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STUDIES ON THE GRAFTING REACTION BETWEEN POLYMERS HAVING A LARGE NUMBER OF REACTIVE GROUPS AND THE FORMATION OF COMPATIBILIZED BLENDS

By

Li Nie

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ABSTRACT

STUDIES ON THE GRAFTING REACTION BETWEEN POLYMERS HAVING A LARGE NUMBER OF REACTIVE GROUPS AND THE FORMATION OF COMPATIBILIZED BLENDS

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The formation of graft copolymers in the course of grafting reactions between two polymers each having a large number of reactive groups can result in compatibilized blends. Cellulose acetate (CA) and styrene maleic anhydride random copolymers (SMA) were selected in this study. The inclusion of SMA into CA can improve the dimensional stability of CA, one of the major shortcomings of CA.

Grafting reaction happens in solution between the hydroxyls of CA and the anhydrides of SMA. The grafting process was studied in detail to understand the various parameters that are important to the rate of SMA grafting conversion. The compatibilized blends have greatly improved dimensional stability in comparison to CA while maintaining good mechanical properties.

Phase size and homogeneity in ternary blends depend on the structures of graft copolymers and the amount of graft copolymers in the mixtures. Studies based on transmission electron microscopy showed that uniform phase size distribution appears when there are substantial amounts of graft copolymers. Polydispersity in reactive polymers was found to be desirable for free chain solubilization based on the current understanding on the solubilization phenomena.

A thorough theoretical analysis based on a kinetic approach was done to look into the various parameters that are important for the build up of graft copolymers up to the point of gelation. The grafting system is defined as two reactive polymers A and B having a large number of reactive groups *a* and *b*, where *a* react irreversibly with *b* in a homogeneous state. The grafting reaction of CA with SMA falls into this system. It was found that the percentage conversion of the reactive polymers is quite limited in order to avoid too high a system's weight-average molecular weight. The presence of high molecular weight tail in the polydisperse reactive polymers will reduce the extent of graft conversion of the reactive polymers.

A self-consistent kinetic theory was developed and a general procedure was provided to look into the extent and the effect of intramolecular reaction in the defined grafting system. The self-consistency is satisfied via a normalization procedure that reflects the hidden redistribution of polymer species away from the complete randomness due to differences in volume exclusion for different species. The self-consistency in past gelation theories as a whole was not adequately addressed in incorporating the presence of intramolecular reaction. This part of the work makes an important contribution to the completeness of the gelation theory.

to my parents, my wife and my beloved son

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NOMENCLATURE

A	storage index of the generating function for monodisperse polymer A
A_m $(m=i,i',\cdots)$	storage index of the generating function for polydisperse polymer A
b	model parameter in Schulz distribution reflecting polydispersity
B	storage index of the generating function for monodisperse polymer B
B_n $(n=j,j',\cdots)$	storage index of the generating function for polydisperse polymer B
B_{ij}	binary interaction energy density (energy/unit volume)
C_A^0	initial molar concentration of polymer A
C_B^0	initial molar concentration of polymer B
$\overline{C}_g$	reduced concentration of graft copolymers
C_{ij}	molar concentration of polymer species containing i A chains and J B chains
$\overline{C}_{ij}$	reduced molar concentration of polymer species having i A chains and J B chains
$\overline{C}_T$	reduced concentration of all polymer species
$C_{i,i',\cdots;j,j',\cdots}$	concentration of polymer species having $i,i',\cdots$ numbers of polymer A of different molecular weight and $j,j',\cdots$ numbers of polymer A of different molecular weight
$\overline{C}_{i,i',\cdots;j,j',\cdots}$	reduced concentration of polymer species having $i,i',\cdots$ numbers of polymer A of different molecular weight and $j,j',\cdots$ numbers of polymer A of different molecular weight
E	variable relating to grafting conversion of polydisperse polymer A

f_A	fraction of polymer A found in graft copolymers (molar basis)
f_{ref}	grafting conversion of an arbitrary chosen chain fraction
f_A^{cri}	grafting conversion of A at gel point (molar basis)
f_A^w	grafting conversion of polymer A (weight basis)
$f_{\overline{M}n_A^0}$	grafting conversion of the reference free chain component of polymer A having a molecular weight equivalent to the number-average molecular weight of the initial A
G	generating function in case of polydisperse A and B
$G(A,B,Z)$	generating function in case of monodisperse A and B
G_I $(I=A, B, Am, Bn, Z)$	partial derivative of the generating function
ΔG_m	free energy of mixing
l	length of the statistically equivalent unit
M_A	molecular weight of monodisperse polymer A
M_B	molecular weight of monodisperse polymer B
$\overline{M}_{k_A}$	reduced molecular weight of free chain component of polymer A
$\overline{M}_{l_B}$	reduced molecular weight of free chain component of polymer B
$\overline{M}_n$	number-average molecular weight of reaction mixture
$\overline{M}_n^0$	initial number-average molecular weight of reaction mixture
$\overline{M}_w$	weight-average molecular weight of reaction mixture
$\overline{M}_w^0$	initial weight-average molecular weight of reaction mixture
$\overline{M}_w^f$	weight average molecular weight of free chains
n	number of dispersed SMA phase per unit volume
$\overline{n}_A$	average numbers of linkages of polymer A segment of the graft copolymers

n_{iso}	total numbers of isomers that can be constructed out of the simplest graft copolymer
N_i	numbers of reactive groups i in polymer chain
N_I	constitutional units of polymer I
$N_{a_ib_j}$	numbers of statistical equivalent units between two reactive groups with coarse-grained gaussian distribution
N_{ball}	numbers of structural units of the coordination ball
$N^0(\overline{M}_{k_A})$	molar fraction of chain component of the initial polymer A having molecular weight of $\overline{M}_{k_A}$
$N^0(\overline{M}_{l_B})$	molar fraction of chain component of the initial polymer A having molecular weight of $\overline{M}_{l_B}$
$\overline{p}_a$	mean probability of $\{a_i\}$ reactive groups meeting with $\{b_j\}$ reactive groups of the simplest graft copolymer
$\overline{p}_b$	mean probability of $\{b_j\}$ reactive groups meeting with $\{a_i\}$ reactive groups of the simplest graft copolymer
$P_{a_ib_j}$	probability of a_i reactive group meets with b_j reactive group
P^g_{ij}	fraction of grafting reaction for the generation of polymer species having i A chains and j B chains
P^c_{ij}	fraction of grafting reaction for the consumption of polymer species having i A chains and j B chains
$P^g_{i,i',\cdots;j,j',\cdots}$	probability of grafting reaction for the generation of species having $i,i',\cdots$ numbers of polymer A of different molecular weight and $j,j',\cdots$ numbers of polymer A of different molecular weight
$P^c_{i,i',\cdots;j,j',\cdots}$	probability of grafting reaction for the consumption of species having $i,i',\cdots$ numbers of polymer A of different molecular weight and $j,j',\cdots$ numbers of polymer A of different molecular weight
r	grafting reaction rate of the system
R	ratio of the numbers of reactive groups consumed in the polydisperse case to that of monodisperse case at the same weight basis grafting conversion of polymer A

R_a	ratio of the numbers of reactive group *a* of polymer A consumed in the polydisperse case to the monodisperse case at the same molar concentration and percentage conversion of polymer A
$R_{spherel}$	radius of the coordination ball
$\overline{S}$	number-average interfacial area of the two phases
T_g	glass transition temperature
ν_A	numbers of constitutional units carried by each reactive group of polymer A
ν_B	numbers of constitutional units carried by each reactive group of polymer B
V_i	total volume of component *i*
V_{ball}	volume of coordination ball
$\overline{V}_i$	molar volume of component *i*
w_i	weight fraction of component *i* in bulk
$W(M)$	weight fraction molecular weight distribution function
x	molar ratio of polymer A to polymer B
Z	variable relating to grafting conversion of monodisperse polymer A
α_p	fraction of u grafted SMA having the same chance of collision for reaction as the grafted SMA chain
β	normalization factor
σ	model parameter in log-normal distribution reflecting polydispersity
ϕ_i	volume fraction of component *i*
ϕ_i'	volume fraction of polymer *i* in the bulk
ϕ_i''	volume fraction of structural units *i* in the copolymer
φ_a	number fraction of constitutional units containing reactive group *a* of chain A in the reaction system excluding solvent
φ_b	number fraction of constitutional units containing reactive group *b* of chain B in the reaction system excluding solvent

δ	interfacial penetration depth
δ_i	solubility parameter $(cal/cm^3)^{0.5}$
$\zeta, \eta, \zeta_m, \eta_n$	implicit variables
θ	bond angle between two constitutional units
λ	system's probability of intramolecular reaction
λ_{ij}	probability of intramolecular reaction from species having *i* polymer A chain and *j* polymer B chains
λ_{11}^{A}	mean intrinsic probability of intramolecular reaction for reactive groups on chain A of the simplest graft copolymer
λ_{11}^{B}	mean probability of intramolecular reaction for reactive groups on chain B of the simplest graft copolymer
λ_{ij}^{A}	mean intrinsic probability of intramolecular reaction for reactive groups on chain A of the graft copolymer having *i* A chains and *j* B chains
λ_{ij}^{B}	mean probability of intramolecular reaction for reactive groups on chain B of the graft copolymer having *i* A chains and *j* B chains
$\Gamma(b+2)$	Garma function
Δ_i	contribution to the probability of intramolecular reaction from the *i*th neighbor
$\Theta(or\ \Theta_A\ or\ \Theta_B)$	model parameter
ψ	rotational angle

Chapter 1. INTRODUCTION

1.1 TRUST FIELD OF THE WORK

This work falls in the fields of polymer blends/alloys and block/graft copolymers. It is about the compatibilization of one reactive polymer with another reactive polymer each having large numbers of reactive groups. The two reactive polymers are immiscible. Control on the phase size and homogeneity of the compatibilized blends and the potential of gelation during the course of grafting reaction are two important characteristics of such system.

1.2 THERMODYNAMICS OF POLYMER BLENDING

Blending two or more polymeric materials provides a simple way for tailoring the properties of the available materials, i.e., performance of materials (mechanical properties, impact properties, optical properties, solvent resistance and heat distortion temperature), processability, and cost effectiveness. The new material often exhibits combined properties when the blending components are miscible. Whether or not the two polymers are miscible depends on the free energy of mixing. According to Flory-Higgins's theory, the free energy of mixing for two polymers A and B in the assumed homogeneous state satisfies

$$\frac{\Delta G_m}{(V_A + V_B)} = B_{AB}\phi_A\phi_B + RT\left[\frac{\phi_A \ln \phi_A}{\overline{V}_A} + \frac{\phi_B \ln \phi_B}{\overline{V}_B}\right] \tag{1.1}$$

where ϕ_i is the volume fraction of component i , B_{AB} is the binary interaction energy density, $\overline{V}_i$ is the molar volume of component i and V_i is the actual volume of the components comprising the mixture. For high molecular weight polymers, the entropy of mixing diminishes and the free energy of mixing is determined mainly by the enthalpy of mixing.

1.3 MISCIBLE BLENDS

Polymers can be miscible when there are some kinds of specific intermolecular interactions (SII) so that the enthalpy of mixing is negative (exothermal). The SII [cowie, 1985] may include acid-base interaction, hydrogen bonding, π-bonding etc. Chemical modification can lead to favorable interactions in some blend systems. In recent years, there have been increasing activities in finding miscible blends involving random copolymers. Many miscible systems were found with copolymers at a certain copolymer composition for the given blending pair. What has been found theoretically is that the unfavorable interactions within the random copolymer itself can be diluted by the presence of a proper polymer. It, therefore, provides opportunities for miscibility at a certain composition range, the so called miscibility window [Alexandrovich et al., 1977; Aptel and Cabasso, 1980; Eisenberg et al., 1982; Vukovic et al., 1983; Brinke et al., 1983; Kambour et al., 1983; Paul and Barlow, 1984; Liberman and Gomes, 1984; Pearce et al., 1984; Balazs et al., 1985; Shiomi et al., 1986; Bourland and Braunstein, (a)1986, (b) 1986; Gardiner and Cabasso, 1987; Aoki, 1988; Kim et al., 1989; Defieuw et al., 1989; Zhu et al., 1990; Jo and Lee, 1990; Brannock and Paul, 1990; Sun and Cabasso, 1991; Krause, 1991]. Current practice in miscible systems has been on the finding of new miscible blends under the guidance of this established theory. Nevertheless, among the vast variety of polymers commercially available nowadays the majority are still immiscible, even though more and more miscible blends have been found and will certainly continue to be found.

1.4 IMMISCIBLE BLENDS

Unfavorable interactions between the structural units of two polymers cause immiscible blends. Immiscible blends are characterized by the presence of macrophase separations.

Figure 1-1 shows an example of macroscopic phase separation of the blend of cellulose acetate/poly(styrene-co-maleic anhydride) (CA/SMA) prepared by extrusion process (typical of immiscible blends). There is complete demixing at the interface. The poor control on phase sizes and the lack of interfacial mixing lead to poor material properties, i.e., tensile strength, elongation, impact strength, and optical properties. The original meaning of blending is often lost because of this.

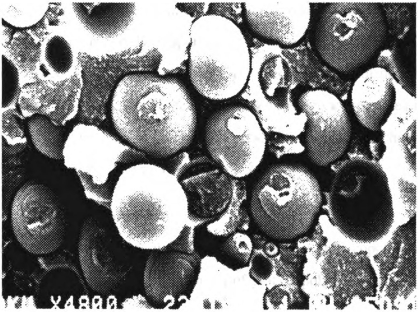


Figure 1-1 SEM picture of the melt blend of CA-SMA showing macro-phase separation and interfacial debonding (SMA being the dispersed phase)

1.5 COMPATIBILIZED BLENDS

1.5.1 Graft copolymer as compatibilizer

The presence of graft copolymers (I avoid mentioning block copolymers for the sake of coherence for my system) in the blends often helps make a better dispersion of the phase size and improves interfacial bonding [Paul, (a) 1978]. The ultimate performance of the material depends on the phase size and phase structure [Noshay and McGrath, 1977;

Bucknall, 1977]. The control on the phase size and morphology depends very much on the structures and the amount of the graft copolymers in addition to processing conditions. The amount of graft copolymers can vary from a few percent to nearly pure graft copolymers. Pure graft copolymers exhibit the limiting phase size (microdomain) and morphological behaviors. Commercial products are often characterized as ternary mixtures. This is particularly true for systems involving graft copolymers, i.e., high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS). The most exciting discovery has been the extraordinary improvement of the impact properties of glassy polymers with the inclusion of rubbery materials. Optimum properties are obtained through careful design of the architecture of graft copolymers as and careful control on the content of graft copolymers so as to have the desired phase sizes and phase structures in the allolys [Echte, 1989]. To achieve this one needs to go back to the basics as to how the grafting scheme is selected to give the best process in the first place.

1.5.2 Synthesis of graft copolymers

There is, perhaps, no particular reason to synthesize graft copolymers instead of block copolymers. The route for the formation of graft copolymers comes from the fact that active sites or reactive groups are more likely to be generated or present on the chain backbone in a random manner.

There are basically two ways to synthesize graft copolymers:

(a) graft copolymerization of monomers onto the polymer backbone

(b) graft coupling between two reactive polymers

In case of graft copolymerization the active or reactive sites on the polymer backbone initiate the polymerization of monomers to form graft copolymers. The active or reactive sites on the polymer backbone can be part of the polymer structure, they can also be generated right before graft copolymerization or during graft copolymerization by some initiating methods. The synthesis of graft copolymer both past and present adopts mostly graft polymerization via a free radical reaction, because of the availability of large numbers of vinyl monomers. Free radicals are generated on the polymer backbone by redox, UV irradiation and high energy radiation [Ceresa, 1976; Stannett and hopfenberg, 1971; Stannett, 1982, 1985; Mukherjee and Goel, 1985; Samal et al., 1986]. The radicals initiate the polymerization of monomers to form graft copolymers. Extensive studies have been conducted on the graft polymerizations of vinyl monomers onto cellulose and its derivatives [Stannett, 1982, 1985; Samal etal., 1986], nylons [Mukherjee and Goel, 1985] and poly(vinyl chloride) [Ceresa, 1976]. Most of the studies were focused on surface modification to alter the surface properties of the materials. One of the major problems in graft polymerization has been the poor control of the amount of homopolymer production, the structures of the graft copolymers, and the chain lengths of the grafted chains and homopolymer chains.

Graft polymerizations through ring-opening, condensation and ionic methods have been studied very little compared to free radical graft polymerizaitons. Ring-opening graft copolymerization of ethylene oxide with cellulose forming hydroxylethylcellulose is well-known. Sundet and Thamm [1977] reported studies on the synthesis and properties of the graft copolymers of pivalolactone with carboxylated polymers by ring-opening polymerization. Kobayashi et al. [1988] reported ring-opening graft polymerization of 2-Oxazolines onto cellulose and cellulose diacetate with the hydroxyls being tosylated. Ring-opening polymerization is perhaps not a good route for the synthesis of graft copolymers since the initiating groups on the backbone are often numerous, and chain transfer could lead to poor control of molecular weight of the polymerized chain (low degree of polymerization).

Ionic graft polymerization includes cationic and anionic processes, the advantages of ionic graft polymerization come from the fact that the molecular weight and molecular weight distribution can be well controlled. Nevertheless, ionic graft polymerization is little studied. Kennedy et al. [1974] studied aluminum alkyl-initiated cationic grafting of isobutylene onto the alylic and/or tertiary chloride sites present in poly(vinyl chloride). However, chain transfer to monomer limits the efficiency of this process. Falk et al. [1973] studied initiation of styrene by metallated polybutadiene. Ionic copolymerizations are more useful for the synthesis of block copolymers. The disadvantage of ionic reaction is the stringent requirement on impurities.

Coupling reaction requires the matching of reactive groups on two reactive polymers. Rempp [1968] reported studies on backbone coupling by the interaction of a living polystyrene anion with macromolecules bearing ester side groups, e.g., poly(methyl methacrylate), the interaction results in the displacement of a methoxyl group and formation of a ketone graft linkage. Narayan [1990] developed a new synthetic approach to tailor-made cellulose-polystyrene graft copolymers with precise control over molecular weights, degree of substitution and backbone-graft linkage via displacement reaction of polystyrylcarboxylate anion with the mesylate groups on the cellulose backbone. The polystyrylcarboxylate anion was prepared by anionic polymerization. In a different reaction route, Holohan et al. [1991] prepared polydimethylsiloxane graft copolymers via the coupling reaction of bisphenol-A-based polyhydroxyether (phenoxy) with chlorosilyl-terminated polydimethylsiloxane (PDMS). The monofunctional PDMS oligomers were prepared by anionic polymerization of hexamethylcyclotrisiloxane using BuLi as initiator and chlorodimethylsilane or dichlorodimethylsilane as the terminating agent.

1.6 *IN SITU* GENERATION OF GRAFT COPOLYMERS TO FORM COMPATIBILIZED BLENDS

Compatibilized blend can be prepared with the addition of graft copolymer to function as a compatibilizer. It can also be prepared by reactive processing such as reactive extrusion where the graft copolymers are generated *in situ*. The most common way to make compatibilized blends is by reactive processing [Dean, 1985; Angola et al., 1988; Chen et al., 1988; Perron and Bourbonais, 1988; Kim and Park, 1991]. Solution or bulk grafting can be employed depending on the nature of the given system.

In recent years, there have been increasing activities in the area of reactive polymers and reactive processing. The variety of functionalized polymers has grown, both in the nature of polymer backbone and in the array of functional groups [Benham and Kinstle, 1986]. This provides opportunities for the synthesis of graft copolymers and the development of new compatibilized blens and alloys. For example, one series of reactive polymers are the maleic anhydride based reactive polymers, the most important and celebrated family of reactive polymers [Sweeney, 1988]. Maleic anhydride is unique because of its reluctance to homopolymerization and its double functionalities: double bond and anhydride.

The first successful commercial development was based on reactive blending of polyamide and ethylene-propylene modified rubbers containing grafted carboxylated or anhydride groups. Approximately 1 wt% of carboxyl or anhydride groups was sufficient to create a graft product by condensation reaction with the amino terminated polyamide, as described by Cimmino and coworkers [1984] and others [Flexman, 1979; Wu, 1983, Chen and Kennedy, 1987]. There have been many studies utilizing the fast reaction between anhydride (or carboxylic acid) and amino groups on the polymer chain ends [Venkatesh et al., 1983; Dean, 1985; Chen et al., 1988; Angola et al., 1988; Perron and Bourbonais, 1988; Campbell et al., 1990; Chang and Hwu, 1991; Kim and Park, 1991]. A similar idea of simple grafting was also applied by DOW Chemicals in a system based on styrenic copolymers containing oxazoline groups. These resins were mixed reactively with carboxylated polyolefins [Sneller 1985; Baker and Saleem, 1987]. MA modified polymers such as Polypropylene [Gaylord et al., 1980], rubbery ethylene-propylene copolymer (EPDM), polyethylene (PE), Polystyrene (PS), etc., provide opportunities for the production of graft copolymers and its alloys. In a closely related field, extensive studies have been done on reactive filler-matrix blends and composites [Broutman and Sahu, 1971; Scott et al., 1987; Takase and Shiraishi, 1989; Tsubokawa and Kogure, 1991].

1.7 CLASSIFICATION OF GRAFTING SYSTEM VIA COUPLING REACTION

Coupling reactions between two reactive polymers can be classified into three categories according to the numbers of reactive groups on the backbones of the two reactive polymers: (a) one or two reactive groups on both polymers; (b) one or two reactive groups on one polymer and a large number of reactive groups on another polymer; (c) a large number of reactive groups on both polymers. The first category is often seen in block copolymer systems. Copolymerization and chemical modifications of homopolymers often result in a large number of reactive groups on the polymer backbones. Most condensation polymers bear reactive groups on the chain ends. There are, therefore, many combinations that fall into the last two categories. The most complicated graft copolymers in terms of structure will be produced in systems of the third category, and gelation occurs at a certain extent of a grafting reaction.

1.8 CELLULOSE ACETATE/POLY(STYRENE-CO-MALEIC ANHYDRIDE) GRAFTING SYSTEM

Cellulose esters are one important family of modified natural polymers. They are prepared in multiton quantities with degrees of substitution (D.S.) ranging from that needed for hydrolyzed, water-soluble monoacetate (biodegradable), plastic secondary diacetate (DS=2.45, films, fibers, molding articles, filters) to those of fully substituted triacetate (photographic films, textile fibers) and specialty mixed esters (cellulose acetate propionate, cellulose acetate butyrate). Although cellulose ester plastics is noted for their toughness, face gloss, smoothness, and excellent optical clarity, its usefulness is restricted by many unfavorable factors. It is well known that cellulose diacetate has a dimensional stability problem when exposed to a high humidity environment. This is one of the biggest problems for applications in fibers and films. The other shortcomings are its high cost, high processing temperature and very limited compatibility with other synthetic resins [Brewer and Bogan, 1985]. So far only poly(4-vinyl pyridine) [Aptel and Cabasso, 1980] and poly(styrenephosphonate ester) at certain degree of phosphorylation [Gardiner and Cabasso, 1987; Sun and Cabasso, 1991] were reported to be miscible with cellulose acetate. These weak points hamper its competitiveness with most synthetic polymers, and there has been a declining demand in the market since 1965. Combining Cellulose acetate with other synthetic polymers can result in new functionalities and is one of the ways to combat these shortcomings.

Styrene maleic anhydride random copolymers (SMA) with different maleic anhydride (MA) levels are commercially available. These resins are characterized by: excellent melt flow properties that provide ease of injection molding and extrusion; retention of stiffness under exposure to high heat and stress loading; inherent low moisture absorption which results in negligible change in dimension under high humidity; low thermal expansion coefficients over a broad range of temperatures and low mold shrinkage.

The reaction between the anhydrides on the SMA backbone with the hydroxyls on the CA backbone provides a synthetic scheme for the production of graft copolymers. Compatibilized blends can be produced through such grafting reactions. The use of the grafting reaction between hydroxyl and anhydride is rarely seen in the open literature. Part of the reason could be for the relatively low reaction rate between the anhydride and the hydroxyl. One report utilizing such a reaction was given by Lambla et al. [1988] on the crosslinking of styrene maleic anhydride copolymer with dihydroxyloligostyrene in the molten state. It is important to point out here that the grafting reaction between hydroxyl and anhydride is of potential interest, given the fact that a vast number of natural polymers have hydroxyl groups. Combining natural polymers with synthetic polymers using such a grafting scheme could lead to important commercial development in the future even though the chemistry is not new.

The compatibilized blends are expected to have improved dimensional stability because of the inclusion of hydrophobic SMA. It is important that the optical clarity of CA be retained after the inclusion of SMA, since it is one of the most important selling points for CA. The potential application for such compatibilized blends could be in fibers and films for the replacement of cellulose triacetate (better dimensional stability). The problem with cellulose triacetate is the use of methylene chloride in fiber spinning and film casting. Concerns over the environment lend such a solvent unfavorable. Another potential application of the new alloys is new membrane material for ultrafiltration and reverse osmosis where the inclusion of SMA might help improve the compaction problem of CA membrane in the skin layer during operation. Compaction in the skin layer over the operation time reduces the flux of water permeation [Baayens and Rosen, 1972; Ohya et al., 1981; Funk et al., 1986].

1.9 TWO IMPORTANT ISSUES

There are two important issues that are general for the grafting systems of the third category: (a) when to stop the grafting reaction so that the system's weight-average molecular weight (WAMW) is kept at a reasonable value from a processing point of view; (b) how the structures of the graft copolymers and the free chains, namely the effective chain length of the grafted chains and the ungrafted chains, differ, and what the effect of polydispersity is in promoting homogeneous phase size. Heterogeneity is often not good in terms of properties. The presence of macroscopic phase size results in a loss of optical clarity that could be crucial for some applications.

1.10 OBJECTIVES OF THE RESEARCH

The combination of CA and SMA belongs to the third category as was classified above due to the large numbers of reactive groups on both CA and SMA. In this study, the grafting reaction between CA and SMA was carried out in solution. A thorough study on the compatibilization of CA with SMA covers many subjects: (a) the study on the grafting reaction itself; (b) the development of graft copolymers; (c) characterization of the structures of the graft copolymers; (d) phase size and phase homogeneity of the reaction products; and (e) evaluation of some of the properties of the new materials. A detailed study is not only important for the case of CA-SMA itself but also important in unveiling some points that are common to the system represented by this particular CA-SMA combination. The objectives of this research were three folds:

1. to examine the compatibilization of CA with SMA: the grafting reaction; the characterization of the reaction products; and the evaluation of some of the properties of the new blends.
2. to look at the phase size and phase homogeneity in relation to the structures of the graft copolymers and the content of graft copolymers in this particular grafting system. The results from this study shall apply to other cases under similar conditions.
3. to look in detail into the buildup of the graft copolymers of the grafting system, namely the branching process of the grafting reaction. Such an analysis is extremely important not only from the standpoint of understanding the complex system better but also from a control point of view in terms of processing.

1.11 ORGANIZATION OF THE THESIS

Chapter 1 covers a general background of the field and the work as is shown above. Chapter 2 gives the experimental methods employed. Chapter 3 covers studies on the grafting reaction, the characterization of the reaction products and the evaluation of some properties of the reaction products. Chapter 4 gives experimental studies on the phase behaviors of the grafting reaction products. Chapter 5 covers theoretical analysis of the branching process of grafting reaction between two reactive polymers each having a large number of reactive groups (without the consideration of intramolecular reaction). Chapter

6 covers analysis of the effect of intramolecular reaction on the branching process of the grafting system. Conclusions and suggestion for further work were given in chapter 7.

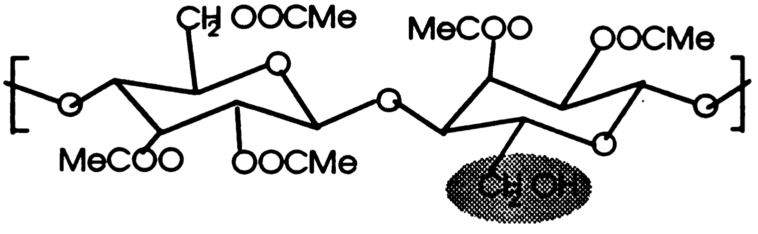
1.12 TERMINOLOGY

The term "polymer blends and alloys" is widely used in the open literature and industry. However, until now there has been no precise definition for "polymer blends" and "alloys". In the recently published superb and fundamental book by Utracki et al. [1989], "polymer blend (PB)" was defined as the "the all-encompassing term for any mixture of homopolymers or copolymers", "polymer alloys" was defined as "a sub-class of PB reserved for polymeric mixtures with stabilized morphologies", "compatible polymer blends" was defined as "a utilitarian term, indicating commercially useful materials, a mixture of polymers without strong repulsive forces that is homogeneous to the eye". There is no distinction between the terms "Alloys" and "compatibilized blends" according to above definitions. Alloys and compatibilized blends were used in the thesis for blends showing desirable properties. No attempt was made to clarify the definitions of "alloys" and "compatibilized blends".

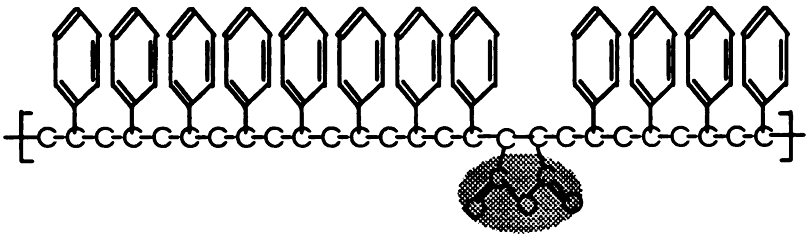
Chapter 2. EXPERIMENTAL

2.1 MATERIALS

Cellulose acetate (CA, D.S.=2.45, Mw=103,000, Mn=46,000) was provided by Courtaulds plc. Styrene maleic anhydride random copolymers (SMA132: 4.75% maleic anhydride, Mw=274k, Mn=136k; SMA232: 7.08 wt% maleic anhydride, Mw=249k, Mn=126k; SMA332: 12.2% maleic anhydride, Mw=193k, Mn=100k) were provided by ARCO Chemical Company. The content of anhydride in SMAs was determined by back titration in xylene with sulfuric acid (dissolved in ethanol), the anhydride was neutralized with potassium hydroxide for 24 hours, phenolphthalein was used as an indicator. SMA stands for SMA232 through out the thesis if not specified. Figure 2-1 shows the structural units of CA and SMA. There are, on the average, 85 hydroxyls per CA chain and 90 anhydrides per SMA chain from the number-average molecular weight. Gel permeation chromatography (GPC) analyses for the four samples were provided by Viscotek Corporation. Figure 2-2 shows the molecular weight distributions of CA and SMA. 4-Dimethylaminopyridine (DMAP) and anhydrous grade N,N-Dimethylformamide (DMF, 99%) were purchased from Aldrich Chemical Company, INC. Figure 2-3 shows the structure of DMAP.



CA (d.s.=2.5, not completely primary hydroxyl)



SMA (the distribution of MA is random)

Figure 2-1 Structures of CA and SMA

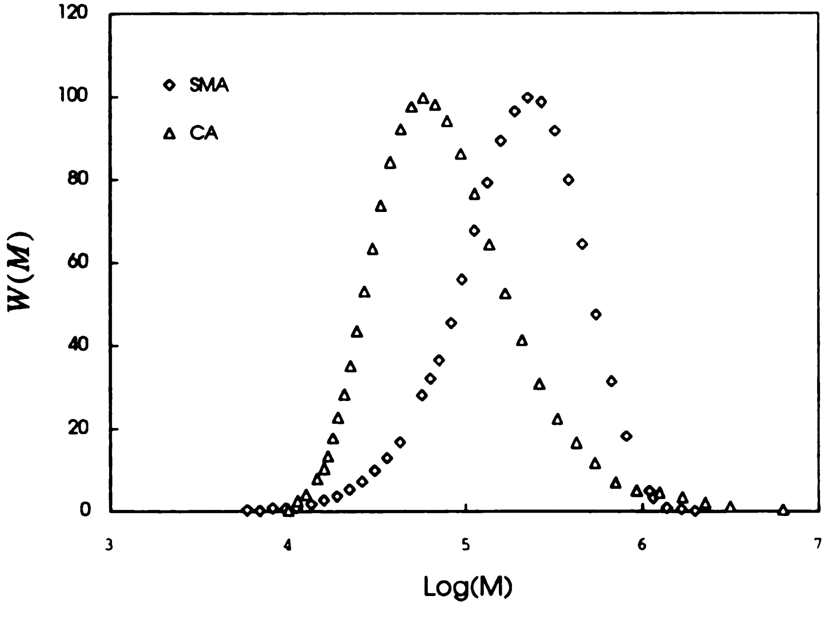


Figure 2-2 Molecular weight distribution of CA and SMA from GPC analysis

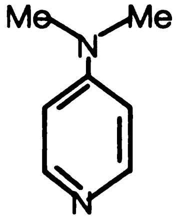


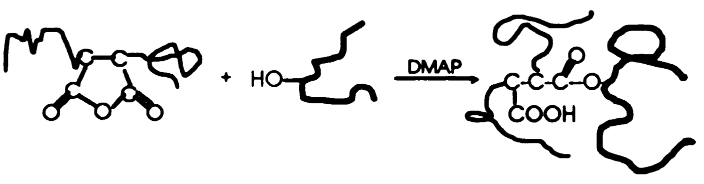
Figure 2-3 Structure of DMAP

2.2 CONSTRUCTION OF PHASE DIAGRAM

Immiscibility between CA and SMA resins persists in the presence of a common solvent, even though the unfavorable contact between CA and SMA is much reduced by the solvent. The phase diagrams were constructed by visual observation on the cloudy point with successive addition of a small amount of solvent at a fixed polymer composition, the same method used by Dobry and Boyer-Kawennoki [1947]. The tie line was obtained by measuring the volume changes after equilibrating the CA solution with SMA solution for three days. The SMA solution of lower density was carefully transferred onto the surface of the CA solution in a tube with volume ticks. The tube was capped with a serum stop and heated gradually to 110°C for equilibration (little head space, excess pressure from air was released with needle).

2.3 GRAFTING REACTION

Grafting reaction happens between the hydroxyl and anhydride to form a half ester with the aid of a catalyst. In the absence of water, the grafting reaction proceeds by



The complexity of the graft copolymers keeps growing because of the large numbers of reactive groups on the chain segments of the graft copolymers. Above reaction route gives the simplest graft copolymer. The grafting reactions were carried out in DMF solution at increased temperature and with stirring. DMAP was used as the catalyst. The cellulose acetate was vacuum dried overnight at 80-100°C and kept under dry nitrogen before anhydrous DMF was transferred to the reactor through the transferring line. Water was added to the reactor through serum stop after the transfer of DMF in looking at the effect of water on the grafting process. DMAP was added after the polymer solution reached to a stable temperature. The reaction temperature was controlled within 0.2°C deviation. After reaction, the solution was cooled down immediately to room temperature, and was precipitated right away with three-time volume of water. Precipitate in the form of porous pulp (low grafting conversion) and porous string (high grafting conversion) was washed with excess amount of hot water every two hours for three times, it was soaked overnight with excess amount of water, further wash was done with methanol for three times. Extensive wash is for the removal of the residual DMF and catalyst. The samples were dried at room temperature to a dry state, and were dried further at 50°C under full vacuum. The amount of sample was weighted under dry condition since CA picks up moisture easily.

2.4 CHARACTERIZATION

2.4.1 Extraction separation

Information on grafting conversion of SMA (wt%) was obtained by Soxhlet extraction with toluene for two days. Carbon-Hydrogen-Nitrogen (CHN) analysis (C%: CA=48.4%, SMA=89.7%) showed less than 3% of CA in the extractable. So only free SMA is extracted. The percentage conversion of SMA is obtained from mass balance. Extraction efficiency depends on the form of sample to be extracted. Precipitates obtained by slowly adding polymer solution (controlled to the concentration of 8g (CA+SMA)/100 ml DMF) into large volume of water is satisfactory for extraction separation. Extraction on the precipitates of simple blends at two compositions (10%SMA, 50%SMA) gave 100% extraction of SMA. No appropriate solvent was found which extracts free CA only.

2.4.2 Analysis by gel permeation chromatography (GPC)

Studies on the molecular weights and molecular weight distributions of the grafting reaction products were attempted using GPC. The column for separation was a Plgel 20m m mixed-A column with a separation capacity ranging from 1k to 40M. Monodisperse polystyrene standards were used for calibration. The analyses were performed on a Viscotek 200 at a flow rate of 1.0 ml/min. with THF and 0.7 ml/min at 50°C with DMF. It was found that there are associations for both CA and SMA in DMF (see Figure 2-4). THF is a good solvent for both CA and SMA (Figure 2-5), the problem came from the grafting reaction products where GPC analyses showed unlikely high molecular weight averages, i.e., the weight-average molecular weight for the half hour reaction sample is more than two millions (see Figure 2-7, Table 3-2 and also theoretical analysis in section 5.4 of chapter 5). It can be explained by the association of SMA chains, free or grafted because of ionic association: grafting reaction with the formation of half-esters and the inevitable hydrolysis of a small amount of anhydrides due to the presence of trace amount of water. A few numbers of carboxylic acid groups on the SMA chain are enough for a substantial ionic association since THF is a non-ionizing solvent [Utracki et al., 1989]. Without theoretical analysis, it could have been taken as the true molecular characteristics of the grafting products since the molecular weight distributions of the grafting reaction products did shift with grafting conversion (Figure 2-7). Adding a small amount of water (2.5 v%) to THF resulted in the associations for both CA and SMA (Figure 2-8). No further attempt was made with GPC analysis.

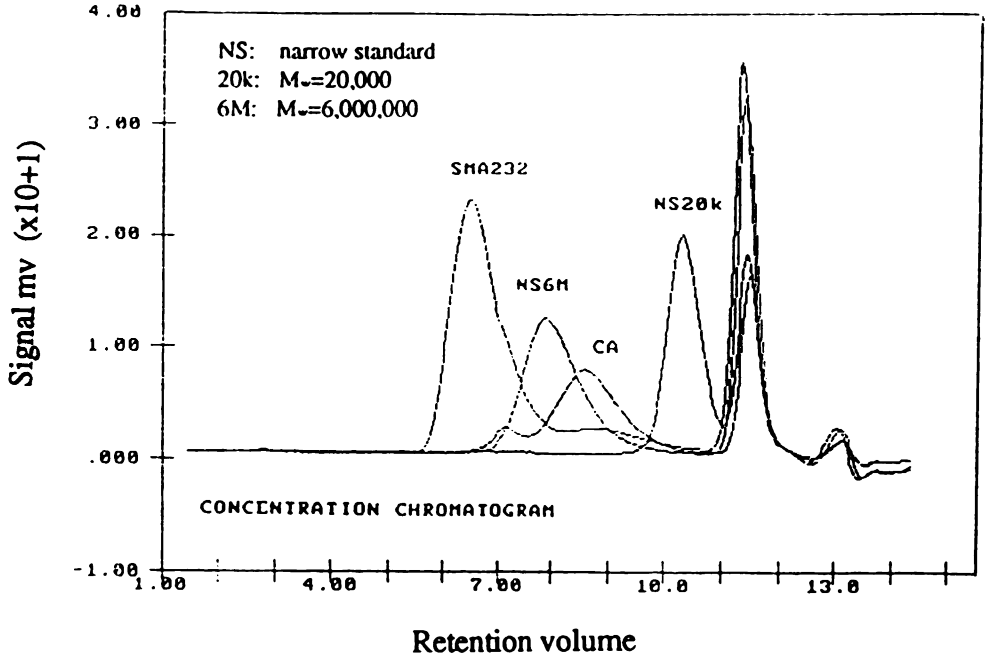


Figure 2-4 GPC evolution showing association of CA and SMA in DMF

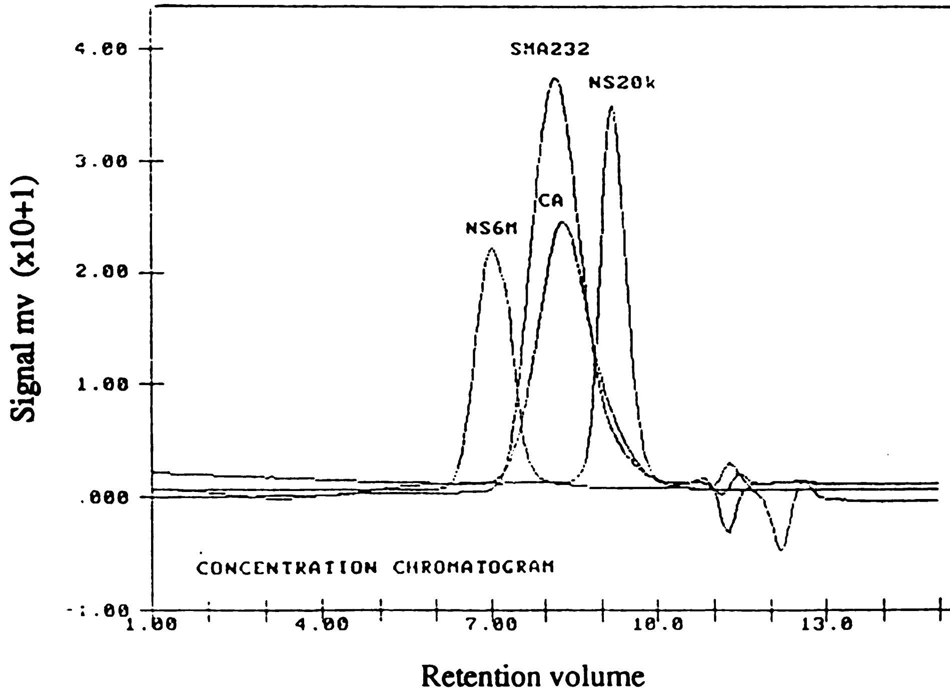


Figure 2-5 GPC evolution showing reasonable molecular distributions of CA and SMA in THF

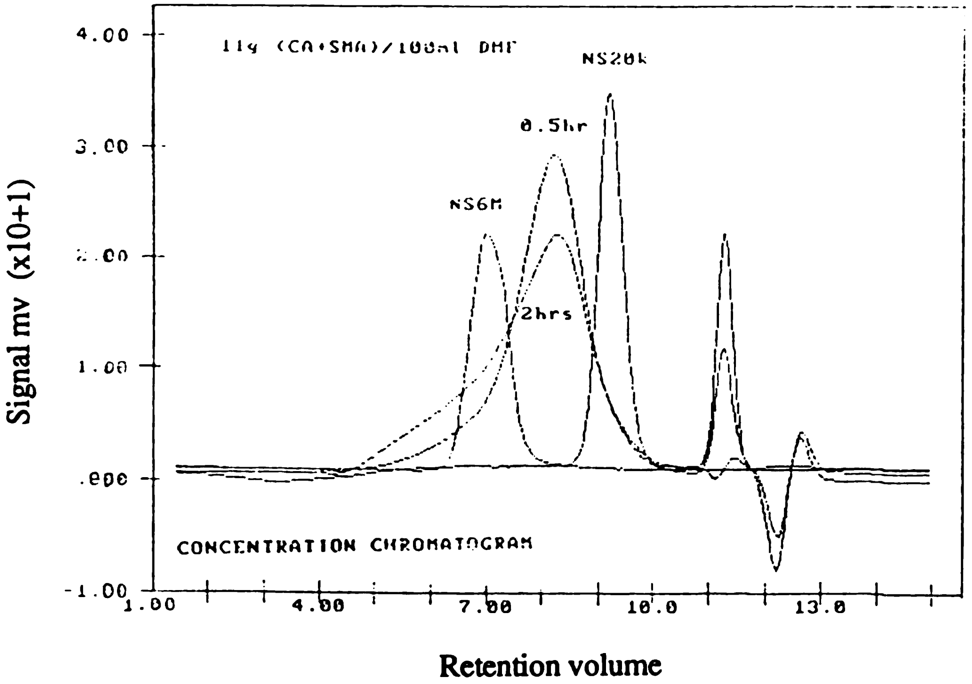


Figure 2-6 GPC evolution showing association in grafting reaction products

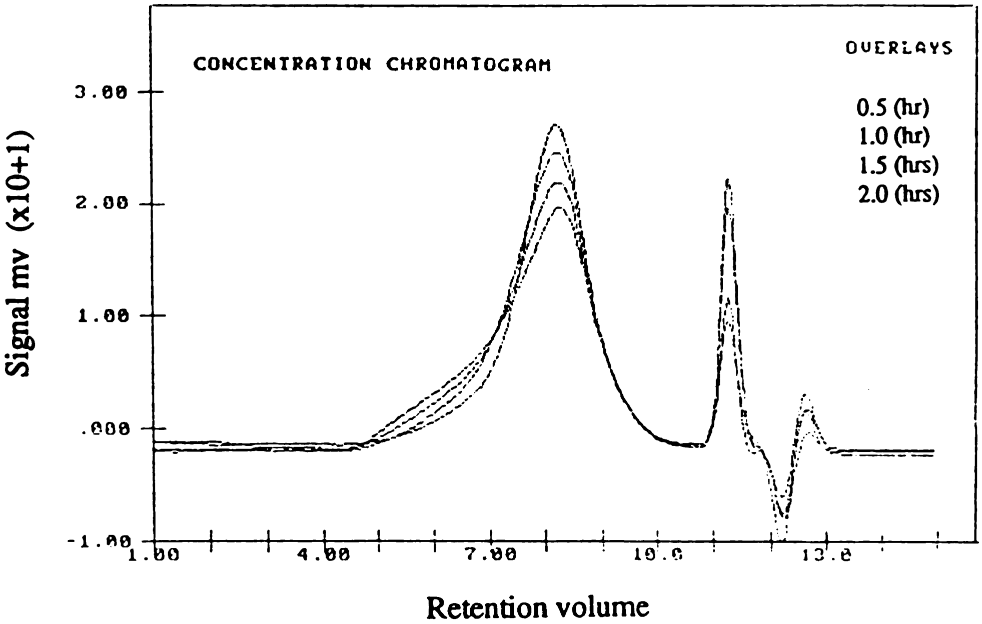


Figure 2-7 GPC evolution showing the shift of molecular weight distribution toward higher molecular weight

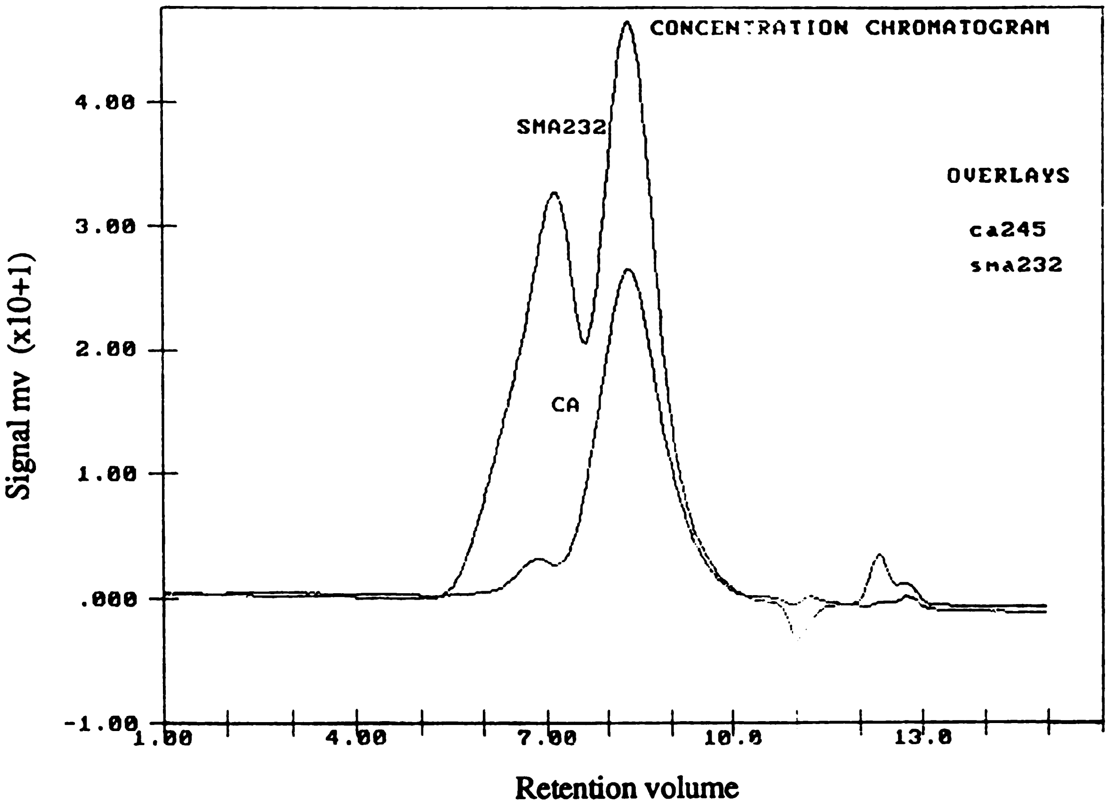


Figure 2-8 GPC evolution showing association for CA and SMA when small amount of water is added to THF

2.4.3 Sample preparation

Films of the grafting reaction products were cast with a film applicator onto clean glass plate and dried at oven temperature of 80°C for 15 minutes. Films for DSC and TEM studies were cast from both acetone/water and THF/water mixture solvents (96v% organic solvent) at a polymer concentration of 0.8-1.0g/10ml. Films for moisture adsorption, tensile properties and dimensional stability were cast from acetone/water mixture solvent (96v% acetone), the polymer concentration was adjusted to proper viscosity for making nice films, it ranged from 0.8g/ml to 1.4g/ml. The solutions were stirred for two days before casting. Small amount of water was added to reduce the solution viscosity. Acetone and THF containing 4 v% water are very effective in reducing the solution viscosity. GPC analyses showed that there are associations for both CA and SMA in the presence of water.

2.4.4 Differential scanning calorimetry (DSC)

DSC studies were conducted to get the glass transition temperature (T_g) of SMA, the glass transition temperatures and the melting temperatures of CA and grafting reaction products (cast films). T_g was taken as the midpoint of a step transition.

2.4.5 Electron microscopy

Transmission electron microscopy (TEM): Phase size and phase homogeneity (homopolymer solubilization) of the film samples were studied by TEM. The phase contrast develops after the ultrathin sections were exposed to the electron beam for a few seconds. This can be attributed to the loss of material from the CA phase (which was appearing lighter) under the electron beam [Thomas and Talmon, 1978]. Staining is not required for this system. Sections of silver color (60-90nm) were ultramicrotomed at room temperature. The TEM studies were performed on a JEOL 100CX transmission electron microscope at an accerating voltage of 80 kV.

Scanning electron microscopy (SEM): Blends of CA-SMA prepared by extrusion process (Baker-Perkins co-rotating intermeshing twin-screw extruder) were studied briefly using SEM to observe the macroscopic phase separation. The SEM studies were performed on a JEOL 35 CF scanning electron microscope at an accerating voltage of 10 kv. The samples were coated with a thin layer of gold.

2.5 PROPERTY EVALUATION

2.5.1 Tensile property

The tensile properties of the cast films were tested according to ASTM D882-83. The tests were performed on a united tensile tester with a crosshead movement at a testing speed of 2%/min. The test samples were cut into dimensions of 4 x 5/16" with a thickness around 0.04". The thickness of a sampls was measured with a caliper having a precision of 0.0005". Before testing, the samples were dried overnight at 60°C and were conditioned at room temperature and also a relative humidity of 60%. All test samples were bubble free. The test results were reported by averaging 10 useful tests.

2.5.2 Moisture adsorption

The moisture adsorptions of the cast films were tested according to ASTM D570-81 at a relative humidity of 95%.

2.5.3 Dimensional stability

The dimensional stabilities (moisture sensitivity) of the films were tested by soaking the films in water for 30 hours at different temperatures. The dimensional changes of the lengths of the films were measured after the film samples were dried naturally for one day. The initial dimensions of the films were taken as the dimensions cut from the glass plates. All samples have a dimension of 8 x 2".

Chapter 3. GRAFTING REACTION AND THE PROPERTIES OF THE GRAFTING REACTION PRODUCTS

3.1 PHASE DIAGRAM OF THE TERNARY MIXTURE

CA is immiscible with SMA (SMA132, SMA232, SMA332). Phase separation happens in solutions even though the presence of a large amount of solvent dilutes greatly the unfavorable interaction between CA and SMA. The phase diagram can be constructed according to the Flory-Higgins theory if the three phenomenological interaction parameters among CA, SMAs and the solvent are available. Scott's [1949] analysis shows semi-quantitatively the important feature of phase behavior in the ternary solution of polymer1 + polymer2 + solvent. For CA and SMA dissolved in DMF, no interaction parameters are available. The phase diagram was constructed by observing the cloudy point experimentally. Figure 3-1 shows the phase diagram of DMF-CA-SMA at 110°C on a weight percentage basis, the tie line is for CA-SMA232 only.

Three important things are noted for grafting reaction from the phase diagram: (1) the shape of phase separation curve is very flat, therefore, a few percentage increase in the polymer concentration from the apex point will cause a drastic phase separation; (2) DMF partitions more in the CA phase than in the SMA phase, the SMA phase will be the dispersed phase if the amount of SMA is less than CA; and (3) the unfavorable interaction between CA and SMA decreases with the content of maleic anhydride in SMA.

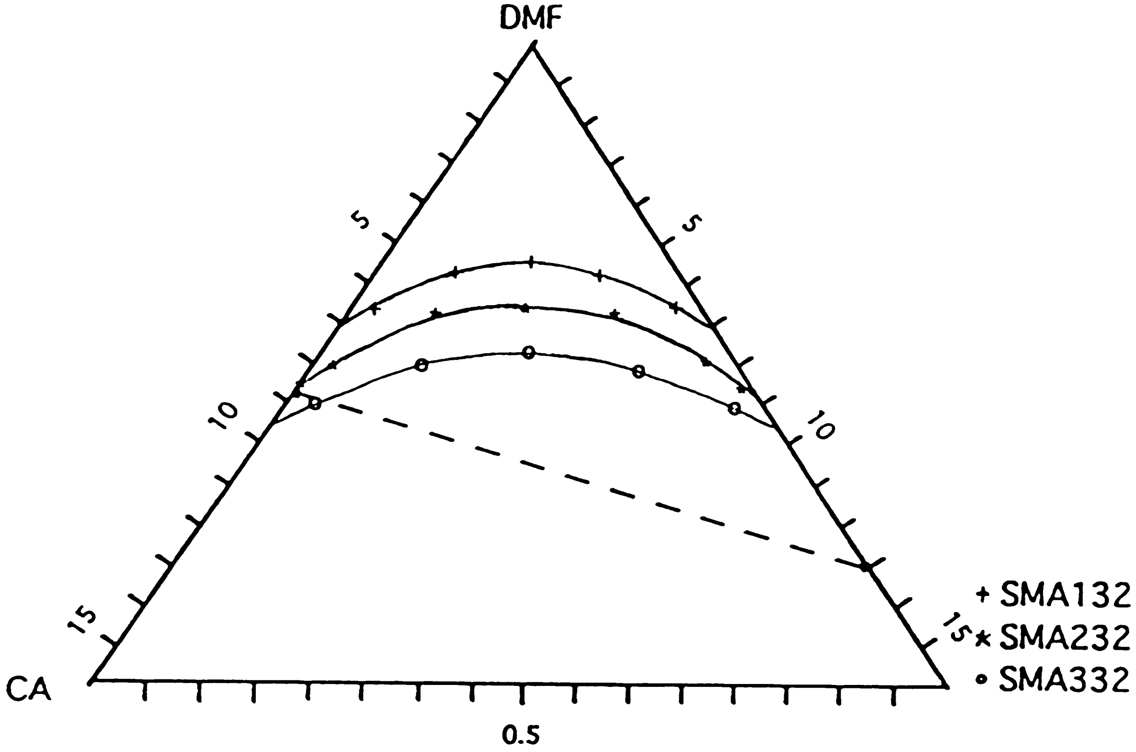


Figure 3-1 Phase diagram of DMF-CA-SMA at 110°C (weight-percentage basis)

To have a better appreciation of the presence of solvent in diluting the unfavorable contact and the content of maleic anhydride of SMA resins in reducing the immiscibility between CA and SMA, one can do a qualitative analysis for the free energy of mixing of the ternary mixture. According to Flory-Higgins's theory, the free energy of mixing in the assumed homogeneous state satisfies

$$\begin{aligned}\frac{\Delta G_m}{RTV} = \frac{\phi_{DMF}}{\overline{V}_{DMF}} \ln \phi_{DMF} + \phi_{DMF}\phi_{SMA}B_{DMF-SMA} \\ + \phi_{DMF}\phi_{CA}B_{DMF-CA} + \phi_{CA}\phi_{SMA}B_{CA-SMA}\end{aligned} \qquad (3\text{-}1)$$

where the combinatorial entropies of CA and SMA have been neglected. B_{ij} is the binary interaction energy density, for non-polar or slightly polar system it is related to the solubility parameters by

$$B_{ij} = \frac{1}{RT}(\delta_i - \delta_j)^2 \tag{3-2}$$

Since DMF is a good solvent for both CA and SMA, the driving force for phase separation comes from the unfavorable interaction between CA and SMA (last term of equation 3-1). Let ϕ'_{CA} be the volume fraction of CA in the absence of solvent, ϕ'_{SMA} be the volume fraction of SMA in the absence of solvent ($\phi'_{CA} + \phi'_{SMA} = 1$), the last term of equation 3-1 becomes

$$\phi_{CA}\phi_{SMA}B_{CA-SMA} = \phi'_{CA}\phi'_{SMA}B_{CA-SMA}(1-\phi_{DMF})^2 \tag{3-3}$$

One see from equation 3-3 that the dilution of the unfavorable interaction is quite sensitive to the amount of solvent in solution, especially at low polymer concentrations. The solutions are often prepared at a concentration of less than 20 wt% polymers due to a high solution viscosity. At this low end, the dilution for the unfavorable interaction between CA and SMA is very sensitive to the change of polymer concentration. As a result, the grafting process is expected to be much affected by the change of polymer concentrations.

SMA resins are commercially available with several maleic anhydride (MA) contents. One can look at the effect of maleic anhydride content of the SMAs on the CA-SMA binary interaction energy density by decomposing the interaction between CA and SMA into the interaction among CA and the monomer units of SMA. Let ϕ''_{ma} be the volume fraction of maleic anhydride in SMA, ϕ''_{sty} be the volume fraction of styrene in SMA ($\phi''_{ma} + \phi''_{sty} = 1$), the binary interaction energy density between CA and SMA, following Paul and Barlow's generalization [1984], becomes

$$\begin{aligned} B_{CA-SMA} &= B_{sty-CA}\phi''_{sty} + B_{ma-CA}\phi''_{ma} - B_{sty-ma}\phi''_{sty}\phi''_{ma} \\ &= B_{sty-CA}(1-\phi''_{ma}) + B_{ma-CA}\phi''_{ma} - B_{sty-ma}(1-\phi''_{ma})\phi''_{ma} \end{aligned} \tag{3-4}$$

The presence of a minus term is due to the unfavorable interaction within the structural units of SMA. It is the presence of such unfavorable interaction within the copolymer itself that leads to the potential of miscibility window in polymer blends involving random copolymers [Brinke et al., 1983; Kambour et al., 1983; Paul and Barlow, 1984]. To fix the idea, let us assume that the binary interaction energy density of B_{ma-CA} is zero (it is supposedly to have a small negative value for the possible weak hydrogen bonding between the hydroxyl of CA and the anhydride), and B_{sty-CA} equals to B_{sty-ma} (δ_{sty}=9.3, δ_{CA}=12.7, δ_{ma}=13.6, δ_{sa}=15.4, (cal/cm^3)$^{0.5}$, sa stands for succinic anhydride, [Grulke, 1989]). It is conservative to have

$$B_{CA-SMA} = B_{sty-CA}(1-\phi''_{ma})^2 \tag{3-5}$$

We see from equation 3-5 that the unfavorable interaction between CA and SMA reduces with increasing MA content in SMA. This explains the shifting of the phase diagram as the MA content of SMA changes. However, the sensitivity of the MA content in reducing the unfavorable interaction is less than the solvent since the important commercial resins have the MA content of less than 25%.

3.2 GRAFTING REACTION

3.2.1 Description of the rate of SMA grafting conversion in the absence of water

Grafting reaction will happen in the diffusive interface when each phase contains only one polymer (the following discussion is for CA-SMA232 only, SMA is meant for SMA232 in rest of the discussion). The phase size decreases as the grafting conversion of SMA increases. This is due to the dispersing power of the graft copolymers once they are formed in the reaction system. Experimentally it was observed that the clarity of the reaction solution changed gradually from opaque to clear. To understand the grafting process, we need to relate the grafting reaction to the percentage conversion of SMA, the only information we can obtain from extraction. The percentage grafting conversion of SMA is defined as

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a

B

$\bar{M}$

th

$$f^{w}_{sma} = 1 - \left(\frac{\int M dC}{\int M dC^{0}}\right)_{sma} = 1 - \left(\frac{\int M dC}{\overline{M}^{0}_{n} C^{0}}\right)_{sma} \tag{3-6}$$

The rate of disappearance for the concentration of free (ungrafted) SMA chain of a certain molecular weight satisfies

$$-\left(\frac{dC_i}{dt}\right)_{sma} = \left(\frac{\alpha_p M_i C_i}{\sum M_i C_i^0 - (1-\alpha_p)\sum M_i C_i}\right)_{sma} \delta n \overline{S} r_{ma} \tag{3-7}$$

where r_{ma} is the rate of MA consumption. $\alpha_p M_i C_i / (\sum M_i C_i^0 - (1-\alpha_p)\sum M_i C_i)$ is the statistical weight of the reaction used for the consumption of the chain species of that particular molecular weight (the numbers of MA reacted on the graft copolymers were neglected in the statistical weight due to the large numbers of MA on the SMA chains). α_p is the fraction of ungrafted SMA chains that have the same chance of collision for reaction as the grafted chains. It is a function of phase size and phase size distribution. Its value should increase with grafting conversion if there were no blocking effect by the graft copolymers. δ is the equivalent interfacial penetration depth for reaction. It should be relatively constant under given conditions. n is the total numbers of the dispersed SMA phase per unit volume. $\overline{S}$ is the number-average interfacial area of the two phases for the given size distribution of the dispersed SMA. Multiplying both side of equation 3-7 by M_i and summing for all the i gives

$$-\left(\frac{\sum M_i dC_i}{dt}\right)_{sma} = \left(\frac{\alpha_p \sum M_i^2 C_i}{\sum M_i C_i^0 - (1-\alpha_p)\sum M_i C_i}\right)_{sma} \delta n \overline{S} r_{ma} \tag{3-8}$$

By substituting equation 3-6 into equation 3-8 and rearranging, we have

$$\frac{df^{w}_{sma\,i}}{dt} = (1 - f^{w}_{sma})\left(\frac{\overline{M}^{f}_{w}}{\overline{M}^{0}_{w}} \frac{PDI}{C^{0}}\right)_{sma} \frac{1}{1 + f^{w}_{sma}(1/\alpha_p - 1)} \delta n \overline{S} r_{ma} \tag{3-9}$$

$\overline{M}^{f}_{w} / \overline{M}^{0}_{w}$ is the reduced weight-average molecular weight of the free SMA chains. *PDI* is the polydispersity index of the starting SMA.

Among several parameters of equation 3-9, only r_{ma} does not change with grafting conversion since the numbers of reactive groups consumed are negligible when the grafting conversion of SMA is less than 80%. The phase sizes and distribution are difficult to quantify since a number of factors contribute it: the extent of immiscibility between CA and SMA; the change of phase size and distribution with grafting conversion; and the stirring strength. As a result, the initial values of and the change of α_p, n, $\overline{S}$ with grafting reaction are not readily available. Actual modeling of the rate of SMA grafting conversion is not attempted in looking at some parameters of equation 3-9.

3.2.1.1 Effect of polydispersity on the change of $\overline{M}_w^f / \overline{M}_w^0$ with grafting conversion

The change of $\overline{M}_w^f / \overline{M}_w^0$ in equation 3-9 depends on the molecular weight distribution of the starting SMA. It satisfies

$$\frac{\overline{M}_w^f}{\overline{M}_w^0} = \frac{\int M / \overline{M}_w^0 (1 - f_{\overline{M}_w^0})^{M/\overline{M}_w^0} W(M) dM}{\int (1 - f_{\overline{M}_w^0})^{M/\overline{M}_w^0} W(M) dM} \tag{3-10}$$

where $f_{\overline{M}_w^0}$ is the grafting conversion of the reference SMA chain having a molecular weight of the weight-average molecular weight of the starting SMA. In case of Schulz distribution we have

$$(\overline{M}_w^f / \overline{M}_w^0)_{sma} = (1 - f_{sma}^w)^{\frac{1}{b+2}} \tag{3-11}$$

b is the model parameter characterizing the polydispersity of the sample. Figure 3-2 shows the change of $\overline{M}_w^f / \overline{M}_w^0$ with grafting conversion at two values of polydispersity for two typical distributions: Schulz and log-normal. We see from Figure 3-2 that the effect of polydispersity on $\overline{M}_w^f / \overline{M}_w^0$ is quite substantial. The reduction of $\overline{M}_w^f / \overline{M}_w^0$ is nearly linear with the percentage conversion of the polymer.

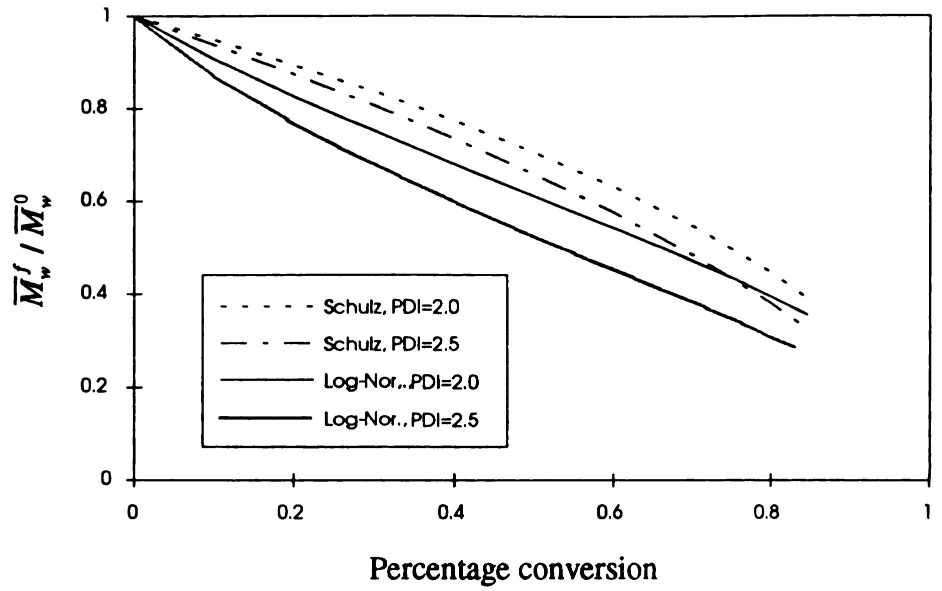

Figure 3-2 Reduced weight-average molecular weight of the free chains of a polymer versus the grafting conversion of the polymer at two values of PDI for two types of distributions

The polydispersity of SMA is 1.98 from GPC analysis. Its molecular weight distribution can be modeled very closely by the Schulz function. Figure 3-3 shows the curve fitting for the molecular weight distribution of SMA using Schulz function.

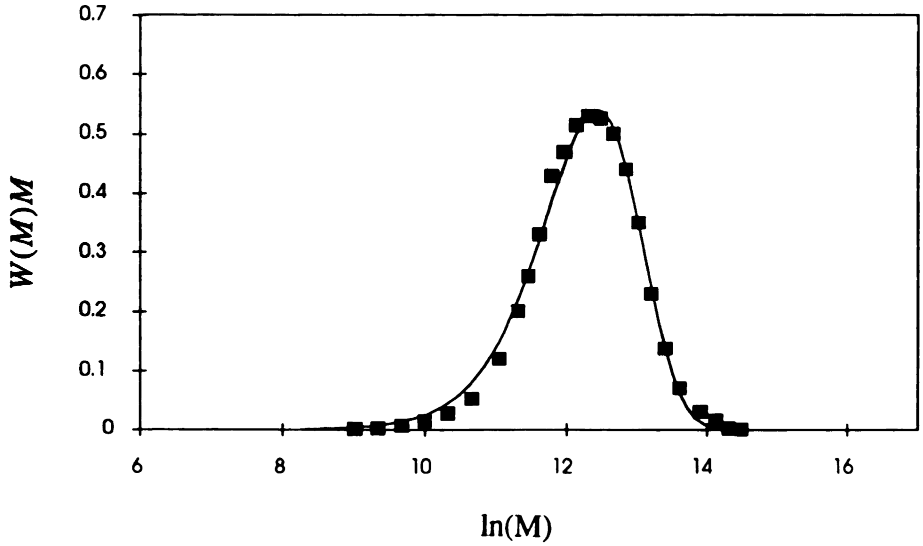

Figure 3-3 Molecular weight distribution of SMA fitted with Schulz function

3.2.1.2 Effect of stirring speed on grafting reaction

The complexity involved in α_p and $n\overline{S}$ comes from both the extent of mixing and the dispersing power of the graft copolymers. The polymer solution is very viscous at a concentration of around 10 wt%. The dispersing force from the stirrer is of viscous shear. The low interfacial tension (diluted in the presence of solvent) at the diffusive interface will result in micron/submicron dispersion for the dispersed SMA phase (indicated by later TEM studies). The high solution viscosity slows down the merging of the dispersed phase to form dispersion of larger size. The formation of graft copolymers during the reaction provides a dispersing force for the dispersed phase to stabilize the dispersion (similar to the role of surfactant). The low interfacial tension and high solution viscosity, plus the stabilizing force from the graft copolymers formed more and more during the reaction, tend to reduce the effect of stirring intensity on the grafting reaction. Table 3-1 shows the effect of stirring speeds on the rate of grafting reaction. It can be seen that the grafting reaction rate increased slightly as the stirring speed increased from 200 rpm to 600 rpm. Therefore the speed of stirring in that range is not particular important for the grafting reaction. A stirring speed of 400 rpm was selected in the rest of the studies.

Table 3-1 Effect of stirring speed on grafting rate*

Speed (rpm)	200	425	600
f^w_{SMA}	0.41	0.43	0.44

* CA:SMA=1:1, 14g polym./100ml DMF,
0.5g cat./100ml DMF, 2hrs., 110^{o}C

3.2.1.3 Effect of polymer concentration

The effect of polymer concentration on the rate of SMA grafting conversion was conducted at three concentrations. Table 3-2 lists the change of SMA grafting conversion with time at three polymer concentrations.

Table 3-2 f_{SMA}^{w} vs. reaction time at different polymer concentrations*

8g/100ml DMF		11g/100ml DMF		14g/100ml DMF	
Time (hrs)	f_{SMA}^{w}	Time (hrs)	f_{SMA}^{w}	Time (hrs)	f_{SMA}^{w}
0.5	0.27	0.5	0.30	1.0	0.33
1.0	0.40	1.0	0.45	2.0	0.46
1.5	0.51	1.5	0.56	3.0	0.54
2.0	0.58	2.0	0.66	4.5	0.63
2.5	0.64	2.5	0.74	5.9	0.72
3.0	0.69				

* CA:SMA=1:1, 0.5g DMAP/100ml DMF, 110°C

We saw from Table 3-2 that the grafting conversion of SMA is very sensitive to polymer concentration. At a concentration of 8g/100ml DMF, the grafting process was very close to homogeneous (the solution turned to clear in less than 10 minutes). A plot of $2[1/(1-f_{SMA}^{w})^{0.5}-1]$ versus time is shown in Figure 3-4. The factor 2 is the value of denominator of the power term in equation 3-11 since *b* equals to zero for a polydispersity of 2. Constant reaction rate r_{ma} is shown from the linear curve fitting.

We can probe somewhat into the effect of phase separation on the grafting process by plotting -ln(1-f) versus reaction time (see Figure 3-5). It happened that at the concentration of 11g(CA+SMA)/100ml DMF the curve is nearly linear. The production of graft copolymer, therefore, helps disperse the homopolymers so to give higher reaction area. This is supported by the gradual transition of the solution clarity from opaque to clear. There is about one fold increase in the reaction area from the beginning to the grafting conversion of 75% since the reduction of $\overline{M}_w^f / \overline{M}_w^0$ in equation 4-9 is close to half at that conversion. However, such dispersion power from the graft copolymers seems to disappear at higher polymer concentration. There is an obvious deviation from the linear relationship at a concentration of 14g/100 ml. The grafting reaction solution never turned clear. The α_p factor in equation 3-9 could be responsible for such behavior. The explanation is that the graft copolymer present at the interface may block somehow the chance of free chains to react. Such blocking action should increase with polymer concentration. As a result, more reaction is given to the graft copolymers at the same grafting conversion as compared to the situation of lower polymer concentration.

It is to point out here that the presence of blocking effect by the graft copolymers is unfavorable for homopolymer solubilization since the effective chain length of the graft copolymer is reduced (see more detailed discussion in chapter 4). As a result, there is a reduction on the solubilization ability of graft copolymers for the free polymers. Tests of free SMA solubilization by comparing the optical clarity of cast film from acetone-water mixture solvent (96% acetone) are shown in Table 3-3. The transparency of the films comes from the homogeneous solubilization of the free SMA into the domains of the grafted SMA Only if the size of domains is well below the wavelength of visible light (see more detailed discussion in chapter 4). We saw from Table 3-3 that the solubilization power of the graft copolymers produced at the highest polymer concentration is less than the other two. Too high a polymer concentration, therefore, is not favorable for producing compatibilized blends with homogeneous phase size.

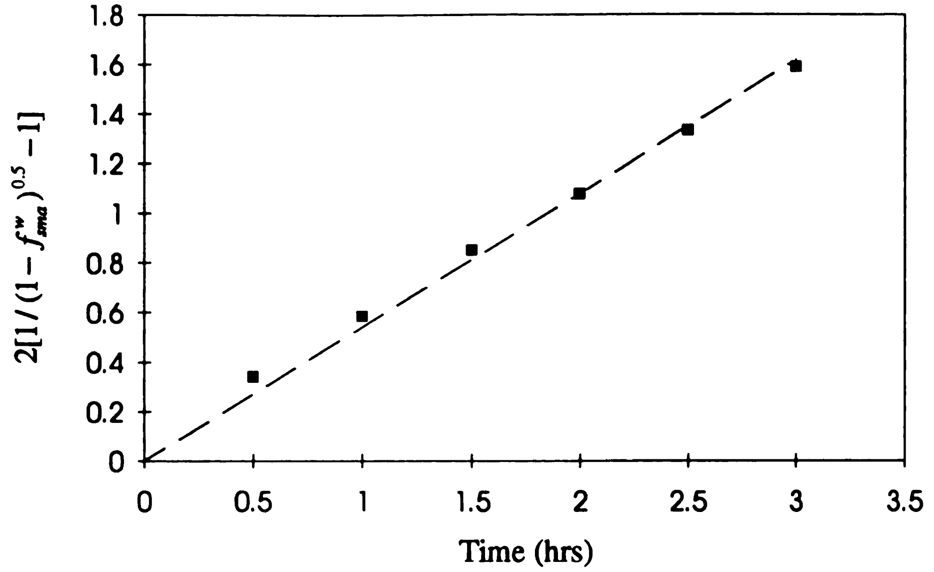

Figure 3-4 Linear fitting for homogeneous grafting reaction showing constant reaction rate

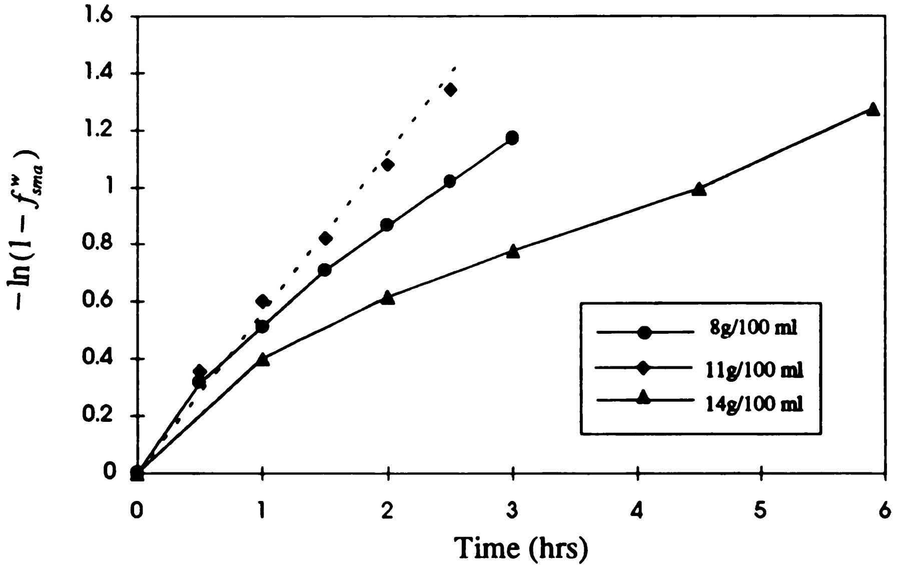

Figure 3-5 Change of $-\ln(1-f^w_{SMA})$ with reaction time at three concentrations

Table 3-3 Film clarity of reaction products prepared at three polymer concentrations*

8g/100 ml	f_{SMA}^{w}	0.27	0.40	0.51	0.58
	clarity	opaque	translucent	transparent	transparent
11g/100 ml	f_{SMA}^{w}	0.30	0.45	0.56	0.66
	clarity	opaque	translucent	transparent	transparent
14g/100 ml	f_{SMA}^{w}	0.33	0.46	0.54	0.63
	clarity	opaque	opaque	translucent	transparent

* Films cast onto glass plate at 80°C, all transparent films have blue tint

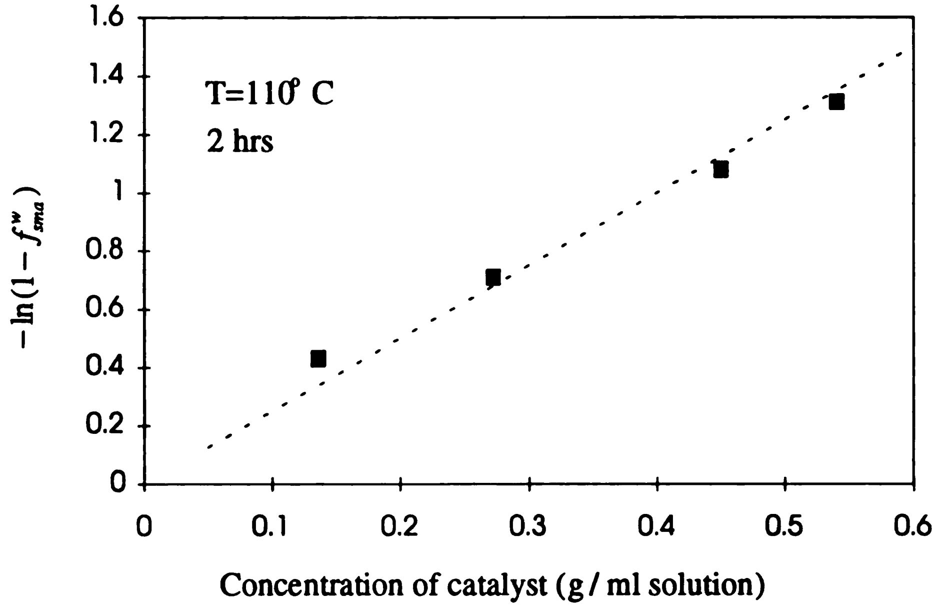

Figure 3-6 First order dependence of reaction rate on the concentration of DMAP catalyst

3.2.1.4 Effect of catalyst concentration

Changing the concentration of the catalyst has little effect on the phase separation of CA and SMA. At a polymer concentration of 11g/100 ml DMF, the increase of SMA grafting conversion is very close to first order with the concentration of free SMA. We can use the same kind of plot as in Figure 3-5 to see the dependence of reaction rate on the concentration of the catalyst. Figure 3-6 shows a first order dependence of the reaction rate on the concentration of DMAP catalyst. The reaction rate, therefore, is directly proportional to the concentration of the catalyst.

3.2.1.5 Effect of reaction temperature

The effect of reaction temperature on the grafting reaction comes from two factors: reaction kinetics and phase heterogeneity. The change of grafting conversion with temperature is shown in table 3-4 for a polymer concentration of 11g/100ml DMF. There is quite an influence of the reaction temperature on the rate of SMA grafting conversion.

Table 3-4 Effect of reaction temperature on the grafting conversion of SMA*

Temp. (°C)	91	100	110	125
f^{w}_{SMA}	0.43	0.58	0.66	0.73

* CA:SMA=1:1, reaction time=2.0 (hrs), 05.g DMAP/100 ml DMF

3.2.1.6 Effect of MA content in SMA on the rate of grafting reaction

Immiscibility between CA and SMA reduces with the content of MA in SMA resins. The grafting reaction between CA and SMA132/SMA332 can be analyzed the same way as in the case of CA-SMA232. The overall feature should be the same except that in case of CA-SMA132 the concentration dependence will shift to lower polymer concentration, and in case of CA-SMA332 the concentration dependence will shift to higher polymer concentration. Increased MA content in SMA and the resultant reduction on the immiscibility between CA and SMA will lead to increased rate of grafting reaction. Table 3-5 shows the grafting conversion of CA with three SMAs at the same polymer concentration. The rate of SMA332 grafting conversion is much faster than SMA232, so does SMA232 to SMA132.

Table 3-5 Effect of MA level on the grafting conversion of SMA *

Sample	MA wt %	(g) DMAP/ 100ml DMF	Reaction time (Hrs)	Grafting conversion
SMA132	4.74%	0.5/100	2.0	0.56
SMA232	7.08%	0.5/100	2.0	0.66
SMa332	12.20%	0.2/100	1.0	0.61

* CA:SMA=1:1, T=110°C, 11g (CA+SMA)/100 ml DMF

3.2.2 Effect of small amount water on grafting reaction

Water is an important factor in this grafting reaction system. The presence of water can result in the hydrolysis of anhydride and the ester groups of cellulose acetate. It will also limit the equilibrium grafting conversion of SMA. Table 3-6 shows the loss of the total amount of polymer mass at three water levels. Both the hydrolysis of the anhydride and the hydrolysis of CA are seen from material balance. The partial hydrolysis of the anhydride caused a slight gain in weight for the polymers (compared to anhydrous case). The hydrolysis of CA resulted in a loss of the polymer mass, it is severe at a water/MA molar ratio of 12. Table 3-7 shows the weight loss of CA at two degrees of substitution, remember there is only half amount of CA for the polymer composition shown in Table 3-6. So only a small amount water can be tolerated in this grafting reaction system.

Table 3-6 Weight change of the reaction products at three water levels and reaction times*

Total weight change (%)		1 hr	2 hrs	4 hrs
H_2O/MA	0	-1.0	-1.1	-1.1
(mole/mole)	6	-0.71	-0.73	-0.80
	12	-1.9	-3.7	-7.7

* T=110°C, (SMA+CA+DMAP)/DMF=(5+5+0.5)/100 (g/ml)

Table 3-7 Weight change of CA at two degrees of substitution

D. S.	unit weight	unit wt. change
1.0	202	-23.8%
2.0	244	-7.9 %
2.5	265	basis

Table 3-8 shows the effect of small amount water on the grafting conversion of SMA. The addition of small amount water caused steady increase on the grafting conversion of SMA. It is, therefore, necessary to control the amount of water in the reaction system even though it is only a small amount. The highest water amount in Table 3-8 corresponds to a water content of 0.45 wt% in DMF. Fortunately, the amount of water in DMF can be readily controlled below 0.5%.

Table 3-8 Effect of small amount water on the grafting conversion of SMA*

H_2O/MA (molar)	0.0	4.0	6.0
f^{w}_{SMA} (1 hour)	0.45	0.48	0.50
f^{w}_{SMA} (2 hours)	0.66	0.70	0.71

* T=110°C, 5.5+5.5+0.5 (CA+SMA+DMAP)/100 ml DMF

3.3 PROPERTIES OF THE GRAFTING REACTION PRODUCTS

The properties of the grafting products depend on the phase size and phase arrangement of CA and SMA in the final products. The inclusion of SMA is meant to improve the performance of CA. It is therefore necessary to disperse SMA into the CA matrix and to have fine dispersion. Acetone is the most common solvent used for CA in film casting and fiber spinning, it is fortunate that SMA is also soluble in acetone. As were shown in chapter 4 films cast from acetone-water mixture solvent gave the desirable matrix phase of CA. A fine and uniform solubilization of ungrafted SMA into the domain of the grafted

SMA chain segments were obtained when the grafting conversion of SMA is above a value of around 50%. Under such conditions, cast films retained optical clarity (with blue tint) since the domain size of the SMA phase is well below 0.1 micron. Property evaluations in the form of cast films were done with such pre-requirements.

3.3.1 DEP as plasticizer

Diethyl phthalate (DEP) is a good plasticizer for CA. The presence of DEP helps increase the toughness of CA films or molding parts. It is essential to have plasticizer in molding formulations for better processability and thermal stability. In this CA-SMA system, DEP is found to be a good plasticizer for both CA and SMA. The effect of DEP is therefore also considered in property evaluation. Table 3-9 shows the reduction of the glass transition temperature (T_g) of SMA with DEP.

Table 3-9 Glass transition temperature of SMA in the presence of DEP

DEP/SMA (g/g)	0.0/1.0	0.1/1.0	0.2/1.0	0.3/1.0	0.4/1.0
T_g (°C)	118	86	65	56	51

Figure 3-7 shows the DSC scan of the CA films cast at room temperature with different amount of DEP. There is no obvious glass transition for CA under such casting conditions. In the presence of DEP the melting temperature of CA decreases with increasing amount of plasticizer. The crystallinity of CA is completely suppressed at a DEP level of 0.4/1.0 (DEP/CA). Figure 3-8 shows the DSC scan of CA films with different amount of DEP cast at 80°C. Under such casting conditions, there is no time for CA to crystallize. It is interesting to observe the appearance of the glass transition temperature of CA. Figure 3-9 shows the DSC scan of a CA-SMA (1:1) grafting product at different DEP content cast at 80°C. The glass transition temperature of SMA is much reduced as the amount of DEP increases. There is quite a amount of DEP partitioned in the SMA phase. It is, however, difficult to tell exactly how much DEP is in the SMA phase since the glass transition temperature of CA is not clearly seen and the exact amount of DEP is not known for the isothermal step needed in the DSC scan in order to remove the moisture. It is also interesting to see the melting like endotherm at a temperature of around 160°C that falls between the T_g of SMA and the T_g of CA. It is not clear what causes such melting like behavior in the alloy films. Conditioning the sample at 190°C for 15 minutes followed by a cooling rate of 20°C/min removes such endotherm for the unplasticized sample (see Figure 3-10).

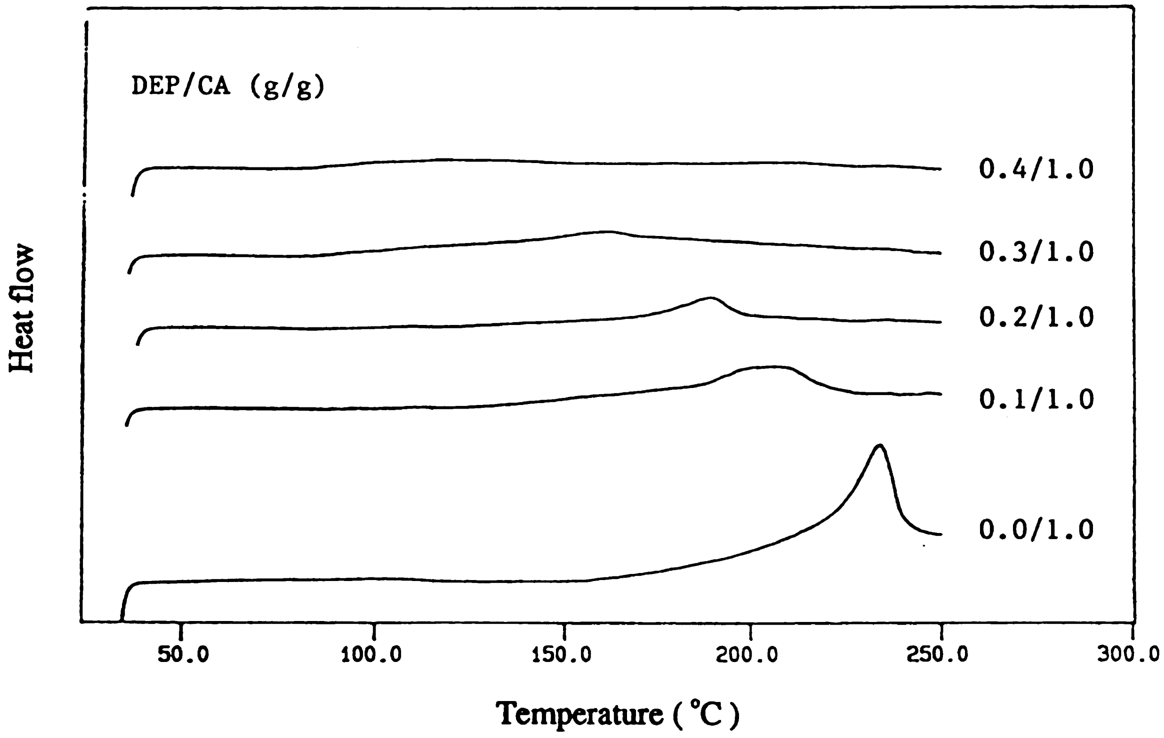

Figure 3-7 DSC scan of the CA films cast at room temperature with different amount of DEP

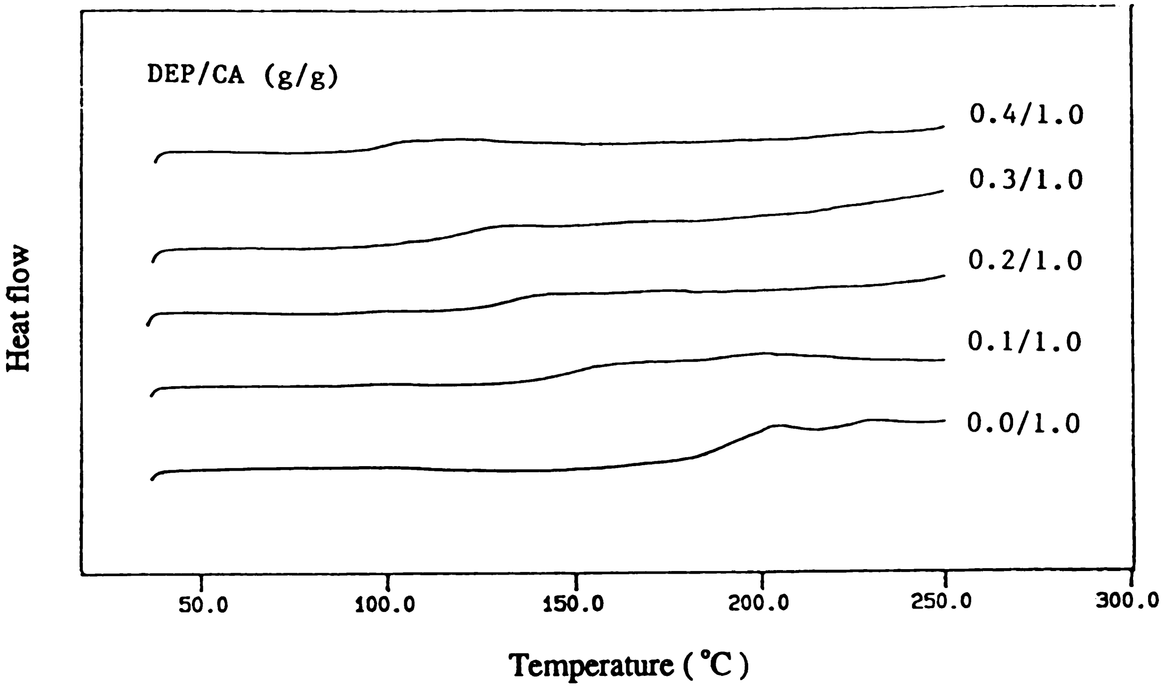

Figure 3-8 DSC scan of CA films with different amount of DEP cast at 80°C

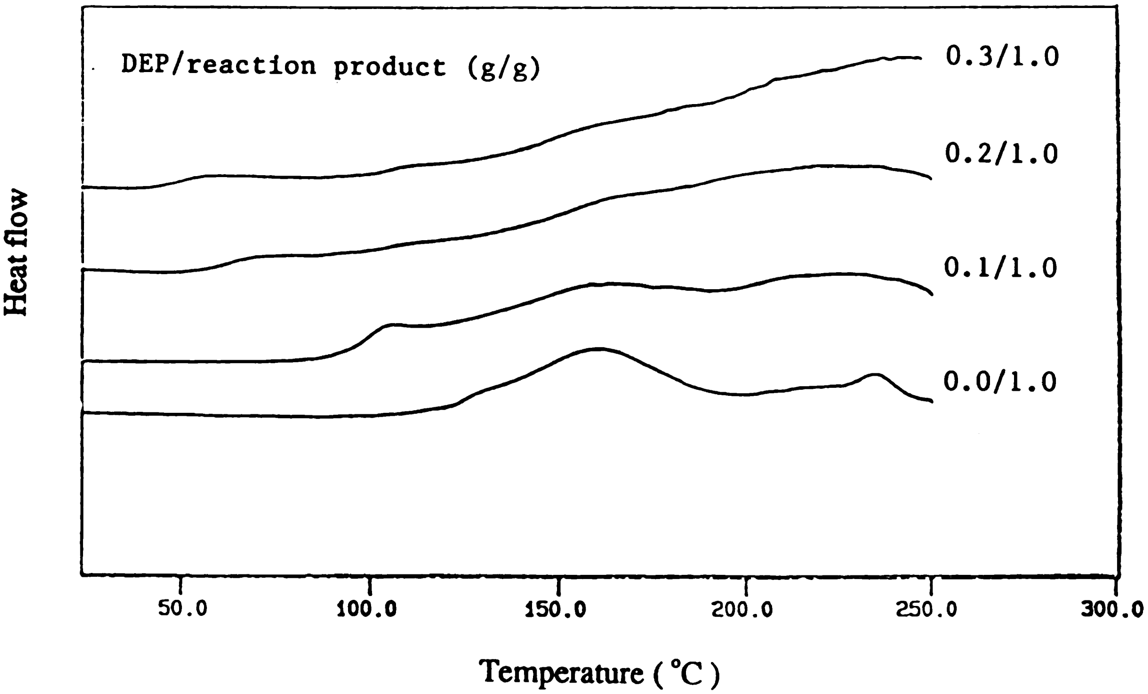

Figure 3-9 DSC scan of CA-SMA grafting product at different DEP content cast at 80°C

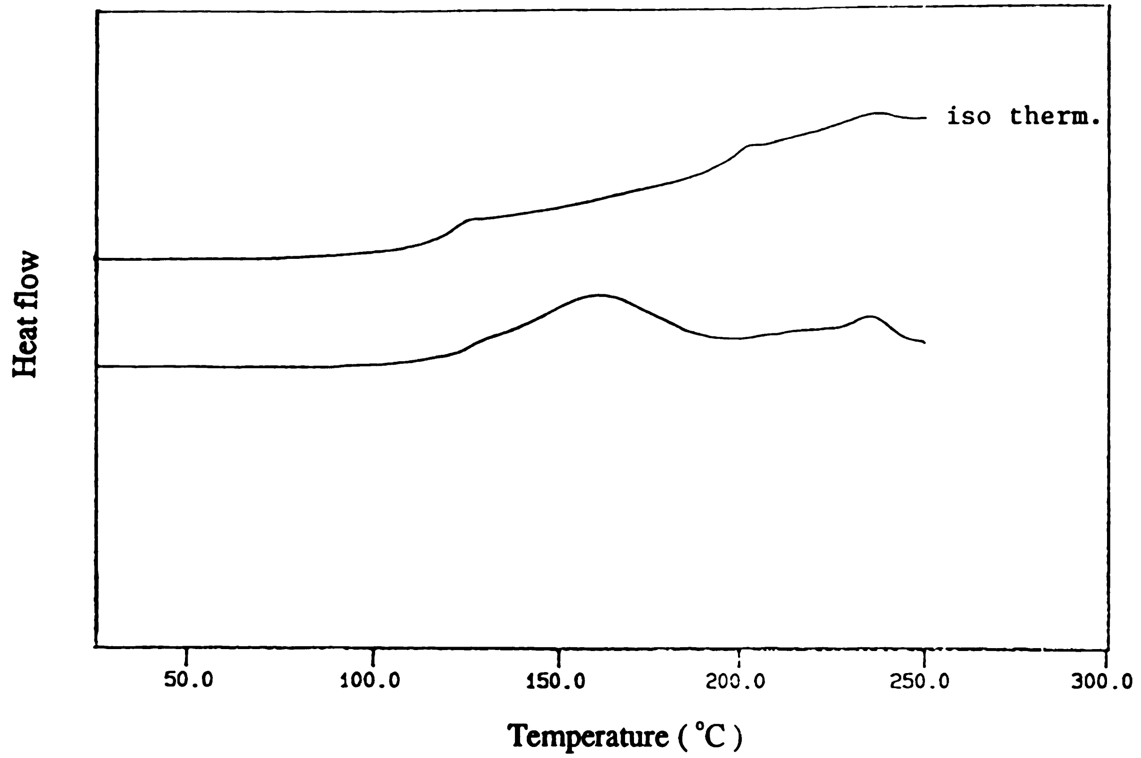

Figure 3-10 DSC scan of film samples with/without isothermal at 190°C for 15 minutes

3.3.2 Tensile properties

One of the most important measures for the compatibilized blends is of tensile properties. According to current understanding, there is a certain degree of demixing between the uniformly solubilized free chains and the corresponding chain segments of the graft copolymers in the microdomains (see background literature of chapter 4). The direct consequence of such demixing could be the loss of tensile strength. The seemingly compatibilized blends, i.e., through the observation of optical clarity, does not necessary possess desirable tensile properties. Tensile properties of the reaction products (CA:SMA=1:1) in the form of cast films were measured with the SMA grafting conversions of 56% and 66% at equal amount of CA and SMA. Cast films of CA were tested for comparison. Since the presence of non-equilibrium factor is always there in the fast casting process, no attempt was made to look into the equilibrium properties. Table 3-10 shows the test results with/without plasticizer. It can be seen that there is basically no difference for the two alloy films at two SMA grafting conversion, therefore, there seems to be no reason to pursue higher grafting conversion from the point of view of mechanical properties whence the films exhibit uniform and microscopic phase size. The alloy films show slightly increased tensile strength in contrast to the most dramatic drop in simple blends under such composition, much increased tensile modulus, but of reduced elongation at break. The difference in those properties between the alloy films and the CA films widens as the amount of DEP increases. The most likely explanation is that DEP partitions more into the SMA phase than the CA phase, this seems to be supported by the results of moisture adsorption. Increased tensile modulus and decreased elongation at break are all good for improving the dimensional stability of the new materials.

Table 3-10 Tensile properties of the cast films with/without DEP

sample	DEP/ sample (g/g)	tensile break x 10^3 psi	modu. x10^3 psi	elon.% break	S.D.% tensile	S.D.% modu.	S.D.% elon.
CA:SMA (1:1) f^{w}_{sma}=0.56	0.0	7.5	0.39	3.1	8.6	3.6	15.2
	0.1	6.1	0.36	3.2	7.8	3.2	12.6
	0.2	5.4	0.34	3.5	7.1	3.3	9.6
CA:SMA (1:1) f^{w}_{sma}=0.66	0.0	7.7	0.38	3.3	9.2	3.4	14.4
	0.1	6.2	0.35	3.5	6.3	3.3	13.3
	0.2	5.7	0.34	3.9	7.6	4.1	10.6
CA	0.0	7.1	0.35	5.4	6.0	3.0	11.3
	0.1	6.3	0.29	8.7	4.8	2.9	10.8
	0.2	6.1	0.27	10.1	5.1	2.3	13.1

3.3.3 Moisture adsorption

CA is moisture sensitive. Substantial amount of moisture adsorption causes dimensional stability problem in film and fiber applications. It is therefore important to look at the moisture adsorption of the grafting products.

Figure 3-11 shows the moisture adsorption of CA, cellulose triacetate (CTA), and one reaction product containing 50% SMA, with/without plasticizer. The moisture adsorption of CTA is measured for comparison. As can be seen the presence of 50% SMA in the new product reduce the moisture adsorption nearly by half. The moisture adsorption is lower than CTA. However, there is apparently no synergistic effect on the reduction of moisture adsorption. This is expected since SMA is immiscible with CA. The presence of DEP helps reduce further the moisture adsorption for all three samples.

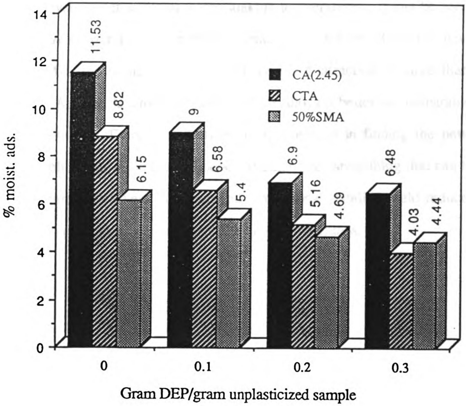

Figure 3-11 Comparison of moisture adsorption for CA, CTA and the alloy

3.3.4 Dimensional stability

The dimensional stability of CA is shown by its dimensional change (contraction) in contact with water. In case of film sample, uneven exposure of film surface to water, i.e., water drop on the surface, can destroy the smoothness of the film. For potential applications in textile fibers, the dimensional stability at increased temperature is extremely important. One of the driving forces in this study is to improve the dimensional stability of CA so that it can have the performance comparable to CTA. The commercial casting process for CTA fiber involves the use of methylene chloride which is environmentally unfriend. Acetone used for CA is a much better solvent in that regard.

The change of the dimension of film samples under water soaking condition at various temperatures can be used as a measure of the dimensional stability of the new materials. Figure 3-12 to Figure 3-15 show the percentage contraction of film samples of different DEP levels under different water soaking temperatures. It can be seen that the inclusion of SMA substantially improves the dimensional stability of the CA based alloys, i.e., at 50% SMA, the reduction of the dimensional contraction is more than 50% in comparison to CA. The dimensional stability of the alloys is better or comparable to CTA at various conditions. There is, therefore, a big potential in finding the new grafting products for applications in films and fibers. Another interesting thing that can be looked at is in new membranes where the improved dimensional stability could reduce the skin layer compaction problem in conventional CA based membranes.

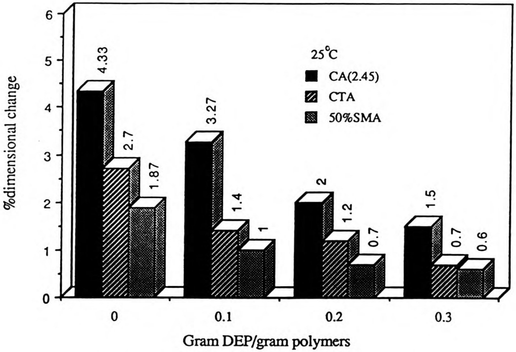

Figure 3-12 Comparison of dimensional changes at 25°C

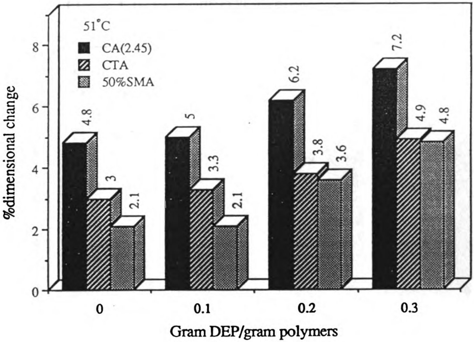

Figure 3-13 Comparison of dimensional changes at 51°C

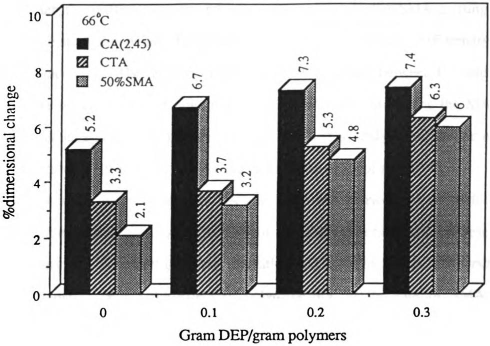

Figure 3-14 Comparison of dimensional changes at 66°C

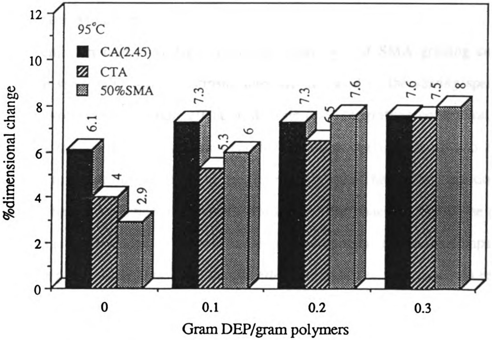

Figure 3-15 Comparison of dimensional changes at 95°C

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3.4 SUMMARY

In this chapter, the grafting reaction and some properties of the CA-SMA grafting reaction products were studied in detail. The phase diagram of the CA-SMA-DMF ternary mixture was constructed first. The dilution of the unfavorable contact between CA and SMA is very sensitive to the amount of polymers dissolved in DMF. Increasing the MA level in SMA reduces the immiscibility between CA and SMA. The analysis on the free energy of mixing by a mean field approach shows qualitatively the order of sensitivity.

The grafting reaction between CA and SMA was carried out successfully in the presence of the DMAP catalyst. The rate of grafting conversion can be described by taking into account the effect of phase separation and the effect of polydispersity of the reactive polymers. While the effect of polydispersity on the rate of SMA grafting conversion can be analyzed exactly, the rate of SMA grafting conversion cannot be described in a simple manner since information on the phase sizes and phase size distribution is not readily available. The complexity of the grafting process is also shown by the dispersion power of the graft copolymers whence they are produced during the course of grafting reactions.

Several parameters involved in the rate expression of SMA grafting conversion were looked separately. (a) The stirring intensity indicated by the stirring speed in the range of 200-600 (rpm) has little effect on the rate of SMA grafting conversion. This is explained by the low interfacial tension and high solution viscosity, these two important factors tend to smear out the effect of mixing intensity. (b) The grafting reaction is very sensitive to the concentration of polymers in solution. The concentration of the polymers in a solution is rather limited in order to avoid too much a reduction on the compatibilizing ability of the graft copolymers, since the net effect of phase heterogeneity is to reduce the effective chain length of the chain segments of the graft copolymers. (c) There is a first order relationship on the intrinsic kinetics between the reaction rate and the concentration of the catalyst. (d) The grafting reaction is very sensitive to the reaction temperature, so is the MA level in SMA. (e) Only a small amount of water is allowed in this grafting reaction system in order to avoid the excess hydrolysis of CA. The presence of a small amount of water promotes grafting reaction.

Tensile properties, moisture adsorption and the dimensional stability were measured for some grafting reaction products in the form of cast films. The film alloys exhibit slightly improved tensile strength, greater tensile modulus and lower elongation at break in comparison to CA, with/without plasticizer. Such tensile properties together with reduced moisture adsorptions are good for improving the dimensional stabilities of the grafting products, i.e., in the presence of 50 % SMA in the alloys, there is more than 50% reduction on the dimensional changes as compared to CA from tests in the form of cast films under various water soaking conditions. The dimensional stabilities of the film alloys are better or comparable to CTA. There is a good potential to find applications for the grafting reaction products in films, textile fibers and separation membranes.

Chapter 4. PHASE BEHAVIORS OF GRAFTING REACTION PRODUCTS

The generation of graft copolymers changes the phase behavior of the ternary mixtures of the grafting reaction products. Controlling the phase size and phase homogeneity of a reaction product is necessary for obtaining many of the desirable performances of the material. It is extremely important to look at that particular aspect of the CA-SMA grafting system. The unique feature of the particular CA-SMA grafting system in terms of phase size and homogeneity shall also be a reflection of the grafting system as was defined in the first chapter. So far no work has been done to look at the phase size and homogeneity in such practical system.

4.1 BACKGROUND LITERATURE

Ternary blends (A+A-g-B+B) are bounded by two extremes of A+B and A-g-B. For immiscible blends, the addition of a small amount of (<10%) block or graft copolymers to the binary blends helps reduce the size of the dispersed phase substantially on the macroscopic scale and improve the mechanical properties of the blends [Locke and Paul, 1973; Meier, 1991]. There is a large body of experimental evidence supporting the interfacial activity of block (or graft) copolymers in mixtures with homopolymer. For example, Gaines and Bender [1972] have demonstrated a lowering of polymer melt surface tension on addition of a styrene/dimethylsiloxane copolymer to polystyrene. Addition of only ~0.2% of the copolymer was shown to give a surface tension close to that of polymethylsiloxane. Reactive extrusion has been the dominant way of making various compatibilized blends.

Pure Block/graft copolymers composed of immiscible chain segments form microphase separation (less than 100 nm). There are interesting morphological behaviors associating with pure block/graft copolymers. It has been established that segregated microphases can be sphere, cylinder, lamellae for pure block copolymers. The type of morphology adopted by the copolymer essentially depends on its composition [Gallot, 1978]. Recently, a new morphology named "ordered bicontinuous double diamond (OBDD)" structures were found in starpolymers [Aggarwal, 1976; Alward et al., 1986; Thomas et al., 1986; Kinning et al., 1986], three-component pentablock copolymer [Hasegawa et al., 1983], and linear diblock copolymer [Hasegawa et al., 1987]. The OBDD phase appeared to be the equilibrium morphology existing between cylinders and lamellae [Hasegawa et al., 1987; Herman et al., 1987].

The equilibrium morphologies in the bulk state can be shifted in the presence of a selective solvent as was shown by Inoue et al. [1970], Shibayama et al. [1983] and Hashimoto et al. [1983]. Cowie [1982] gave a review on the effect of solvent on block copolymer system. Figure 4-1 illustrates three morphologies (OBDD not listed) as well as the effect of selective solvent.

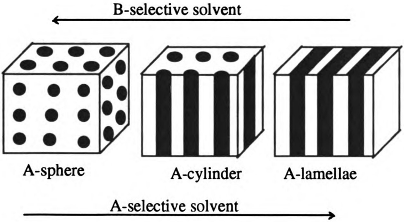

Figure 4-1. Idealized morphologies and the effect of solvent

Meier [1967, 1969, 1973], Helfand [1976, 1978, 1980] and Leibler [1980] have developed statistical mechanics theories to explain quantitatively the equilibrium forces for the three idealized morphologies of block copolymers. The presence of various equilibrium morphologies is associated with the conformational entropy of the chain segments of the block copolymers. Both theoretical prediction and experimental evidences (small-angle neutron scattering) indicated that the chain segments of the block in the bulk are stretched away from the unperturbed state [Meier, 1969; Helfand, 1980; DiMarzio, 1988; Hasegawa et al., 1985; Matsushita et al., 1990].

When homopolymers are admixed with block/graft copolymers (A+A-b/g-B or B+B-b/g-A or A+A-g-B+B), the homopolymers may or may not be solubilized uniformly into the microdomains of the block/graft copolymers, the so called *solubilization phenomena*. *Solubilization phenomena* were studied mostly with block copolymers of a narrow molecular weight distribution made by anionic polymerization. Solubilization of A by A-b-B was reported in an early work by Inoue et al. [1970], in which mixtures of styrene/isoprene diblock copolymer with polystyrene and/or polyisoprene were examined for optical clarity of toluene-cast films and for the microstructure by electron microscopy. The results, though not quantitative, suggest that the amount of solubilized homopolymer could be 2-3 times the volume of the like copolymer block when the corresponding molecular weight ratio was around unity, while films containing a much higher molecular weight homopolymer were invariably opaque. Skoulios et al. [1971] used small angle x-ray scattering (SAXS) and visual observation to determine the solubility of polystyrene of different molecular weights in the styrene domains of a styrene/(vinyl-2-pyridine) diblock copolymer, the vinyl-2-pyridine block was swollen with octanol. On addition of the polystyrene with a molecular weight equal to the copolymer styrene block, the solubility limit was reached when the volume ratio of the polystyrene to the styrene block was roughly unity, while cloudy macrophase separated mixtures resulted when the polystyrene molecular weight was higher. Ptaszynski et al. [1975] also used SAXS to study mixtures of polystyrene of varying molecular weight with a styrene/isoprene diblock copolymer with block molecular weights 40000 and 50000, respectively. Essentially corroborating the above results, they found that at a fixed homopolymer concentration (15% w/w) the mixtures were transparent until a homopolymer molecular weight of 60000 (i.e., 1.5 times the styrene block length) was reached and thereafter the mixtures were visibly cloudy. With polystyrene of molecular weight 10000, the solubility limit was reached when the polystyrene content was around 30%. Thus it was concluded that the statement that the homopolymer molecular weight must be less than or equal to that of the corresponding copolymer block for solubilization to occur represents a good rule of thumb, but that a certain amount of solubilization occurs even at higher molecular weights. Roe and Rigby [1987] has given an excellent review on the studies of solubilization phenomena of homopolymer-block copolymer systems. Recently, Kinning et al. [1988] pointed out the importance of TEM study on the judgment of solubility limit, since homogeneous solubilization does not necessary lead to transparent films.

The theory on homopolymer solubilization is much less studied as compared to the theories on equilibrium morphologies. Meier's theory [1977] on homopolymer-block copolymer system showed general agreement with experiments, that is the length of the homopolymer has to be of the same order of magnitude or smaller in comparison to the corresponding block length for it be soluble in the microdomains of the copolymers, the solubility limit would decrease with increasing homopolymer molecular weight. There is, however, about an order of magnitude difference on the solubility between Meier's prediction and experimental observations. Roe and Zin [1984] argued that the underestimation by Meier's theory arises because the theory assumes a model in which the homopolymer is uniformly distributed within the microdomain, where in practice it is more likely that the homopolymer will concentrate more toward the center of the microdomain to avoid overly stretching the block chains. Xie et al. [1986] did some work to calculate theoretically the free energy of mixing in case of the localized concentration distribution of the homopolymer. Their studies, though not rigorous because of the self-claimed density profile used in their calculations, showed that the amount of homopolymer solubilization is greatly increased in accordance with Roe and Zin's argument [1984]. They suggested further that there is no solubilization limit if the homopolymer can be solubilized into the domain of the copolymer. Shall and Winey's analysis [1992] showed a more detailed density profile in the extreme case of adsorbing layer of the block junction. Recent experimental studies seem to conform the non-uniform distribution of the homopolymers inside the microdomains of the copolymers [Berney et al., 1988; Winey et al., 1991; Hashimoto et al., 1990]. It is apparent that the study on the solubilization phenomena is far from being complete, both theoretically and experimentally, even for the ideal case of block copolymer systems.

The chain length of the copolymer depends on the structure of the copolymer. For homopolymers and complex copolymer system, particularly graft copolymers of complex structures, there is no theoretical prediction on the extent of homopolymer solubilization. Jiang et al. [1986] reported their studies on the effect of molecular architectures of copolymers on the solubilization of polyisoprene, their study showed clearly that the power of solubilization of copolymers for homopolymers has the sequence of diblock>triblock>four-arm block when the molecular weights of the chain segments of the copolymers are close to each other. Eastmond [1979] and Jiang [1985] studied AB-crosslinked copolymers (ABCP) of relatively complicated structures (somehow similar to graft copolymers of this study). They found that the miscibility between ABCP and homopolymer A is rather limited, macrophase separation occurred.

Graft copolymers formed between two reactive polymers each having large numbers of reactive groups will react further to form new graft copolymers during the course of grafting reaction. The net result is the reduction of the effective chain length of the chain segments of the graft copolymers as grafting reaction continues. On the other hand, the reactive polymers are often highly polydisperse. Polydispersity can cause differences in the average chain lengths between the grafted chains and the ungrafted chains. In chapter 5 it will be shown that there is an upper limit on the extent of grafting conversion for the reactive polymers in order to avoid too high a system's weight-average molecular weight (high viscosity). It is, therefore, very important to know in such a practical system how phase size and phase homogeneity changes with grafting reaction, at what extent of grafting reaction there is homogeneous solubilization in the reaction products. TEM was used as a tool to look at these aspects. The studies on the CA-SMA system shall have general implication for the defined grafting system.

4.2 GRAFTING CONVERSION OF CA VERSUS SMA

The grafting conversion of CA is internally related to the grafting conversion of SMA at given compositions. In the assumed state of homogeneous grafting reaction, we can connect the grafting conversion of CA to the grafting conversion of SMA by

$$f_{CA}^{w} = f_{SMA}^{w} \frac{1-\int_0^{\infty}(1-f_{ref})^{\overline{M}/x}\, W_{CA}(M)dM}{1-\int_0^{\infty}(1-f_{ref})^{\overline{M}}\, W_{SMA}(M)dM} \tag{4-1}$$

$$\overline{M} = M / \overline{M}_n^0 \tag{4-2}$$

where *W(M)* is the weight fraction density function of a molecular weight distribution, x is the molar ratio of the molar concentration of CA divided by that of SMA, f_{ref} is the grafting conversion of the reference SMA chains having a molecular weight of the number-average molecular weight of the starting SMA. Figure 4-2 shows that the percentage conversion of CA is much less than the percentage conversion of SMA for a composition of 0-50% SMA. The grafting reaction products used in this part of the study were made at a concentration of 11g/100ml (polymers/DMF). Phase heterogeneity during the early stage of grafting reaction will affect the actual relationship between the grafting conversion of CA and the grafting conversion of SMA. However, it is believed that such effect is minor even though there is no way to characterize experimentally the grafting conversion of CA.

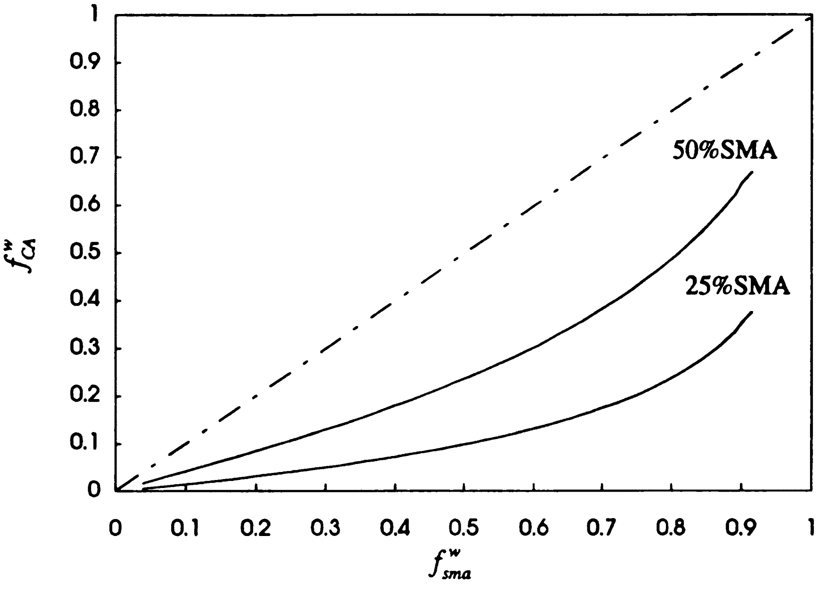

Figure 4-2. Grafting conversion of CA versus that of SMA

4.3 SELECTIVE GRAFTING CONVERSION OF THE HIGH MOLECULAR WEIGHT CHAINS OF THE REACTIVE POLYMERS

The formation of complex graft copolymers in this grafting reaction system has a net effect of reducing the effective chain length of the grafted chain segments. On the other hand, the grafting reaction happens with more grafting conversion of higher molecular weight chain fraction of the reactive polymers. The importance of polydispersity shall not be overlooked in this grafting system. In a homogeneous state, the grafting conversions between two chain fractions having molecular weights of M_i and M_j (CA or SMA) satisfy

$$1 - f_{M_i} = (1 - f_{M_j})^{M_i/M_j} \tag{4-3}$$

This is because the numbers of reactive groups on the chain species are proportional to molecular weight. We can look at the effect of polydispersity in increasing the effective chain length of the chain segments of the graft copolymers by comparing the number-average molecular weight of the free (ungrafted) chains with that of the grafted chain segments. The number-average molecular weights for free SMA and grafted SMA are calculated by

$$(\overline{M}_n^f)_{SMA} = \frac{\int_0^\infty (1-f_{ref})^{\overline{M}} W(M)dM}{\int_0^\infty (1-f_{ref})^{\overline{M}} W(M)/MdM} \tag{4-4}$$

$$(\overline{M}_n^g)_{SMA} = \frac{\int_0^\infty \left[1-(1-f_{ref})^{\overline{M}}\right] W(M)dM}{\int_0^\infty \left[1-(1-f_{ref})^{\overline{M}}\right] W(M)/MdM} \tag{4-5}$$

The ratio of the number-average molecular weight of the grafted SMA chains to that of the free SMA chains is defined as

$$R = \frac{(\overline{M}_n^G)_{SMA}}{(\overline{M}_n^f)_{SMA}} \tag{4-6}$$

Figure 4-3 shows that the number-average molecular weight of the grafted SMA chains is more than twice that of the free chains. The selectivity of the grafting process is quite substantial. If we divide *R* by the average numbers of linkages per grafted SMA chain we have a rough sense of effective chain length (number average) for the grafted and the ungrafted. The average numbers of linkages per grafted SMA chain is defined as

$$\overline{n}_{SMA}^{ma} = \frac{C_{MA}^0 f_{ma}}{C_{SMA}^0 f_{sma}} \tag{4-7}$$

It is related to the molecular weight distribution as well as the grafting conversion of the reference chain species by

$$\overline{n}_{SMA}^{ma} = \frac{-\ln(1-f_{ref})}{1-\overline{M}_n^0\int_0^{\infty}(1-f_{ref})^{\overline{M}}\,W(M)/M\,dM} \tag{4-8}$$

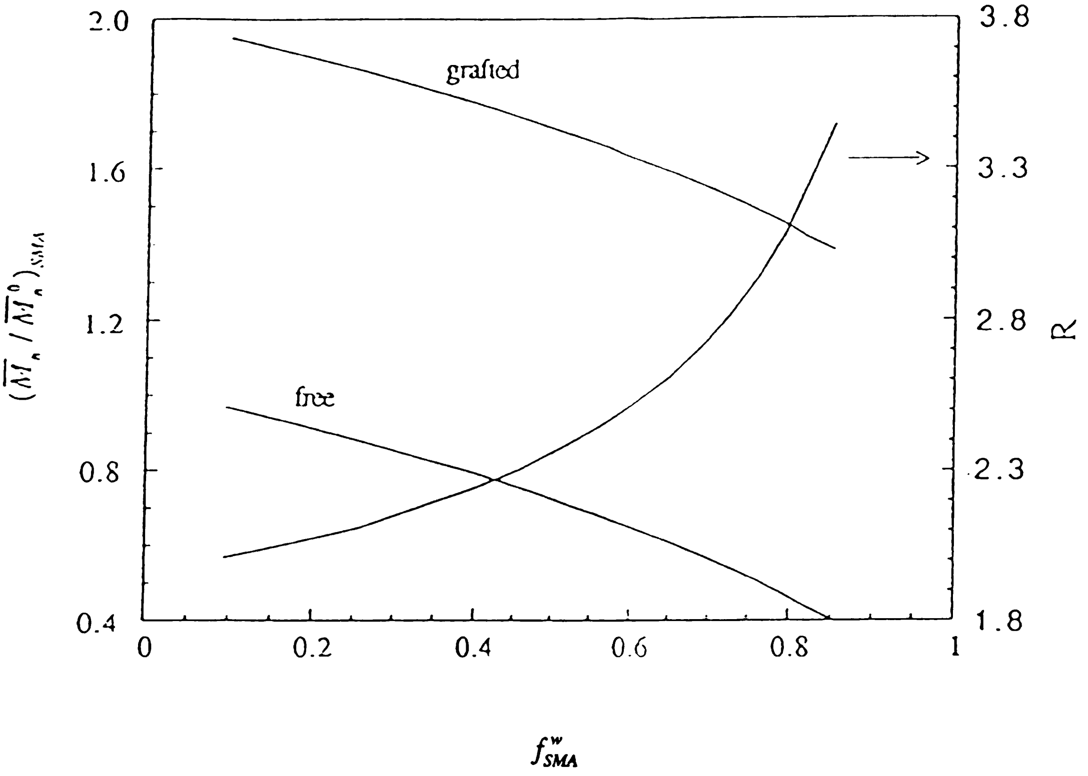

Figure 4-3 Change of the number-average molecular weights for the grafted and ungrafted SMA chains and the ratio of the two with grafting conversion

Figure 4-4 shows the ratio of the effective number-average molecular weight of the grafted chains to the number-average molecular weight of the free chains. We see that such ratio decreases with grafting conversion but is still greater than one (the actual ratio shall be smaller since graft linkage reduces the effective chain length as compared to block linkage). Polydispersity, therefore, shall have a significant effect in the solubilization of free chains into the microdomains of the chain segments of the graft copolymers.

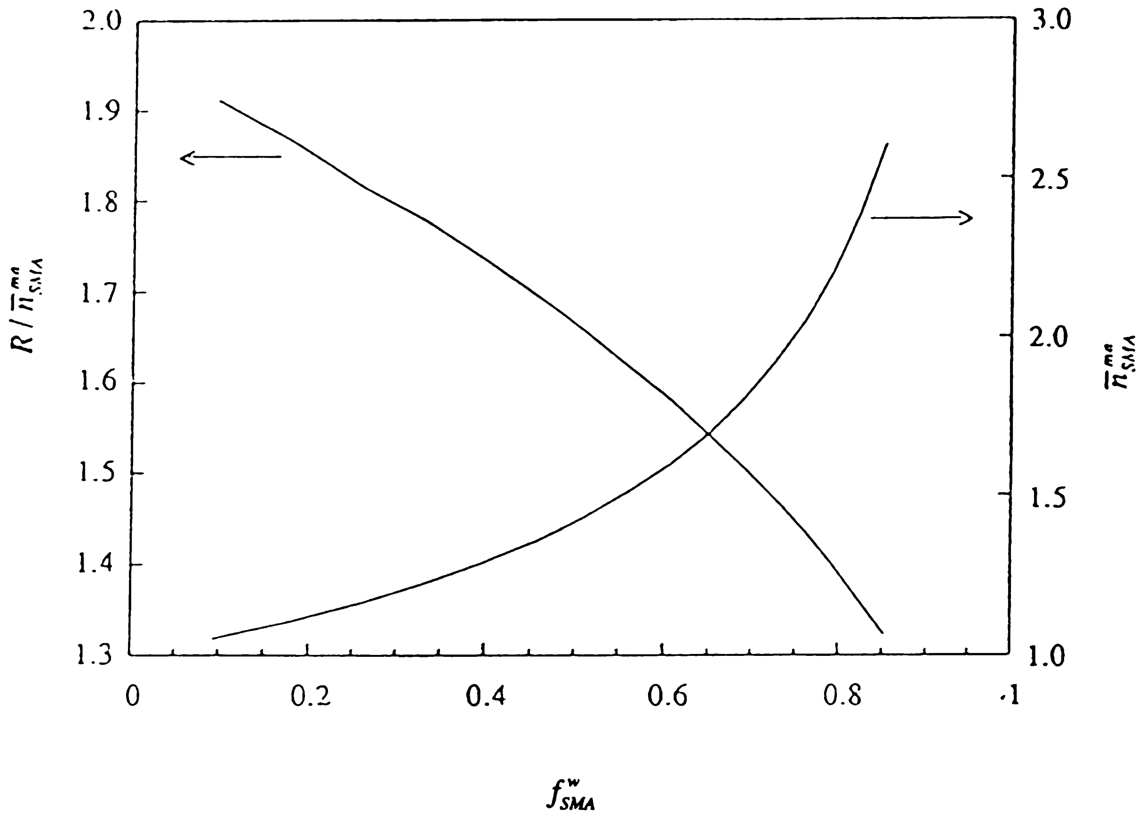

Figure 4-4 Changes of the ratio of the effective number-average molecular weight of the grafted SMA chains to the number-average molecular weight of the free SMA chains and the average numbers of linkages per grafted SMA chain with grafting conversion

4.4 PHASE SIZE AND HOMOGENEITY

Figure 4-5 and Figure 4-6 show two sets of TEM micrographs of the reaction products at different grafting conversions (50% SMA for the first set, 25%SMA for the second set). SMA is the dispersed phase. The films were cast from an acetone-water mixture solvent (96 v% acetone, SMA is swelled only in this mixture solvent). The matrix phase looked homogeneous in the long range. The overall feature of the two sets of micrographs is very similar. Homogeneous solubilization occurs when the grafting conversion of SMA is above a value of around 50%. The composition of SMA has minor effect. At low grafting conversion of SMA (26%, 39%, and 51% of Figure 4-5, 31% and 44% of Figure 4-6), macrophase separation and microphase separation coexist. Films with such phase heterogeneity are not transparent while the others are transparent but with a blue tint. A close inspection on the phase sizes at lower SMA conversions shows a distribution of phase sizes. There is no clear cut of two sizes with order of magnitude difference. The presence of such characteristics cannot be explained simply by the insolubilization of the free chains. Figure 4-7 and Figure 4-8 show two sets of micrographs of the corresponding reaction products cast from THF-water mixture solvent (96 v% THF). The THF-water mixture solvent is close to be non-selective. The SMA phase becomes continuous except for the case of 26% SMA conversion (Figure 4-7). At higher grafting conversion, the phase structures become homogeneous, co-continuous phases were observed. The SMA phase in its matrix state was homogeneous at lower grafting conversion as compared to the case of the dispersed state. There is no separated microphase of SMA. The dispersed CA phase appeared less homogeneous. This is because the grafting conversion of CA is less than the grafting conversion of SMA. Apparently, solubilization of SMA free chain happens at the lowest grafting conversion of SMA. It seems to suggest that there is no solubilization limit when SMA is in its matrix state.

From the four sets of micrographs, we found that phase size homogeneity increases with the grafting conversion of SMA. The homogeneity of SMA was observed at lower conversion in the continuous state than in the dispersed state. The formation of more and more complex graft copolymers causes a net reduction of the chain segments of the graft copolymers as was discussed earlier. Such a reduction of the block length of the graft copolymers does not reverse phase homogeneity with grafting conversion. The desirable feature of this grafting reaction system is explained by the grafting conversion of more high molecular weight chain fractions of the reactive polymers. To illustrate the importance of the selectivity of grafting reaction because of polydispersity, the free SMA

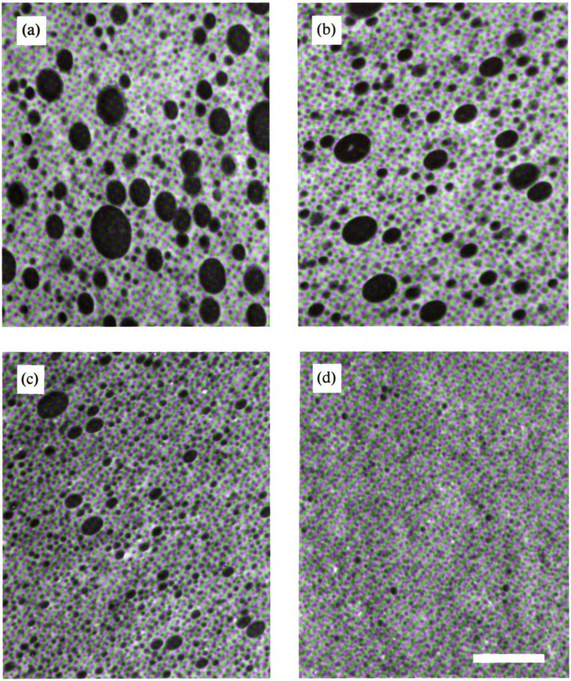

Figure 4-5 TEM micrographs of films cast from acetone-water mixture solvent (96:4) at 70°C with 25% SMA in the alloy. f^{w}_{SMA}: (a) = 0.26, (b) = 0.39, (c) = 0.51, (d) = 0.74. (bar length = one micron).

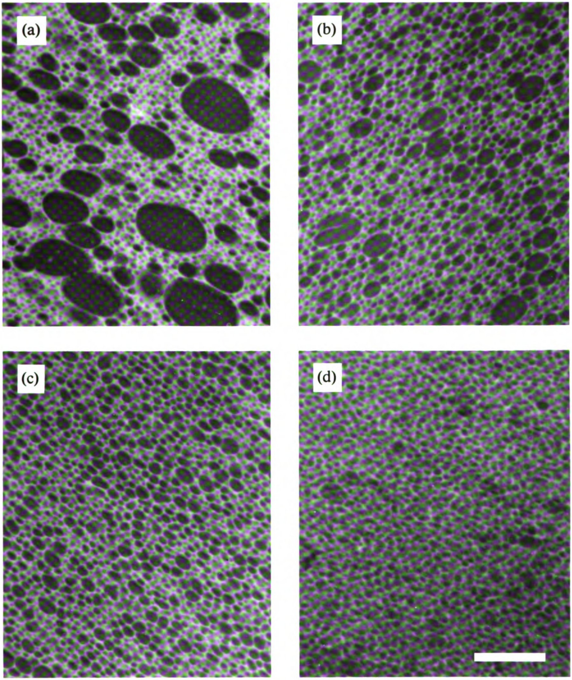

Figure 4-6 TEM micrographs of films cast from acetone-water mixture solvent (96:4) at 70°C with 50% SMA in the alloy. f^{w}_{SMA}: (a) = 0.30, (b) = 0.45, (c) = 0.56, (d) = 0.66. (bar length = one micron).

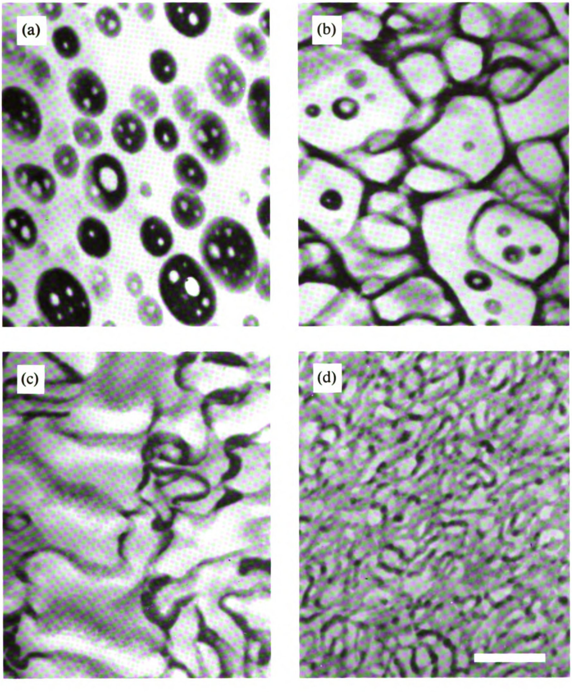

Figure 4-7 TEM micrographs of films cast from THF-water mixture solvent (96:4) at room temperature with 25% SMA in the alloy. f^{w}_{sma}: (a) = 0.26, (b) = 0.39, (c) = 0.51, (d) = 0.74. (bar length = one micron).

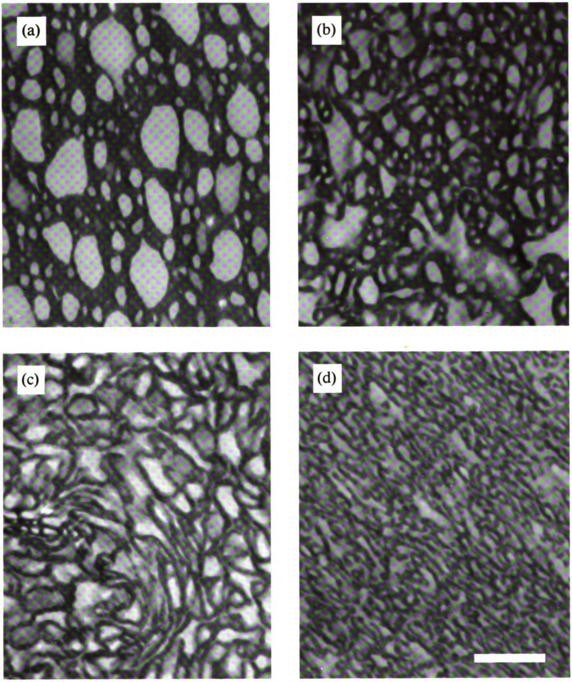

Figure 4-8 TEM micrographs of films cast from THF-water mixture solvent (96:4) at room temperature with 50% SMA in the alloy. f^{w}_{SMA}: (a) = 0.30, (b) = 0.45, (c) = 0.56, (d) = 0.66. (bar length = one micron).

in one reaction product (Figure 4-6 (d)) was extracted and the remaining was mixed with free SMA without going through grafting reaction (The SMA was treated the same way as in the grafting reaction of the reaction product except for the absence of CA so to eliminate the possible change of SMA) to arrive at the same composition. The cast film from acetone-water mixture solvent at the same condition (Figure 4-6(d)) was no longer transparent. Insolubilization or less solubilization of the high molecular weight chains of SMA is seen from such a test. This simple test tells the importance of the effective chain length of the free chains and that of the chain segments of the graft copolymers. It also tells that adding small amount reaction products of high graft copolymer content to the blend of CA/SMA may not provide the same kind of compatibilzing effect by the graft copolymers as the one produced by a reactive extrusion process.

Homogeneous solubilization happened at relatively high grafting conversion. Given the results on the change of system's weight-average molecular weight (WAMW) with grafting conversion, there is, therefore, at equal amount of CA and SMA only a narrow range of SMA grafting conversion from a Practical point of view, so that homogeneous phase size is obtained while the WAMW of the reaction product is still kept at a reasonable value.

4.5 PHASE SIZE AND STABILITY

The appearance of macrophase separation from visual observation of optical clarity and electron microscopy is often used as evidence of the insolubilization of homopolymers or of solubility limit on the amount of homopolymer that can be solubilized if the homopolymers are initially solubilized. The unfavorable enthalpic interaction between basic structural units of chain A and chain B of the block copolymer results in microphase separation and the growth of domain size. The loss of conformational entropy of the confined chains exerts an opposing force for the growth of domain size. Morphological behaviors of block copolymers result from the minimization of the conformational entropy of the confined chain through spatial arrangements [Meier, 1967; Helfand, 1976]. In the presence of homopolymers, the driving force for homopolymer solubilization has to do with the conformational entropy of both confined and free chains. It is the relaxation of the confined chains in the presence of homopolymers that results in homopolymer solubilization. Relaxation because of the presence of homopolymers causes more freedom of spatial arrangement. The homopolymer chains have to be disturbed at the same time, and therefore has less degree of freedom as compared to the undisturbed state. There is a net increase of the combined conformational entropy for the confined chains and the homopolymer chains. The system takes the form of uniform phase size so to have a free energy minimum if the reduction of free energy is more than linear to the amount of solubilized homopolymers. However the reduction of free energy may not be necessary more than linear since the relaxation comes from both phases. Therefore heterogeneous phase size is not necessary an indication of homopolymer insolubilization. On the other hand, as more and more homopolymers are solubilized into the domains of graft copolymers, the driving force for homopolymer solubilization may become so small from a relaxation point of view that dynamic force can easily distort the equilibrium phase structure.

Let us take a look at the dispersed spheres (chain A) in the case of slow relaxation of the confined chains. Let $\overline{V}_A$ be the volume of the confined A chain in its compacted state, $\overline{S}_A$ be the interfacial area per confined chain. We have from material balance

$$\frac{1}{6}\pi d^3 = \frac{n_c \overline{V}_A}{f_A^w} \tag{4-9}$$

The surface area of the sphere becomes:

$$\pi d^2 = n_c \overline{S}_A \tag{4-10}$$

Dividing equation 4-9 by equation 4-10, we have

$$d = \frac{6}{f_A^w} \frac{\overline{V}_A}{\overline{S}_A} \quad (4\text{-}11)$$

If the interfacial area per confined chain does not change with the solubilization of homopolymers, the diameter is reversibly proportional to the fraction of the copolymer. Figure 4-9 shows the change of domain size with the content of copolymer. It is important to point out that the change of phase size is the most drastic at low copolymer content. Therefore the phase heterogeneity on the order of a few time differences in sizes does not necessary mean that the homopolymer is not solubilized in the copolymers. It does tell that the driving force for solubilization is weak if there is no solubility limit for the given system at low graft copolymer content.

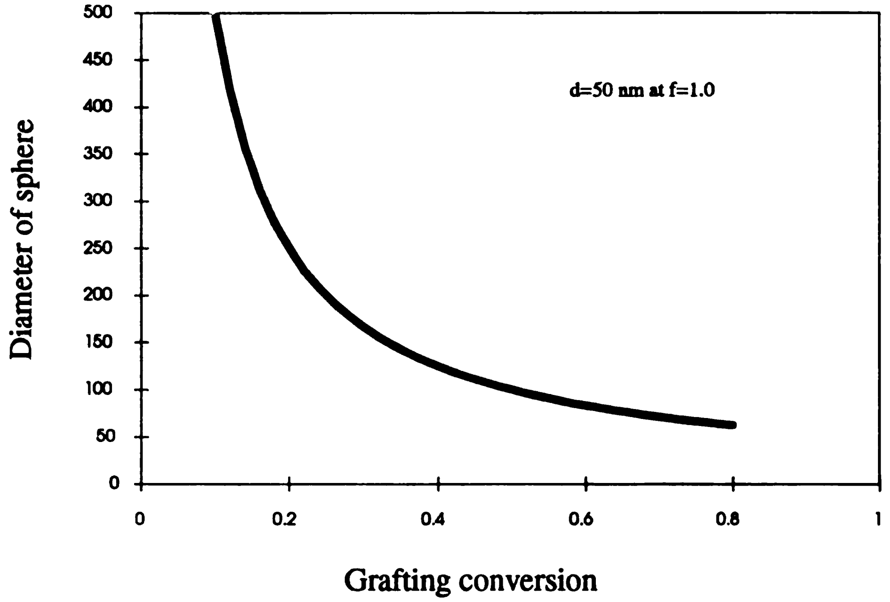

Figure 4-9 Phase size .vs. copolymer content

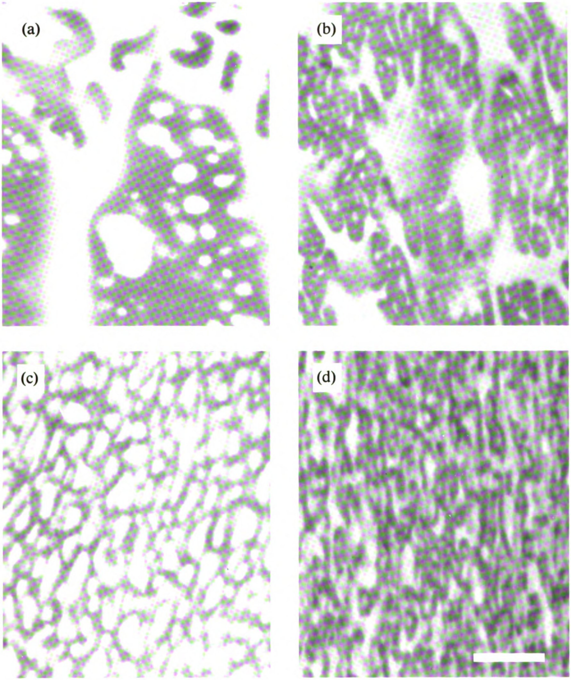

Figure 4-10 TEM micrographs of cast films from THF-Water mixture solvent cast with a film applicator and dried at 50°C. f^{w}_{sma}: (a) = 0.30, (b) = 0.45, (c) = 0.56, (d) = 0.66. (bar length = one micron).

Figure 4-10 shows a set of TEM micrographs for films cast from THF-water mixture solvent with a film applicator. The solvent was evaporated in less than 10 minutes at 50°C. The external force from the film applicator caused drastic change for the samples with macrophase separation. The phase homogeneity at higher grafting conversion was preserved even though the microphases are stretched along the moving direction of the applicator. This set of experiments shows clearly the weak driving force in maintaining the phase structures at low grafting conversion of SMA.

4.6 SUMMARY

Homogeneous phase structures appear in the grafting reaction product of CA-SMA as the grafting conversion of SMA increases. There is a substantial amount of free chain solubilization into the microdomains of the graft copolymers. The formation of complex graft copolymers at high grafting conversion does not lead to the insolubilization of free chains. Such a desirable property is explained from the more grafting conversion of the high molecular weight chain fraction of the reactive polymers, a unique feature for synthesizing graft copolymers in the defined grafting system. While the driving force for homogeneous solubilization at low content of graft copolymers is not clearly understood, the dynamic force can be important in causing the phase size distribution of the dispersed phase. This part of the study shows the importance of polydispersity in promoting homogeneous phase size of the grafting reaction system.

Chapter 5. THEORETICAL ANALYSIS OF THE BRANCHING PROCESS OF GRAFTING REACTION BETWEEN TWO REACTIVE POLYMERS

Graft copolymers formed during the grafting reaction of CA-SMA are capable of grafting further due to the large numbers of reactive groups on the backbones of both CA and SMA. The buildup of the complexity of the graft copolymer structures during the grafting process raises an immediate concern as to how far the grafting reaction can be carried out, since too high a molecular weight average is generally undesirable from a processing point of view. It is important to know theoretically how the system's molecular characteristics changes with grafting reaction, at what extent of grafting reaction the system starts to gel. One of the difficulties in understanding such complex system is the lack of adequate techniques to characterize the grafting reaction products. In case of CA-SMA, the association behavior of the grafting products caused difficulty doing GPC analysis. Theoretical analysis of the CA-SMA system can be done on a more general basis, in which the nature of the grafting chemistry is less important as long as it provides grafting linkages irreversibly.

5.1 BACKGROUND LITERATURE

The term branching process was used by Gordon to describe the development of polymer species in systems capable of gelation. Figure 5-1 is an illustration of branching process of an aggregation system from computer simulation. The grafting process of this grafting system can best be described as a branching process when we neglect the presence of rings.

Figure 5-1. Illustration of the branching process after transformation of the molecular forest of trees into a forest of rooted trees (with permission from Richard F. Voss and Elsevier Science Publishers B. V.)

Theoretical works on the branching process of network forming systems have been done extensively over the past decades. The works are exclusively on the polymerization of monomers to form a three dimensional network at the end of the polymerization. The important things for the characterization of the polymerization system are the content of polymer species of different sizes, molecular weight distribution, molecular weight averages, gel point, sol-gel relationship, and finally the crosslinking density of the network.

Theoretical analyses can be classified into: statistical, percolation, and kinetic. The statistical approach can be classified further into four techniques: (1) Flory and Stockmayer's classic combinatorial method [Flory, 1941, 1953; Stockmayer, 1943, 1944, 1952, 1953]; (2) Gordon's cascade theory [1962]; (3) Macosko and Miller's recursive method [1976]; (4) Durand and Brumeau's approach [1982]. These methods differ in their language and power. Gordon's theory used abstract vectorial probability generating functions. The method is powerful but difficult like the combinatorial method. Macosko and Miller's method uses conditional probability. It is mainly useful for deriving the molecular weight averages and the gel point of the polymerization process. Extension to the consideration of unequal reactivity, intrinsic [Case, 1957; Miller and Macosko, 1978] and/or induced such as the first-shell substitution effect [Grodon and Scantlebury, 1964, 1966; Sarmoria and Miller, 1991; Dotson, 1992], is readily made from above theories since unequal reactivity affects the equivalent reactive groups as a whole. The consideration of unequal reactivity and substitution effect narrow the gap between theory and many actual polymerization systems.

The most important assumption made in the statistical approaches is of random mixing with reaction control, that is the probability of reaction between two reactive species is weighted according to the equivalent numbers of reactive sites on the two species. The equal accessibility of space (any lattice site) by any species represents one extreme case, another extreme case is represented by fixed lattice sites where the species is stuck to it. Simulations on the branching process using a computer on the constructed lattice sites, namely the percolational analyses were developed by Staufeer et. al. [1982], Boots et al. [1985] and Herrmann et al. [1982, 1983]. Difference between the classical theory and the percolation model on the scaling behavior near the critical point was observed. Since the motion of chain segment is so restricted, such simulations are perhaps applicable to the situation when a system starts to gel or after the system has already gelled, i.e., some curing system [Dusek, 1986]. Nevertheless, present percolation models are far from simulating actual network formation, since the bonds are too rigid, the movement of molecules is too suppressed and the chemical rules of bond formation are quite often ignored.

The kinetic approach involves the solution of the differential equations which describe the rate of change of individual species. It is always possible to describe the system based on first principle (material balance) no matter how complex the system is.

The complexity of the problem is embodied in the form of the differential equations, i.e., linear or nonlinear. In the latter case, numerical method is often used to solve the equations. The power of the kinetic approach is best shown in the studies of free radical polymerization of linear chains where complex situations such as the change of kinetic rate coefficients during the course of polymerization, the presence of several mechanisms during the course of polymerization (chain transfer, different ways of termination), changing monomer concentration, reactor selection (PFR, CSTR), can be readily considered in the differential equations [Hamielec and MacGregor, 1983]. The equal reactivity assumption in the statistical derivation is simply a special case. A large number of ingenious methods, i.e., generating functions, transformations and continuous variable approximations [Ray, 1972], have been applied to the solution of the batch, free radical polymerization kinetics for relatively simple system. Numerical method is possible for complex system since the advent of stiff ODE codes [Hindmarsh, 1974]. Skeirik and Grulke [1985] developed a calculation scheme to reduce the extremely large number of differential equations by grouping chain lengths into equal sized groups and still retain the flexibility of the initial kinetic formulations.

Kinetic formulation of nonlinear condensation system was referred to briefly without details or development by Stockmayer [1943]. Stafford [1981] derived a distribution function for a self condensing $A_1 + A_2 + A_i + \cdots$ system by a kinetic approach and extended to several cases including a stoichiometric mixture of $A_1 + A_2 + A_i.+ \cdots + B_1 + B_2 + B_j + \cdots$. In a closely related field on cluster formation or aggregation process, Smoluchowski's coagulation equation (kinetic approach) has been used to study the formation of clusters in the coaggregation process of particles. Computer programs based on kinetic aggregation process (including many of the percolational models) have been developed to study the scaling exponent of the mass versus the mean length of the cluster, the so called fractal [Stanley, 1984]. Ziff [1984] gave a broad discussion on the aggregation kinetics via Smoluchowski's equation. Recently, Tobita and Hamielec [1989, 1991] proposed pseudokinetic rate constant method to simulate network formation in free radical polymerization. Tobita [1992] applied their kinetic theory to emulsion copolymerization of vinyl and divinyl monomers and found highly heterogeneous network structure.

A kinetic approach is developed in this part of the study for the grafting reaction system of two reactive polymers each having large numbers of reactive groups. General discussions were given of the effect of various parameters on the branching process.

A limiting case of infinite numbers of reactive groups on both reactive polymers is the defined system in this part of the work, practically the number of reactive groups on both polymers can be considered as infinite when the numbers of reactive groups are large, say, more than 50 (see discussion section) so far as grafting reaction is concerned.. No theoretical analysis has been given to such system. CA and SMA is one particular case that falls to such system.

5.2 THEORETICAL DEVELOPMENT

Grafting reactions are generally heterogeneous since most polymers are immiscible. Heterogeneity complicates the analysis. Theoretical Analysis assuming a homogeneous grafting process represents the limiting case, homogeneous grafting can be found in solution processes. Since the numbers of reactive groups on the polymer chains are so large, the substitution effect can be neglected. A homogeneous, kinetically controlled, irreversible grafting reaction is considered. Two assumptions are made in the kinetic approach: (1) equal reactivity of the reactive groups on the polymer backbones; (2) no intramolecular reaction. Neglecting temporarily the effect of intramolecular reaction does not affect us in finding out the main features of the grafting process. The importance of intramolecular reaction will be discussed in chapter 6. All discussions are made in respect to the percentage (weight basis) conversion of one reactive polymer to graft copolymers since that information can be obtained by extraction study, it is perhaps the only information one can obtain in grafting system.

5.2.1 Monodisperse reactive polymers

5.2.1.1 Balance equation

Let A and B represents the two reactive polymers having large numbers of reactive groups *a* and *b* respectively. With the assumptions mentioned above, the kinetic equations which describe the rate of change of the concentration of individual species are generalized by

$$\frac{dC_{ij}}{dt} = \frac{1}{2}\sum_{k=0}^{i}\sum_{l=0}^{j} r_{kl+(i-k)(j-l)} + \frac{1}{2} r_{\frac{i}{2}\frac{j}{2}+\frac{i}{2}\frac{j}{2}} - r_{ij+ij} - \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} r_{ij+pq} \tag{5-1}$$

where subscript notation *ij+pq* means grafting reaction of component *ij* with component *pq*. Subscript on the left side is assigned for polymer A. Subscript on the right side is assigned for polymer B. $r_{i/2j/2+i/2j/2}$ appears when *i* and *j* are both even since there is no component with non-integer index, extra r_{ij+ij} term is counted because self grafting reaction kills two species simultaneously compared to reaction with other components.

The rate expression of equation 5-1 can also be written as

$$\frac{dC_{ij}}{dt} = (P_{ij}^{g} - P_{ij}^{c})r \tag{5-2}$$

where P_{ij}^{g} is the fraction of the total reaction rate r for the generation of graft copolymer *ij*. P_{ij}^{c} is the fraction of the total reaction rate for the consumption of graft copolymer *ij*. Since the polymers have infinite numbers of reactive groups, the rate of grafting conversion for polymer A satisfies

$$C_A^0 \frac{df_A}{dt} = (1 - f_A)r \tag{5-3}$$

where $(1-f_A)$ is the fraction of the total reaction rate for the consumption of A in case of infinite reactive groups. Combining equation 5-2 with equation 5-3 gives

$$d\overline{C}_{ij} / df_A = (P_{ij}^g - P_{ij}^c) / (1-f_A) \tag{5-4}$$

where the reduced concentration $\overline{C}_{ij}$ is defined by

$$\overline{C}_{ij} = \frac{C_{ij}}{C_A^0} \tag{5-5}$$

The reduced initial concentration of B becomes

$$\overline{C}_B^0 = \frac{\overline{C}_B^0}{C_A^0} = x \tag{5-6}$$

where x is the molar ratio of the two reactive polymers.

The grafting reaction environment is the same for any particular reaction. The chance for a particular reaction of component ij with component kl to form component $(i+k)(j+l)$ is proportional to $(il+jk)\overline{C}_{ij}\overline{C}_{kl}$. The chance for all reactions to occur at any moment is proportional to $\overline{C}_A^0\overline{C}_B^0$. The fraction of the total reaction rate for the formation of any particular component is the summation of all the chances for the formation of that component divided by the chance of all reactions. The expression for P_{ij}^g is generalized as

$$P_{ij}^g = \frac{1}{2x}\left\{\sum_{k=0}^{i}\sum_{l=0}^{j}[k(j-l)+l(i-k)]\overline{C}_{kl}\overline{C}_{(i-k)(j-l)}\right\} \tag{5-7}$$

where the separated plus term in equation 5-1 is adsorbed to give equation 5-7. Accordingly, the expression for P_{ij}^c is generalized as

$$P_{ij}^c = \frac{1}{x}\left[(ix+j)\overline{C}_{ij}\right] \; (i = 0,1,\cdots n, \; j = 0,1,\cdots m) \tag{5-8}$$

where the separated minus term in equation 5-1 is adsorbed to give equation 5-8.

5.2.1.2 Concentrations of polymer species

From expressions of P_{ij}^{g} and P_{ij}^{c} of equation 5-7 and equation 5-8, we can solve equation 5-4 analytically with the initial conditions

$$f_A = 0,\ \overline{C}_A^0 = 1,\ \overline{C}_B^0 = x,\ \overline{C}_{ij}^0 = 0\ (ij \neq 10 \neq 01) \tag{5-9}$$

The solution is generalized as

$$\overline{C}_{ij} = g_{ij}(1-f_A)^{i+\frac{j}{x}}\left[-\ln(1-f_A)\right]^{i+j-1}\frac{1}{x^{i-1}} \tag{5-10}$$

where

$$\begin{aligned} g_{ij} &= \frac{1}{2(i+j-1)}\sum_{k=0}^{i}\sum_{l=0}^{j}\left[k(j-1)+l(i-k)\right]g_{kl}g_{(i-k)(j-l)} \\ &(i = 1,2,\cdots m+1;\ j = 1,2,\cdots n+1) \end{aligned} \tag{5-11}$$

$$\begin{aligned} &g_{10} = g_{01} = 1, \quad g_{i0} = g_{0j} = 0 \\ &(i = 0,2,3,4,\cdots m+1;\ j = 0,2,3,4,\cdots n+1) \end{aligned} \tag{5-12}$$

Since there is no intramolecular reaction, the total reduced concentration of all species satisfies

$$\frac{d\overline{C}_T}{dt} = \frac{d\left(\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\overline{C}_{ij}\right)}{dt} = -\frac{r_{ma}}{C_A^0} \tag{5-13}$$

by combining equation 5-13 with equation 5-3 and integrating, we have

$$\overline{C}_T = x+1+\ln(1-f_A) \tag{5-14}$$

The total reduced concentration of the graft copolymers $\overline{C}_g$ becomes

$$\overline{C}_g = \overline{C}_T - \overline{C}_A - \overline{C}_B = x+1+\ln(1-f_A)-(1-f_A)-x(1-f_A)^{1/x} \tag{5-15}$$

Equations 5-13, 5-14, 5-15 are valid only for grafting conversions before the onset of gelation. Equation 5-10 is valid for post-gel grafting conversion according to Flory's argument. This is obvious since equation 5-1 describes species of finite size. Intramolecular reaction happens only to the single gel of infinite size. The presence of gel does not change the expression for P_{ij}^c.

5.2.1.3 Molecular weight averages and gel point

The reduced number-average molecular weight (NAMW) and weigh-average molecular weight (WAMW) of all species are calculated by

$$\frac{\overline{M}_n}{\overline{M}_n^0} = \frac{1+x}{\overline{C}_T} \tag{5-16}$$

$$\frac{\overline{M}_w}{\overline{M}_w^0} = \frac{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}(i + jM_B / M_A)^2 \overline{C}_{ij}}{1+(M_B / M_A)^2 x} \tag{5-17}$$

Equation 5-17 can be easily programmed to get the reduced WAMW in relation to molar ratio , molecular weight ratio of the reactive polymers and grafting conversion. A more compact form can be sought by seeking the generating function of equation 5-1 or equation 5-4. The various molecular weight averages can be obtained from the moments of the generating function.

Let us define the generating function as

$$G(A,B,Z) = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} A^i B^j \overline{C}_{ij}(Z) \tag{5-18}$$

where

$$Z = -\ln(1 - f_A) \tag{5-19}$$

By multiplying equation 5-4 by $A^i B^j$ and summing for all the i and j, we have

$$G_Z = \frac{1}{x} ABG_A G_B - AG_A - \frac{1}{x} BG_B \tag{5-20}$$

The initial condition becomes

$$G(A,B,0) = A + Bx \tag{5-21}$$

G_A, G_B, and G_Z are the partial derivatives. Equation 5-20 belongs to a nonlinear first order partial differential equation with three independent variables. We can solve it using the method of characteristics [Rhee et al., 1986] with the initial condition of equation 5-21 (see Appendix A). The results are:

$$G(A,B,Z) = \zeta + x\eta - \zeta\eta Z \tag{5-22}$$

$$A = \zeta EXP[(1-\eta)Z] \tag{5-23}$$

$$B = \eta EXP[(1-\zeta)Z] \tag{5-24}$$

$$G_A = \zeta / A \tag{5-25}$$

$$G_B = x\eta / B \tag{5-26}$$

Apparently $\zeta = \eta = 1$ when $A = B = 1$.

The WAMW is related to the generating function by

$$\overline{M}_w = \left. \frac{M_A^2 \frac{\partial}{\partial A}(AG_A) + 2M_A M_B G_{AB} + M_B^2 \frac{\partial}{\partial B}(BG_B)}{M_A G_A + M_B G_B} \right|_{\substack{A=1 \\ B=1}} \tag{5-27}$$

By manipulation of equations 5-23, 5-24, 5-25, 5-26, we have for the reduced WAMW (see Appendix A):

$$\frac{\overline{M}_w}{\overline{M}_w^0} = \frac{1 + 2ZM_B / M_A + x(M_B / M_A)^2}{\left[1 + x(M_B / M_A)^2\right](1 - Z^2 / x)} \tag{5-28}$$

From equation 5-28, we have at the critical point of gelation

$$Z^2 = x \tag{5-29}$$

Substituting expression for Z, we have

$$-\ln(1-f_A^{cri}) = x^{0.5} \tag{5-30}$$

5.2.2 Polydisperse reactive polymers

5.2.2.1 Balance equation

Polymers can be highly polydisperse when they are made by condensation polymerization, free radical polymerization, and ring-opening polymerization with chain transfer. For polydisperse reactive polymers, it is necessary to relate the grafting conversion to weight-base grafting conversion. The new kinetic description has to reflect the grafting history of each individual species of a particular molecular weight when the individual component of certain molecular weight of the polymers is labelled individually. The kinetic expression of equation 5-1 can be readily extended to accommodate the situation with polydisperse reactive polymers.

Let us designate the species concentration by

$$C_{i,i',\cdots;j,j',\cdots}$$

where $i,i',\cdots$ stand for numbers of chains of polymer A of different molecular weight, $j,j',\cdots$ stands for numbers of chains of polymer B of different molecular weight. The kinetic expression of equation 5-4 becomes

$$\frac{d\overline{C}_{i,i',\cdots;j,j',\cdots}}{df_{\overline{M}n_A^0}} = \frac{P^g_{i,i',\cdots;j,j',\cdots} - P^c_{i,i',\cdots;j,j',\cdots}}{1-f_{\overline{M}n_A^0}} \tag{5-31}$$

where $\overline{M}n_A^0$ is the reference free chain component of polymer A having molecular weight of the number-average molecular weight of initial polymer. $\overline{C}_{i,i',\cdots,j,j',\cdots}$ is defined as

$$\overline{C}_{i,i',\cdots;j,j',\cdots} = \frac{C_{i,i',\cdots;j,j',\cdots}}{C_A^0} \tag{5-32}$$

With such identification, we can extend $P^{g}_{i,i',\cdots;j,j',\cdots}$ and $P^{c}_{i,i',\cdots;j,j',\cdots}$ into

$$P^{g}_{i,i',\cdots;j,j',\cdots}=\frac{1}{2x}\sum_{i_A=0}^{i}\sum_{i'_A=0}^{i'}\cdots\sum_{j_B=0}^{j}\sum_{j'_B=0}^{j'}\cdots\left\{\begin{array}{l}\left(\sum\limits_{k=i,i',\cdots}k_A\overline{M}_{k_A}\right)\left[\sum\limits_{l=j,j',\cdots}(l-l_B)\overline{M}_{l_B}\right]+\\ \left(\sum\limits_{l=j,j',\cdots}l_B\overline{M}_{l_B}\right)\left[\sum\limits_{k=i,i',\cdots}(k-k_A)\overline{M}_{k_A}\right]\end{array}\right\}$$

$$\cdot\overline{C}_{i_A,i'_A,\cdots;j_B,j'_B,\cdots}\,\overline{C}_{i-i_A,i'-i'_A,\cdots;j-j_B,j'-j'_B,\cdots} \tag{5-33}$$

$$P^{c}_{i,i',\cdots;j,j',\cdots}=\frac{1}{x}\left(x\sum_{k=i,i',\cdots}k\overline{M}_{k_A}+\sum_{l=j,j',\cdots}l\overline{M}_{l_B}\right)\cdot\overline{C}_{i,i',\cdots;j,j',\cdots} \tag{5-34}$$

where x is defined the same as in monodisperse case. The reduced molecular weights of free chains and chain segments on the graft copolymers are defined as

$$\overline{M}_{k_A}=\frac{M_{k_A}}{\overline{M}^{0}_{nA}};\ \overline{M}_{l_B}=\frac{M_{l_B}}{\overline{M}^{0}_{nB}} \tag{5-35}$$

The initial conditions are:

$$f_{\overline{M}^{0}_{nA}}=0;$$

$$\begin{array}{c}\overline{C}^{0}_{i,i',\cdots;j,j',\cdots}=0\ \text{except}\\ \overline{C}^{0}_{0,k,\cdots;0,0,\cdots}=N^{0}(\overline{M}_{k_A})\quad(k=i,i',\cdots,\ k=1)\\ \overline{C}^{0}_{0,0,\cdots;0,l,\cdots}=x\cdot N^{0}(\overline{M}_{l_B})\ \ (l=j,j',\cdots,\ l=1)\end{array} \tag{5-36}$$

where $N^{0}(\overline{M}_{k_A})$ and $N^{0}(\overline{M}_{l_B})$ are, respectively, the number fractions of the polymers A and B of certain molecular weight.

5.2.2.2 Concentrations of polymer species

The analytical solution of equation 5-31 is readily extended from equation 5-10 to arrive at the concentration of polymer species:

$$\overline{C}_{i,i',\cdots;j,j',\cdots}=g_{i,i',\cdots;j,j',\cdots}\cdot\frac{1}{x^{\sum_{k=i,i',\cdots}k-1}}(1-f_{\overline{M}^{0}_{nA}})^{\sum_{k=i,i',\cdots}k\overline{M}_{k_A}+\frac{1}{x}\sum_{l=j,j',\cdots}l\overline{M}_{l_B}}\cdot\left[-\ln\left(1-f_{\overline{M}^{0}_{nA}}\right)\right]^{\sum_{k=i,i',\cdots}k+\sum_{l=j,j',\cdots}l-1} \tag{5-37}$$

with

$$g_{0,k,\cdots;0,0,\cdots} = \begin{cases} N^0(\overline{M}_{k_A}) & k=1 \\ 0 & k \neq 1 \end{cases} \qquad (k = i, i', \cdots)$$

$$g_{0,0,\cdots;0,l,\cdots} = \begin{cases} N^0(\overline{M}_{l_B}) & l=1 \\ 0 & l \neq 1 \end{cases} \qquad (l = j, j', \cdots) \tag{5-38}$$

$$g_{i,i',\cdots;j,j',\cdots} = \frac{1}{2(\sum\limits_{k=i,i',\cdots} k + \sum\limits_{l=j,j',\cdots} l - 1)} \cdot \sum_{i_A=0}^{i} \sum_{i'_A=0}^{i'} \cdots \sum_{j_B=0}^{j} \sum_{j'_B=0}^{j'} \cdots \left\{ \begin{aligned} &\left(\sum_{k=i,i',\cdots} k_A \overline{M}_{k_A} \right) \left[\sum_{l=j,j',\cdots} (l - l_B) \overline{M}_{l_B} \right] + \\ &\left(\sum_{l=j,j',\cdots} l_B \overline{M}_{l_B} \right) \left[\sum_{k=i,i',\cdots} (k - k_A) \overline{M}_{k_A} \right] \end{aligned} \right\}$$

$$\cdot g_{i_A, i'_A, \cdots; j_B, j'_B, \cdots} g_{i-i_A, i'-i'_A, \cdots; j-j_B, j'-j'_B, \cdots} \tag{5-39}$$

Stockmayer [1952] gave a compact form for the concentration of species in multi-component polymerization system of $\{A_{f_i}\} + \{B_{g_j}\}$ through classic combinatorial derivation. By referring to his result, we have a neat expression for $g_{i,i',\cdots;j,j',\cdots}$, of equation 5-39. The new expression

$$g_{i,i',\cdots;j,j',\cdots} = \prod_{k=i,i',\cdots} \frac{(\overline{M}_{k_A} N^0(\overline{M}_{k_A}))^k}{k!} \cdot \prod_{l=j,j',\cdots} \frac{(\overline{M}_{l_B} N^0(\overline{M}_{l_B}))^l}{l!}$$

$$\cdot \left(\sum_{k=i,i',\cdots} \overline{M}_{k_A} k \right)^{\sum\limits_{l=j,j',\cdots} l-1} \left(\sum_{l=j,j',\cdots} \overline{M}_{l_B} l \right)^{\sum\limits_{k=i,i',\cdots} k-1} \tag{5-40}$$

is obtained in the limit of polymers having infinite numbers of reactive groups.

The percentage grafting conversion f_A^w is related to $f_{\overline{M}_{nA}^0}$ by

$$f_A^w = 1 - \frac{\sum\limits_{k=i,i',\cdots} M_{k_A} C_{0,k,\cdots;0,0,\cdots}}{\overline{M}_{nA}^0 C_A^0}$$

$$= 1 - \sum_{k=i,i',\cdots} \overline{M}_{k_A} \overline{C}_{0,k,\cdots;0,0,\cdots} = 1 - \sum_{k=i,i',\cdots} \overline{M}_{k_A} N^0(\overline{M}_{k_A})(1 - f_{\overline{M}_{nA}^0})^{\overline{M}_{k_A}} \tag{5-41}$$

5.2.2.3 Molecular weight averages and gel point

The reduced NAMW and WAMW of the system satisfy

$$\frac{\overline{M}_n}{\overline{M}_n^0}=\frac{1+x}{\overline{C}_T}=\frac{1+x}{1+x+\ln(1-f_{\overline{M}_{nA}^0})} \tag{5-42}$$

$$\frac{\overline{M}_w}{\overline{M}_w^0}=\frac{1}{\dfrac{\overline{M}_{wA}^0}{\overline{M}_{nA}^0}+x\dfrac{\overline{M}_{wB}^0}{\overline{M}_{nB}^0}\left(\dfrac{\overline{M}_{nB}^0}{\overline{M}_{nA}^0}\right)^2}$$

$$\cdot\sum_{i=0}^{\infty}\sum_{i'=0}^{\infty}\cdots\sum_{j=0}^{\infty}\sum_{j'=0}^{\infty}\cdots\left(\sum_{k=i,i',\cdots}k\overline{M}_{k_A}+\frac{\overline{M}_{nB}^0}{\overline{M}_{nA}^0}\sum_{l=j,j',\cdots}l\overline{M}_{l_B}\right)^2\overline{C}_{i,i',\cdots;j,j',\cdots} \tag{5-43}$$

Again, we can introduce a generating function to reduce equation 5-43 into a compact expression. Let

$$G=\sum_{i=0}^{\infty}\sum_{i'=0}^{\infty}\cdots\sum_{j=0}^{\infty}\sum_{j'=0}^{\infty}\cdots(A_i^iA_{i'}^{i'}\cdots B_j^jB_{j'}^{j'}\cdots\overline{C}_{i,i',\cdots;j,j',\cdots}(E)) \tag{5-44}$$

be the generating function in the polydisperse case, where

$$E=-\ln(1-f_{\overline{M}_{nA}^0}) \tag{5-45}$$

By multiplying equation 5-31 by $A_i^iA_{i'}^{i'}\cdots B_j^jB_{j'}^{j'}\cdots$ and summing for all the species, we have

$$G_E=\frac{1}{x}\sum_m\sum_n\overline{M}_{A_m}\overline{M}_{B_n}A_mB_nG_{A_m}G_{B_n}-\sum_m\overline{M}_{A_m}A_mG_{A_m}-\frac{1}{x}\sum_n\overline{M}_{B_n}B_nG_{B_n} \tag{5-46}$$
$$(m=i,i',\cdots;\ n=j,j',\cdots)$$

The initial condition of equation 5-36 becomes

$$G\big|_{E=0}=\sum_m A_mN^0(\overline{M}_{A_m})+x\sum_n B_nN^0(\overline{M}_{B_n}) \tag{5-47}$$

Solving equation 5-46 by the method of characteristics gives

$$G=\sum_m\zeta_mN^0(\overline{M}_{A_m})+x\sum_n\eta_nN^0(\overline{M}_{B_n})-E\sum_m\sum_n\zeta_m\eta_nN^0(\overline{M}_{A_m})N^0(\overline{M}_{B_n})\overline{M}_{A_m}\overline{M}_{B_n} \tag{5-48}$$

$$A_m = \zeta_m \exp\left[\overline{M}_{A_m} E(1 - \sum_n \eta_n N^0(\overline{M}_{B_n})\overline{M}_{B_n})\right] \tag{5-49}$$

$$B_n = \eta_n \exp\left[\frac{\overline{M}_{B_n} E}{x}(1 - \sum_m \zeta_m N^0(\overline{M}_{A_m})\overline{M}_{A_m})\right] \tag{5-50}$$

$$G_{A_m} = \zeta_m N^0(\overline{M}_{A_m}) / A_m \tag{5-51}$$

$$G_{B_n} = x\eta_n N^0(\overline{M}_{B_n}) / B_n \tag{5-52}$$

$$(m = i, i', \cdots;\ n = j, j', \cdots)$$

$\zeta_m = \eta_n = 1$ when $A_m = B_n = 1$. The system's WAMW is related to the generating function by

$$\overline{M}_w = \begin{pmatrix} \sum_m M_{A_m}^2 \frac{\partial(A_m G_{A_m})}{\partial A_m} + 2\sum_m \sum_{m'} M_{A_m} M_{A_{m'}} G_{A_m A_{m'}} + 2\sum_m \sum_n M_{A_m} M_{B_n} G_{A_m B_n} + \\ 2\sum_n \sum_{n'} M_{B_n} M_{B_{n'}} G_{B_n B_{n'}} + \sum_n M_{B_n}^2 \frac{\partial(B_n G_{B_n})}{\partial B_n} \end{pmatrix} / (\sum_m M_{A_m} G_{A_m} + \sum_n M_{B_n} G_{B_n})$$

(5-53)

at $A_m = B_n = 1$. By manipulating equations 5-49, 5-50, 5-51, 5-52, 5-53, we have (see Appendix A)

$$\frac{\overline{M}_w}{\overline{M}_w^0} = \frac{1 + x\frac{\overline{M}_{wB}^0}{\overline{M}_{wA}^0}\frac{\overline{M}_{nB}^0}{\overline{M}_{nA}^0} + 2E\frac{\overline{M}_{wB}^0}{\overline{M}_{nA}^0}}{\left(1 + x\frac{\overline{M}_{wB}^0}{\overline{M}_{wA}^0}\frac{\overline{M}_{nB}^0}{\overline{M}_{nA}^0}\right)(1 - \frac{E^2}{x}\frac{\overline{M}_{wA}^0}{\overline{M}_{nA}^0}\frac{\overline{M}_{wB}^0}{\overline{M}_{nB}^0})} \tag{5-54}$$

We have at the critical point of gelation:

$$-\ln(1 - f_{\overline{M}_{nA}^0}^{cri}) = \sqrt{\frac{x}{\frac{\overline{M}_{wA}^0}{\overline{M}_{nA}^0}\frac{\overline{M}_{wB}^0}{\overline{M}_{nB}^0}}} \tag{5-55}$$

$(f_A^w)^{cri}$ and $f_{\overline{M}_{nA}^0}^{cri}$ are connected through equation 5-41.

5.2.3 Average numbers of graft linkages on each polymer A segment of the graft copolymers

Solubilization of ungrafted polymers into the domains of graft copolymers depends very much on the molecular weights of the ungrafted polymer and the effective chain length of the polymer segments of the graft copolymers. The average numbers of linkages of each polymer A segment of the graft copolymers ($\bar{n}_A$) is defined as

$$\bar{n}_A = \frac{C_a^0 f_a}{C_A^0 f_A^m} \tag{5-56}$$

where C_a^0 is the molar concentration of reactive group *a*, f_a is the molar conversion of *a*, f_A^m is the molar conversion of polymer A. The conversion of reactive groups is related to the conversion of polymer A having the molecular weight of $\overline{M}_{nA}^0$ by

$$C_a^0 f_a = -C_A^0 \ln(1 - f_{\overline{M}_{nA}^0}) \tag{5-57}$$

By substituting equation 5-57 into equation 5-56, we have

$$\bar{n}_A = \frac{-\ln(1 - f_{\overline{M}_{nA}^0})}{f_A^m} \tag{5-58}$$

The effect of polydispersity on the change of system's molecular weight averages with grafting conversion can be understood further by comparing the numbers of reactive groups consumed in the polydisperse case to that of monodisperse case at the same percentage conversion of polymer A and the same concentration of reactive groups *a*. More grafting conversion of higher molecular weight polymers is seen from such comparison. We can look at the difference by defining the ratio R_a as the numbers of functional groups consumed in the polydisperse case to that of the monodisperse case. It follows that

$$R_a = \frac{f_a^{poly}}{f_a^{mono}} = \frac{\ln(1 - f_{\overline{M}_{nA}^0})\Big|_{f_A^w}}{\ln(1 - f_A^w)} \tag{5-59}$$

5.3 DISCUSSION

5.3.1 Monodisperse reactive polymers

Table 5-1 lists the grafting conversion of polymer A at the gel point in relation to molar ratio. The gel point is delayed to higher grafting conversion as the molar ratio of polymer B to polymer A increases. Grafting conversion of A shall not exceed the critical point for the purpose of grafting reaction instead of crosslinking.

Table 5-1 Critical Grafting Conversion vs. Molar Ratio

x	1.0	1.5	2.0	3.0	6.0	12.0
f_A^{cri}	0.63	0.71	0.76	0.82	0.91	0.97

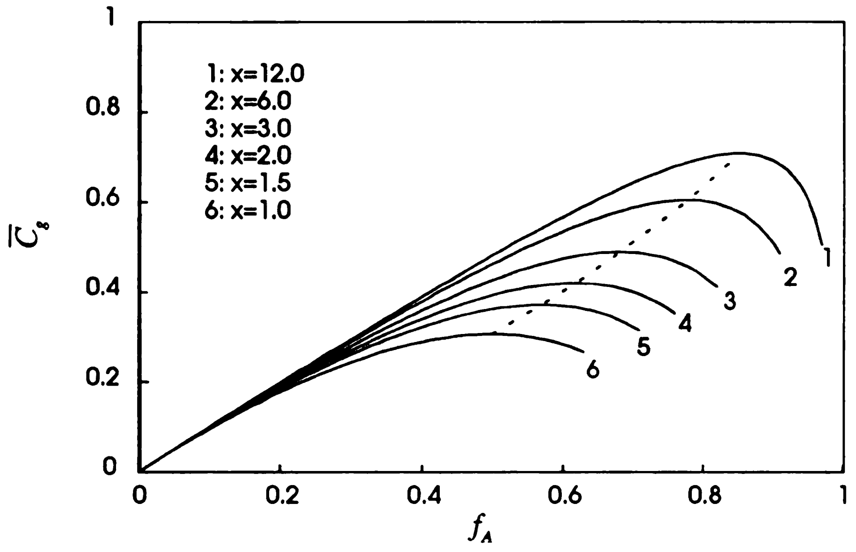

Figure 5-2 System's reduced graft copolymer concentration in relation to grafting conversion and molar ratio.

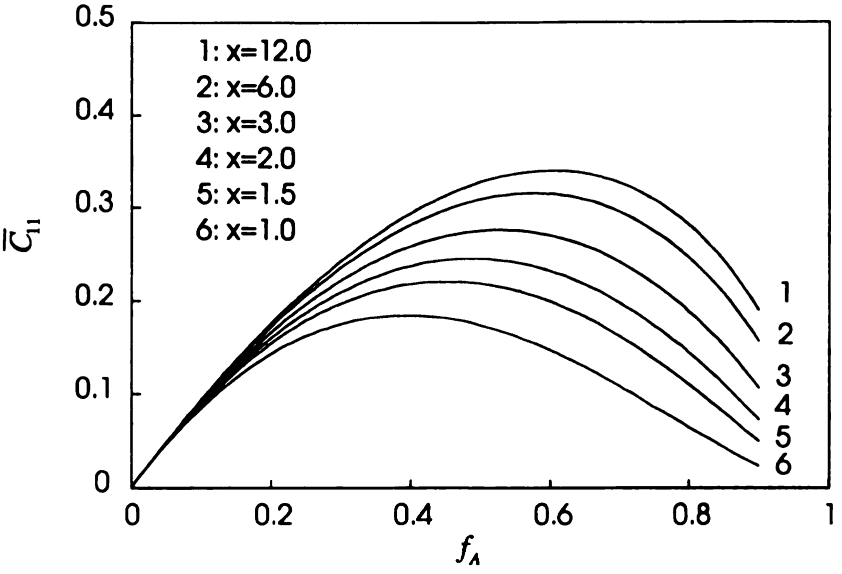

Figure 5-3 Reduced concentration of the simplest graft copolymer in relation to grafting conversion and molar ratio.

Figure 5-2 and Figure 5-3 show respectively the reduced concentration of total graft copolymers and the concentration of the simplest graft copolymer in relation to molar ratio and grafting conversion of polymer A. The plot in Figure 5-2 stops at the gel point since equation 5-15 is valid only in the pre-gel region. The delay of the gel point with increasing molar ratio is partly explained by the existence of more graft copolymers or more of the simplest graft copolymer (Figure 5-3). The dotted line in Figure 5-2 corresponds to the maximum concentration of all graft copolymers at different molar ratios.

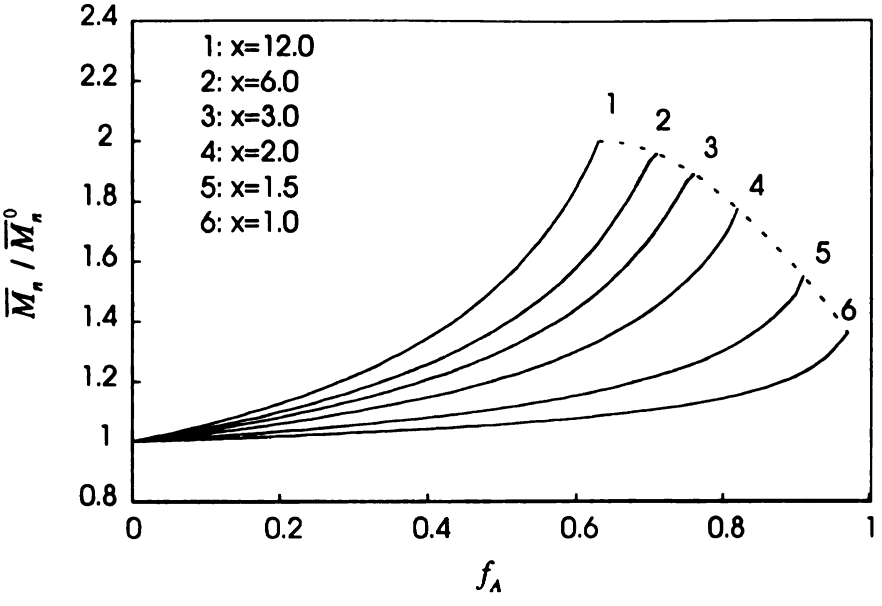

Figure 5-4 System's reduced number-average molecular weight in relation to grafting conversion and molar ratio.

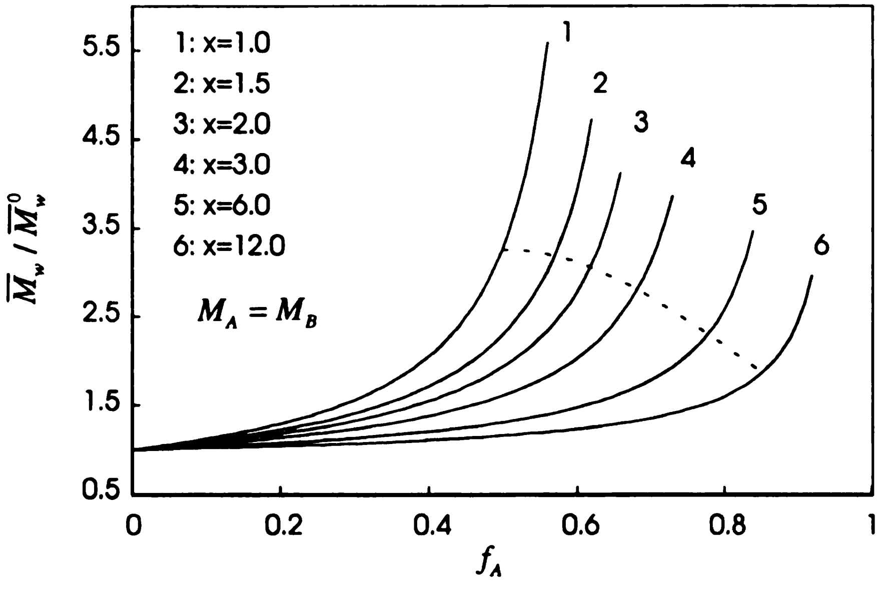

Figure 5-5 System's reduced weight-average molecular weight in relation to grafting conversion and molar ratio.

Figure 5-4 and Figure 5-5 show respectively system's reduced NAMW and WAMW. The reduced NAMW is finite and less than two at the gel point. The WAMW rises more quickly than the NAMW and becomes infinite at the gel point. Control of the upper grafting conversion limit relates to processing properties, mainly the melt viscosity or solution viscosity. This property is related more closely to the WAMW than the NAMW since what matters primarily is the size of the molecules that make up the bulk of the sample by weight [Williams, 1971]. The control of grafting conversion should be confined to the percentage conversion when the reduced WAMW has a reasonable value. Since grafting reaction starts with high molecular weight reactive polymers, the reduced WAMW is very limited. The dotted line in Figure 5-5 corresponds to maximum concentration of all the graft copolymers. We can use this line as a transition line, that is, the WAMW grows smoothly with grafting conversion when the grafting conversion is below that line, it grows quickly once the grafting conversion is above that line. In equation 5-28, the WAMW is also a function of molecular weight ratio M_B / M_A of the reactive polymers. This factor is less sensitive for the change of WAMW compared to the molar ratio and grafting conversion. However the composition of the system (w_A) is much affected by that ratio since w_A, x, and M_B / M_A are related by

$$x\frac{M_B}{M_A}=\frac{w_A}{1-w_A} \qquad (5\text{-}60)$$

Two most important points coming out of the discussions of monodisperse reactive polymers are: (a) grafting conversion of reactive polymer A (if A is to be included into B) is limited in order to avoid gelation, the critical grafting conversion is very sensitive to composition for the given molecular weight of the reactive polymers; (b) grafting reaction should be stopped long before the system starts to gel in order to avoid too high a system's WAMW.

5.3.2 Effect of polydispersity

The effect of polydispersity is contained in equations 5-54, 5-55. Its influence on the gel point and molecular weight averages comes mainly from two factors: (a) the polydispersity index (PDI); (b) the molecular weight distribution function. It is important to point out that only the distribution function of the polymer A is needed in reference to the percentage conversion of A.

Polymers made by condensation polymerization, free-radical polymerization, and ring-addition polymerization with chain transfer, are highly polydisperse. The molecular weight distribution is obtained theoretically for the ideal case with known simple mechanisms. The real production processes are often more complex than the ideal case, this is particularly true for free-radical polymerization where parameters for different mechanisms are often not available. In free-radical emulsion polymerization the gel effect or the Trommsdorff effect complicates further the situation. Long chain tail is often seen due to that effect from gel permeation chromatography (GPC) study. Removing the low molecular weight fraction of some production process causes new distribution function for the remaining product. Therefore, detailed distribution function for the description of the linear polymer product is often not available. Nevertheless, several known distribution functions are commonly used in the discussion of molecular weight distributions of linear polymers. The two-parameter Schulz and the Wesslau (log-normal) distributions are two of the representative distribution functions. The Schulz distribution is an extension of the theoretical Schulz-Flory most probable distribution that describes the ideal linear condensation system and the free-radical system at certain conditions [Peebles, 1971]. Therefore the Schulz distribution function has a theoretical basis. The Wesslau distribution function is also empirical, which is invited for the often seemingly normal distribution of the GPC evolution curve. The log-normal distribution is recovered when the calibration curve of logarithmic molecular weight versus evolution volume is linear (which happens to be the case for most linear polymers of not too high a molecular weight). It also shows the important feature of long chain tail (in emulsion polymerization). Figure 5-6 shows the Schulz and Wesslau distributions at two values of polydispersity. The two distribution functions are:

Schulz

$$W(M) = \frac{(-\ln a)^{b+2}}{\Gamma(b+2)} M^{b+1} a^{M} \tag{5-61}$$

Wesslau

$$W(M) = \frac{1}{\sigma\sqrt{\pi}M} \exp(-\frac{1}{\sigma^2} \ln^2 \frac{M}{M_p}) \tag{5-62}$$

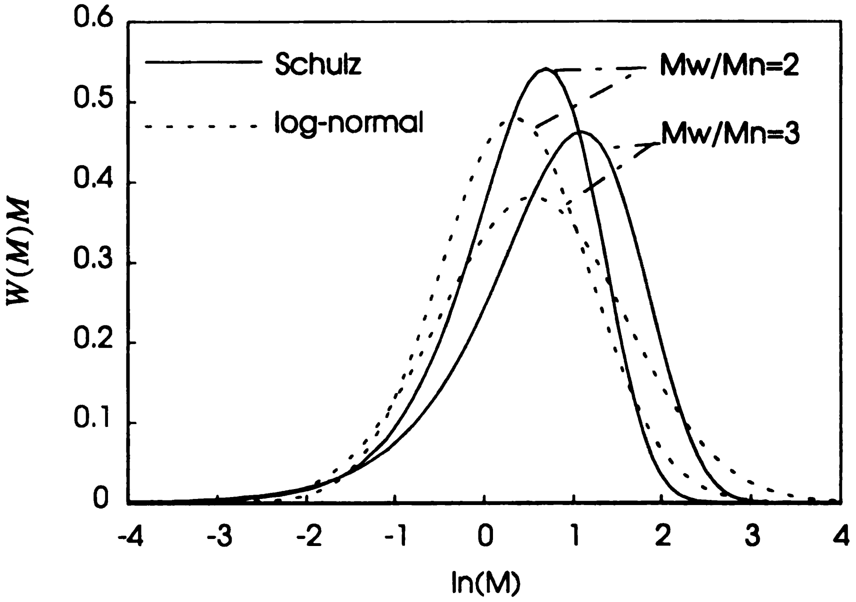

Figure 5-6 Weight fraction molecular weight distributions of Schulz and Wesslau functions at two P.D.I. values.

The effect of polydispersity on the control of grafting conversion is discussed for the case of Schulz distributions and Wesslau distributions. The goal is to have a general feeling on the effects of polydispersity and to see how much difference the distribution difference is going to make at the same polydispersity.

In the case of Schulz distribution, f_A^w and $f_{\overline{M}_{nA}^0}$ is connected by

$$-\ln(1-f_{\overline{M}_{nA}^0}) = (b_A+1)\left[(1-f_A^w)^{\frac{-1}{b_A+2}} - 1\right] \tag{5-63}$$

For log-normal distribution, simple numerical calculation is needed for the correspondence of f_A^w and $f_{\overline{M}_{nA}^0}$ through the following equation:

$$f_A^w = 1 - \int_0^\infty (1-f_{\overline{M}_{nA}^0})^{M/\overline{M}_{nA}^0} W_A(M)dM \tag{5-64}$$

Table 5-2 lists the grafting conversions of A at the gel point when the two reactive polymers have the same PDI. In case of Schulz distribution of A, the critical grafting conversion decreases with polydispersity, for example, at equal molar amount A and B, the critical grafting conversion is 63% for monodisperse polymer, but the critical grafting conversion is 56% at PDI of 2.0, 54% at PDI of 3.0. The differences on critical grafting conversion are small when PDI increases from 2.0 to 3.0. In case of Log-normal distribution of A, the critical grafting conversion of A is reduced further in comparison to Schulz distribution at the same PDI. The effect of PDI on critical conversion is far more sensitive in case of Log-normal distribution. From equation 5-55, it is obvious that increasing the polydispersity of B will reduce the critical grafting conversion at fixed polydispersity of A. Table 5-3 lists the critical conversion of A with monodisperse B. The effect of polydispersity of A alone is to increase the critical grafting conversion of A when the molar ratio is close to one and to decrease it when the molar ratio is much more than one.

It is apparent that the change of critical grafting conversion of polymer A depends on the polydispersity of both polymers and the composition of grafting condition. The critical grafting conversion is very sensitive to the presence of high molecular weight tail, an undesirable factor for the purpose of grafting.

Table 5-2 Effect of Polydispersity of the Reactive Polymers on Critical Grafting Conversion at Various Molar Ratio*

x\PDI	1.0	2.0	3.0	2.0	3.0
		Schulz		Log-	nor.
1.0	0.63	0.56	0.54	0.52	0.47
1.5	0.71	0.61	0.59	0.58	0.53
2.0	0.76	0.66	0.63	0.62	0.56
3.0	0.82	0.71	0.68	0.68	0.61
6.0	0.91	0.80	0.77	0.77	0.70
12.0	0.97	0.87	0.83	0.84	0.78

* $PDI_A=PDI_B$

Table 5-3 Effect of PDI of A on Critical Grafting Conversion at Various Molar Ratio*

x \ PDI	1.0	2.0	3.0	2.0	3.0
		Schulz		Log-	nor.
1.0	0.63	0.66	0.68	0.67	0.60.
1.5	0.71	0.71	0.73	0.72	0.67
2.0	0.76	0.75	0.77	0.75	0.70
3.0	0.82	0.80	0.80	0.79	0.75
6.0	0.91	0.87	0.87	0.85	0.82
12.0	0.97	0.92	0.91	0.90	0.88

* $PDI_B=1.0$

Figure 5-7 shows the reduced WAMW of the two distributions of A in relation to grafting conversion and molar ratio (PDI=2.0). The molecular weight takeoff is earlier for log-normal distribution than the Schulz distribution. The difference in the transition region between the two distribution is about 2-3% grafting conversion. The tailing in the log-normal distribution is responsible for that. The relative small changes of gel point for PDI range of 1.5-2.5, plus the small shifts due to distribution differences indicate that the accuracy of the GPC analysis and the distributions of it should not be much emphasized as long as the PDI value is in that range, even though the critical grafting conversion is quite sensitive to the presence of high molecular weight tail. In addition to overall shift of the reduced WAMW with polydispersity, the transition zone sharpens with increasing PDI, which is obvious by comparing Figure 5-5 and Figure 5-7. The dotted line in Figure 5-7 corresponds to the case of Schulz distribution.

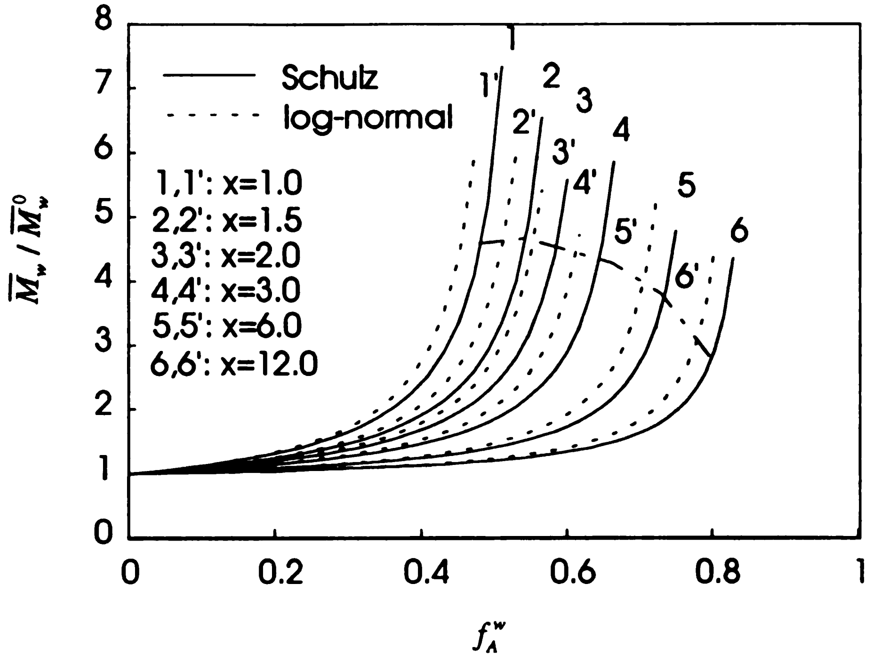

Figure 5-7 Reduced system weight-average molecular weight of Schulz and Wesslau distribution functions with P.D.I. of 2 and equal molecular weight averages for both A and B in relation to grafting conversion and molar ratio

It is very desirable to look the change of system's molecular weight distribution with grafting conversion. The difference between the molecular weight distribution of the graft copolymers and that of the remaining free A and B widens as grafting conversion increases. Unfortunately, the system's molecular weight distribution can not be generalized to a simpler expression even though the individual species content is unraveled in equations 5-37, 5-40, 5-41. To simulate the distribution based on known concentrations of polymer species, one has to slice the distribution into several pieces.

One needs, say, seven to ten slices each for A and B to have a reasonable representation of the distribution at a polydispersity of 2. This means a calculation program involving more than fourteen dimensions. If each dimension has, say, five steps (each sub-index used for the labeling of the polymer species increases from zero to four), the whole calculating program will run for tremendous amount of time to give the results.

5.3.3 Average numbers of graft linkages of each polymer A segment of the graft copolymers

In the case of Schulz distribution, the average numbers of linkages of each polymer A segment of the graft copolymers becomes

$$\bar{n}_A = \left[(1-f_A^w)^{\frac{-1}{b_A+2}} - 1 \right] \cdot \frac{b_A+1}{1-(1-f_A^w)^{\frac{b_A+1}{b_A+2}}} \qquad (5\text{-}65)$$

The relative amount of functional groups consumed in the polydisperse case to monodisperse case becomes

$$R_a = \frac{(b_A+1)\left[(1-f_A^w)^{\frac{-1}{b_A+2}} - 1 \right]}{-\ln(1-f_A^w)} \qquad (5\text{-}66)$$

Numerical solution is needed for log-normal distribution.

Figure 5-8 shows the average numbers of linkages of each polymer A segment of the graft copolymers for the two distributions in relation to grafting conversion. We see that the average numbers of functional groups consumed is less than 2.5 when the grafting conversion of A is below 80% by weight. Therefore the amount of reactive groups consumed is very small. If the reactive groups on both A and B are 50, then at 80% conversion, the percentage conversion of reactive groups of the grafted chain is less than 5%, the numbers of reactive groups consumed can be neglected for the statistical weighting difference between the free chain and the grafted chain segment of the same molecular weight in the kinetic formulation. When grafting conversion is below 60%, the difference in the average numbers of linkages of each polymer A segment of the graft copolymers between the polydisperse case with a PDI of 3.0 and the monodisperse case is slight. The difference widens only at much higher grafting conversions.

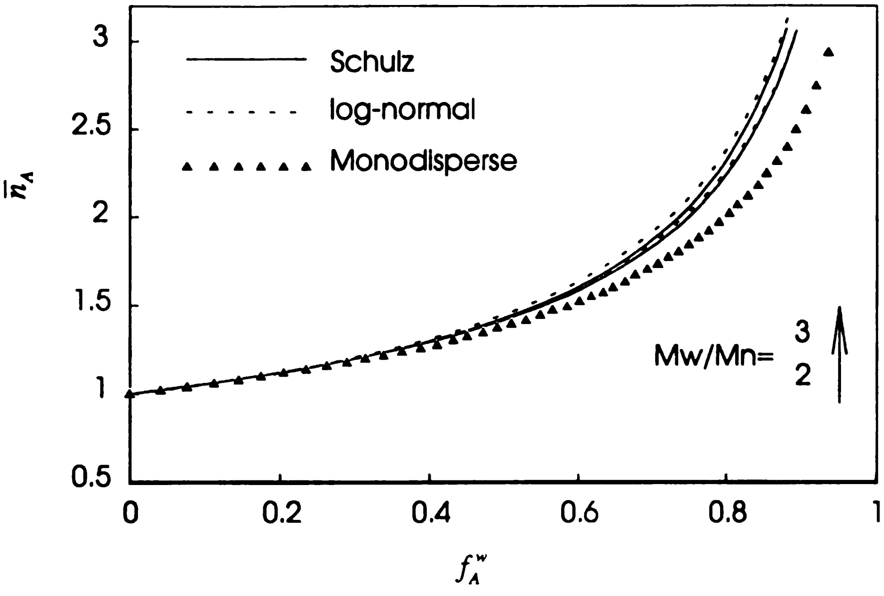

Figure 5-8 Average numbers of linkages of A chain of the graft copolymers versus grafting conversion.

Figure 5-9 shows the change of R with grafting conversion of polymer A. We can see that the amount of functional groups consumed is substantially reduced with increasing PDI of polymer A no matter which way the WAMW shifts with PDIs of the two reactive polymers. There is more difference in R_a between Schulz distribution and Wesslau distribution. The much lower consumption with increasing polydispersity of polymer A at the same grafting conversion (compared to monodisperse case) indicates more grafting conversion of higher molecular weight chain fractions of the reactive polymers. A direct calculation is shown in Section 4-3 of Chapter 4 for the particular case of CA-SMA system.

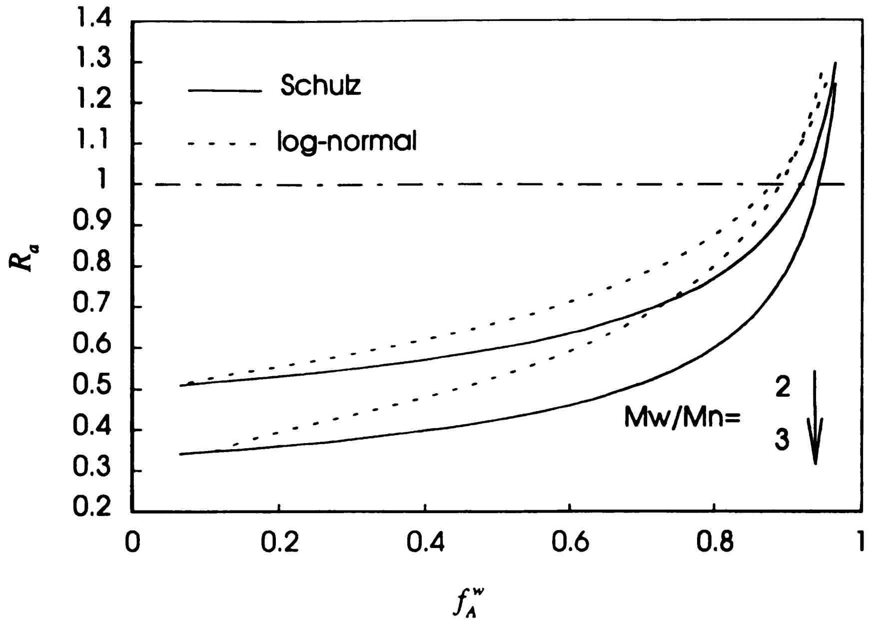

Figure 5-9 Comparison of the amount of reactive groups *a* of A consumed in polydisperse case to that of monodisperse case at different grafting conversion.

5.4 CA-SMA GRAFTING SYSTEM

There are on the average 85 hydroxyl groups per CA chain (one per two modified anhydroglucose units) and 90 anhydride per SMA232 chain (one anhydride per 13 styrenic units). The numbers of reactive groups consumed is negligible, therefore the theoretical derivation is applicable for this CA-SMA grafting system. Figure 5-10 shows the theoretical calculation of the change of system's WAMW with percentage conversion of SMA in the assumed homogeneous state. It is observed that the percentage conversion of SMA is limited around 60±5% at equal amount of CA and SMA, and 70±5% a quarter amount of SMA in the polymer mixture. At a polymer concentration of 11g/100ml DMF, the reaction solution is heterogeneous at the beginning of grafting reaction, heterogeneity has net results of weighting toward more reaction for the graft copolymers and the creation of one on one local composition of reactants. Therefore the presence of heterogeneity at the early stage of grafting reaction will limit the SAM grafting conversion at the same WAMW of the system. It is extremely important to do GPC analysis to see how the presence of heterogeneity is going to reshape the grow of system's WAMW with SMA conversion and also the molecular weight distribution of the grafting reaction products. Unfortunately the association behavior of the grafting reaction products in carrier solvents caused great difficulty doing GPC analyses (see Chapter 2).

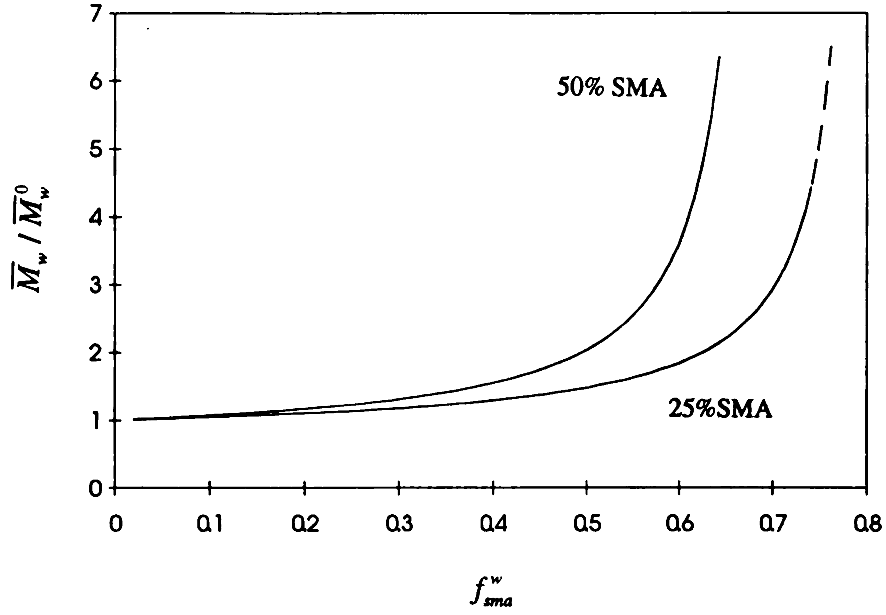

Figure 5-10 Theoretical prediction on the change of system's WAMW with SMA grafting conversion at two compositions

This part of the studies neglects the presence of intramolecular reaction during the grafting process. The kinetic approach can be extended to take account intramolecular reaction into consideration where the chain characteristics and dilution become important. A study of its effect on the branching process of our system will be discussed in chapter 6, where a thorough theoretical development is given for the grafting system. For the particular case of CA-SMA system, the extent of intramolecular has only minor effect on the system's WAMW even though its influence on the grafting process can not be simply neglected in general.

5.5 SUMMARY

In this chapter, the branching process of grafting reaction between two reactive polymers each having large numbers of reactive groups is studied systematically. A kinetic approach is employed to arrive at various expressions for the molecular characteristics of the grafting process. Both monodisperse and polydisperse polymers are considered.

Discussion from the case of monodisperse reactive polymers reveals many important things on the branching process. The two most important points are: (a) critical grafting conversion is limited and depends on the composition of the two reactive polymers; (b) the take off of system's WAMW starts long before the on set of gelation therefore limits further the extent of grafting conversion in such grafting system. When the two reactive polymers are highly polydispersive, the critical grafting conversion behaves in a complicated manner depending on several factors: PDI, distribution, composition. Increasing PDI lowers the critical grafting conversion when the polydispersities of two reactive polymers are close to each other. It is found that the presence of high molecular weight tail in the polydisperse reactive polymer reduces the critical grafting conversion of the reactive polymer, an undesirable factor for the purpose of grafting. The practical grafting conversion for a reasonable WAMW can be much affected when the PDIs becomes extremely high (much more than 3). The study also shows that simulating the molecular weight distribution of grafting process is not readily done because of excessive calculation time.

The theoretical analyses is applied to the CA-SMA grafting system. Calculation based on the assumed homogeneous state indicates that the grafting conversion of SMA is limited to 60±5% with equal amount of CA and SMA, and 70±5% with a quarter amount of SMA in the polymer mixture. The presence of heterogeneity at the early stage of grafting reaction will limit further the grafting conversion of SMA. The theoretical analysis is of great importance when there is difficulty doing GPC analysis because of associations of the grafting reaction products in the carrier solvents.

Chapter 6. EFFECT OF INTRAMOLECULAR REACTION ON THE BRANCHING PROCESS OF GRAFTING REACTION BETWEEN TWO REACTIVE POLYMERS

Intramolecular reaction happens within the species itself with the formation of ring or loop. Some authors like to call it cyclization reaction. Intramolecular reaction is a universal phenomenon in reaction systems, particularly with polymers. In this grafting system, intramolecular reaction happens only to the graft copolymers since the reactive groups on polymer A react only with the reactive groups on polymer B.

Grafting reaction of the defined system starts with long chain reactive polymers. The large numbers of reactive groups on the two reactive polymers call for an analysis on the influence of intramolecular reaction of the graft copolymers on the grafting process. The take-off of system's weight-average molecular weight (WAMW) and the onset of gelation shift because of intramolecular reactions.

In a broad sense, the issue on the effect of intramolecular reaction remains to be an old problem that has not be dealt with completely from a theoretical point of view [Dusek, 1985; Sarmoria et al., 1990]. There is, in author's view, provided no general procedure to incorporate intramolecular reaction into the theoretical models. The most important contribution of this part of the work to the completeness of theory with regard to the effect of intramolecular reaction is the implementation of spatial correlation because of volume exclusion, as was urged by Gordon back in the 70's [Gordon, 1974]. The distribution of polymer species is no longer homogeneous as is commonly assumed in the mean field approach. The physics of inhomogeneity (locality) has to be incorporated into the theory in considering the presence of intramolecular reaction.

6.1 BACKGROUND LITERATURE

The studies on the influence of intramolecular reaction have been mainly on several monomer polymerization systems. Examples of condensation type reactions are seen from the systems of oxypropylene triol/hexamethylenediisocyanate and epoxy curing. Recently, the most studied are free radical vinyl-divinyl polymerizations, i.e., systems of methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) and vinyl acetate/divinyl adipate [Dotson, 1992]. Both theoretical analyses and numerous experimental observations indicate that intramolecular reactions account for a finite fraction of the total reaction and delay the growth of molecular weight averages as well as the onset of gelation [Flory, 1953; Stockmayer, 1945; Frisch, 1955; Kilb, 1958; Gordon and Scrantlebury, 1967; Dusek, 1968, 1980; Stepto, 1974; 1979; Stafford, 1981; Stanford and Stepto, 1982; Kumar et al., 1986; Landin and Macosko, 1988; Scranton and Peppas, 1990; Zhu et al., 1993]. Extensive intramolecular reaction will lead to the formation of microgels before the system gels [Dusek et al., 1980; Stafford, 1981]. Intramolecular reaction before the onset of gelation leads to the formation of loops (elastically ineffective, Dusek, 1985) that is often not desirable since they do not contribute to the modulus of the material (instead, they contribute to the loss modulus, G"). Part of the loops formed may become elastically effective as gelation continues since active sites from other chain segments may attach to the loops, of course, elastically ineffective loops will continue to be formed as gelation proceeds [Dotson et al., 1992]. The properties of the network material formed can be markedly affected by these reactions [Stepto, 1979; Dusek, 1980; Stanford and Stepto, 1982; Shah and Parsons, 1980]. Intramolecular reaction is responsible for the formation of crosslinked gels. All reactions are intramolecular when there is finally one single gel.

The probability of intramolecular reaction comes from two aspects: (a) random probability of reactive groups on the same chain to meet together; (b) chain conformational energetics. The rotational potential difference gives energetically weighted probability of intramolecular reaction. The most favorable situation for intramolecular reaction appears when the spacing of the reactive groups is to form a 5-7 member ring [Stafford, 1981]. For some monomers, the spacing of the unreacted groups of the growing branched chains can be that close thereby promoting intramolecular reactions. Long chain polymeric species forms random coil as long as the chain is not stiff. Theoretical analysis often omits the rotational potential difference. Random coil of gaussian distribution was commonly used for long chains for the convenience of mathematical descriptions.

Early in the 50's, Jacobson and Stockmayer [1950] derived the probability of ring formation and the extent of it in the polymerization of a difunctional monomer using gaussian conformational statistics for the growing chain. The probability that a chain is in a ring conformation is proportional to $N^{-3/2}$ (N is the number of links), therefore the probability of ring formation decreases with increasing ring size. Their theory was further developed by Kilb [1958] and applied to polycondensation of a f-functional monomer with a difunctional monomer, expression for the gel point was obtained in an approximate manner. Frisch [1955] gave a slightly different expression for the gel point in the same system. Stepto [1974] examined Kilb's and Frisch's theory by experiments, and gave a more accurate condition for the gel point in an RA_2 +RB_f system [Ahmad et al., 1978]. The problems with these theories lie in the fact the physical meaning of the model parameters defined in the theories was not clearly defined. One of the important errors in their derivation was the assumption of equal probability of intramolecular reaction for different polymer species. Another problem is seen on the selection of the concentration of the reactive groups. Statistical methods were used in deriving the expressions for the gel point among those theories. No attention was paid to the molecular weight averages of the system.

Vinyl-divinyl system is different from condensation systems in term of mode of chain propagation and termination. Several studies looked into the details of the probability of intramolecular cyclization [Dusek and Ilavsky, 1975; Dusek and Spevacek, 1975,1980; Tobita and Hamielec, 1989; Dotson, 1991]. The terms, *primary cyclization* and *secondary cyclization,* were used to distinguish different types of cyclizations (see Figure 6-1). Tobita and Hamielec [1989], Dotson [1991], and Zhu et al. [1993] derived expressions for the probability of primary cyclization and secondary cyclization. Dotson [1991] discussed qualitatively the incorporation of intramolecular reaction into the recursive method developed by Macosko and Miller [1976].

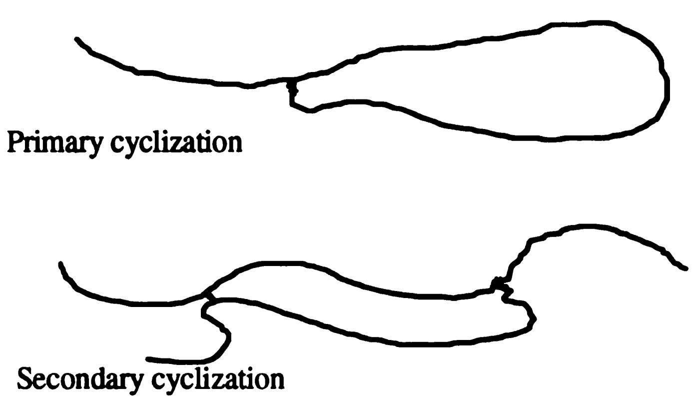

Figure 6-1 Definition of primary and secondary cyclization, so on so forth

Kinetic approach has been extended to include intramolecular reactions in nonlinear polymerization system [Plate and Noah, 1979]. In self polymerization, the rate of intramolecular reaction was written as

$$r_{n,j}^{cyc} = k\overline{Z}_{n,j}[C_{n,j}] \tag{6-1}$$

where $\overline{Z}_{n,j}$ is the probability that a molecule of chain length n undergoes cyclization by intramolecular reaction of two functional groups separated by j repeat units. Monte Carlo simulation [Plate and Noah, 1979] was developed to look at the value of $\overline{Z}_{n,j}$ in relation to n and j. Apparently for species with complex structure, such simulation is hardly conceivable. Kumar et al [1986] made distinctions of the same molecular weight chain of different ring numbers. Kinetic equations were written out with additional balance equations for those ring species. Numerical solution was attempted for a discussion on the effect of intramolecular reaction.

Despite extensive studies on the influence of intramolecular reaction in several monomer polymerization systems, there is still a lack of general procedure in a complete sense. What is also missing is the presence of spatial correlation among polymer species when we consider the presence of intramolecular reaction. The system has to be disturbed away from the ideal case of complete randomness when we consider the presence of intramolecular reaction, that is, the collisions given for intramolecular reaction can not be given to intermolecular reactions at the same time. Two polymer species having high probability of intramolecular reaction shall have less probability of reacting with each other because of volume exclusion. The mutual space exclusion among polymer species has to be settled down in a normalized sense to meet the constant density requirement. There is nonuniform distribution of polymer species for a otherwise random distribution of polymer species weighted according to the total mass of each polymer species (complete randomness for collisions) if we focus at the surroundings of any one particular polymer species. Every polymer species creates its own local environment and likely causes the nonuniformity for the system as a whole. As a first order approximation, the composition of polymer species can still be considered as uniform down to the scale of polymer species, to the extreme of high probability of intramolecular reaction, there can be compositional inhomogeneity. No Attention has been paid to such a stochastic correlation in both the statistical and kinetic approaches. There is, therefore, a missing physics in those theories. Such physical concept has not been incorporated into the gelation theory up to now even though it has been recognized long time ago by Gordon [1974] and Stauffer [1982]. It is the missing of such important physical reality that makes the theory incomplete when one talks about the presence of intramolecular reaction.

In this part of the work, a complete theory is developed based on the kinetic formulation while looking into the grafting system. Monodisperse reactive polymers are considered in the theoretical development. The effect of polydispersity on the probability of intramolecular reaction and its effect in the grafting process is discussed qualitatively following the understanding from the monodisperse case. A brief discussion is given to the particular case of CA-SMA grafting system.

6.2 THEORETICAL DEVELOPMENTS

6.2.1 Probability of intramolecular reaction

Clearly, for intramolecular reaction to occur, two reactive groups on the same polymer chain need to come into a small reactive volume, which has a length scale on the order of Angstrongs. There is always the issue whether the reaction is diffusion controlled or reaction controlled, reaction control means the time scale for reaction is much longer than the time scale for the movement of the polymer chain. Fortunately for many cases, reaction control is a reasonable assumption even for fast free radical reaction [Dotson, 1991]. There is also the issue of long-range excluded-volume effects on the mean dimensions of a polymer chain in the presence of solvent. The mean volume of the coil may be expanded or compressed depending on solvent power, i.e., in the presence of good solvent, the radius of gyration of a linear chain scales like n^{ν} where ν=3/5, rather than 1/2 as is the case for an unperturbed chain [Flory, 1953; deGennes, 1979]. The end-to-end distribution function is no longer gaussian. The presence of excluded volume effect will vastly increase the complexity of the problem [Freed, 1987]. In the following treatment, reaction control is assumed and whenever possible gaussian distribution is invited to carry out the analysis while acknowledging the error involved.

For our grafting reaction system, the long polymer chain and large numbers of reactive groups of the two reactive polymers lead to two simplifications: (a) the long chain nature of the reactive polymers gives rise to the picture of random coil (excluding rod-like chain); (b) no weighting difference for reaction between free chain and grafted chain of A or B since the consumed reactive groups are negligible compared to the numerous reactive groups on the chains.

Intramolecular reaction happens only to the graft copolymers since the reactive polymers bear only one kind of reactive groups in our system. The probability of intramolecular reaction is different for different graft copolymers. The probability of intramolecular reaction of the whole system is the sum of contributions from each graft copolymer in the system with proper weighting.

The probability of intramolecular reaction for a reactive group depends on its location on the chain segment relative to the site of grafting linkage. The probability of intramolecular reaction of the graft copolymer is the average over all the structural isomers if no distinction is made between structural isomers in the kinetic expression. Such a mean approach greatly simplifies mathematical description, otherwise the numbers of kinetic equations will be vastly increased. In the following development average probability from the structural isomers was used in the kinetic formulation in implementing the presence of intramolecular reaction.

There is a statistically equivalent mean volume (from the probability of intramolecular reaction) if we focus on one chain segment of a graft copolymer. The local environment surrounding the chain segment of the graft copolymer is sketched conceptually as in Figure 6-2 by: (a) considering every ungrafted chain and every chain segment of the graft copolymer as structural units; (b) clustering solvent molecules as clusters having total volume of solvent existed in that mean volume. Such an clustering is really not necessary except for the purpose of making the concept more straight forward. The probability of intramolecular reaction for the center unit A is obtained by counting the numbers of unit B surrounding the center of A, how many of them are connected to it and how many of them not. The same is for the probability of intramolecular reaction for the center unit B. The equivalent numbers of structural unit of that coordination ball depend on chain configuration and dilution.

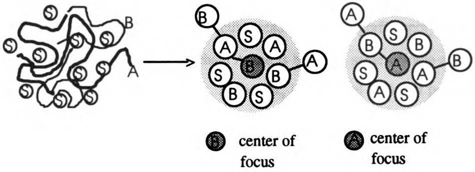

Figure 6-2 2-d conceptualization of the local environment of a graft copolymer.

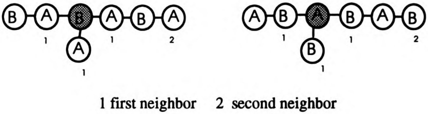

Figure 6-3 Naming of chain segments of a graft copolymer.

Units of other type connected directly to the focused unit in the center is named as the first neighbor, units of other type connected next to the focused unit is named as the second neighbor, so on so forth. Figure 6-3 illustrates the naming of structural units. The units connected directly to the center unit have more chance to react intramolecularly than units not directly connected to it. The probability of intramolecular reaction is different locally for the center of interest of structural unit A or B on the same graft copolymer.

6.2.1.1 Intrinsic probabilities of intramolecular reaction for the chain segments of A and B of a simple graft copolymer

Let us look first at the mean intrinsic probability (average from structural isomers) of intramolecular reaction of a simple graft copolymer before arriving at the general expression for the probability of intramolecular reaction of the graft copolymers. Let us assume that the constitutional units on chain A and B have the same volume and the same chain flexibility for the sake of simplicity. Let n_A, n_B be the total moles of polymer A and B, N_A, N_B be the total number of constitutional units of polymer A and polymer B, N_a, N_b the numbers of constitutional units each bearing one reactive group, φ_a, φ_b and φ_s the number fraction of constitutional units each having one reactive groups a and b and the equivalent number fraction of solvent in the system, ν_A and ν_B the number of constitutional units carried by each reactive group of chain A and B (even inert spacing). ν_A and ν_B equal to one when each constitutional unit has one reactive groups. Figure 6-4 illustrates the structure of one isomer of a simple graft copolymer.

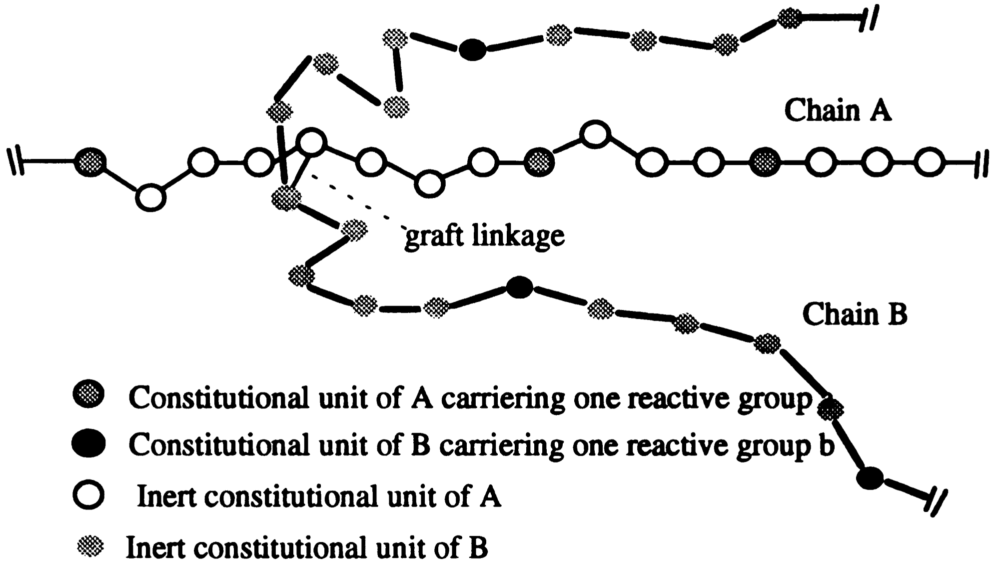

Figure 6-4 Structure of one isomer of a simple graft copolymer

Let $P^k_{a_i b_j}$ be the probability of a_i reactive group meeting with b_j reactive group for the k type isomer, $\overline{P}_a$ the mean probability of $\{a_i\}$ reactive groups meeting with $\{b_j\}$ reactive groups, $\overline{P}_b$ the mean probability of $\{b_j\}$ reactive groups meeting with $\{a_i\}$ reactive groups for the simple graft copolymer. We have

$$v_A = N_A / N_a \tag{6-2}$$

$$v_B = N_B / N_b \tag{6-3}$$

$$\overline{P}_a = \frac{\sum_{k=1}^{n_{iso}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} P^k_{a_i b_j}}{N_a n_{iso}} \tag{6-4}$$

$$\overline{P}_b = \frac{\sum_{k=1}^{n_{iso}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} P^k_{a_i b_j}}{N_b n_{iso}} \tag{6-5}$$

where n_{iso} are the total numbers of isomers of the simple graft copolymer (different location of graft linkage). It is assumed here that there is equal probability for the formation of any particular isomer. If we define N_{ball} as the real number of constitutional units of the coordination ball surrounding a constitutional unit having one reactive group (one unit in the center, solvent molecules have the same volume, we can always convert to the equivalent number of units for solvent), the mean intrinsic probabilities of intramolecular reaction for chain A and B of the simple graft copolymer become

$$\lambda^A_{11} = \frac{\overline{P}_a}{N_{ball}\varphi_b} \tag{6-6}$$

$$\lambda^B_{11} = \frac{\overline{P}_b}{N_{ball}\varphi_a} \tag{6-7}$$

where

$$\varphi_a = \frac{N_a}{N_A + N_B x}(1 - \varphi_s) \tag{6-8}$$

$$\varphi_b = \frac{N_b x}{N_A + N_B x}(1-\varphi_s) \tag{6-9}$$

Subscript 11 means one polymer A chain and one polymer B chain. φ_s can be considered to be equal to the volume fraction of solvent without going too far into the detail of the shape of the constitutional units and the actual coordination sphere sorrounding a constitutional unit. In writing down equations 6-6 to 6-9 one assumes that there is no compositional inhomogeneity down to the scale of the surrounding of a constitutional unit. Such assumption is valid unless there is very high degree of branching. If we define

$$\Theta_A = 1/\lambda_{11}^A \tag{6-10}$$

$$\Theta_B = 1/\lambda_{11}^B \tag{6-11}$$

we have

$$\Theta_B = x\Theta_A \tag{6-12}$$

where x is the molar ratio defined by

$$x = n_B / n_A \tag{6-13}$$

Therefore we know that Θ_A and Θ_B are the numbers of chain A and B in the statistically equivalent mean volume including segment A and segment B of the simple graft copolymer.

6.2.1.2 Average intrinsic probabilities of intramolecular reaction of the chain segments of A and B of any graft copolymer

Generalization for the graft copolymers follows from the basis of equations 6-6, 6-7 and the definition of Θ_A and Θ_B,. The average (from all the A or B chain segments) intrinsic probabilities of intramolecular reaction λ_{ij}^A and λ_{ij}^B of all the chain segments A and B of a graft copolymer are generalized as

$$\lambda_{ij}^{A} = \frac{(i+j-1)/i}{\Theta_B}(1+\Delta_2+\Delta_3+\cdots) \tag{6-14}$$

$$\lambda_{ij}^{B} = \frac{(i+j-1)/j}{\Theta_A}(1+\Delta_2+\Delta_3+\cdots) \tag{6-15}$$

Δ_2, Δ_3 are contributions from the second neighbor and the third neighbor as were defined in Figure 6-3, so on so forth. Equation 6-14 and equation 6-15 are obtained under the assumption of independent gaussian distribution for each chain segment of the graft copolymer, ring effect is not considered. There is certain amount of error associated with the above two equations (apparently there is no simple way to calculate accurately the distribution functions of the constitutional units for any branches on the graft copolymer).

6.2.1.3 Probabilities of intramolecular reaction of the graft copolymers and system's probability of intramolecular reaction

The probability of intramolecular reaction λ_{ij} for a graft copolymer having i A chain segments and j B chain segments in the reaction system is independent of the way which center of focus is selected in analyzing the intrinsic probability of the chain segments of the graft copolymer. It satisfies

$$\lambda_{ij} = i\overline{C}_{ij}\lambda_{ij}^{A} = \frac{j\overline{C}_{ij}}{x}\lambda_{ij}^{B} \tag{6-16}$$

The system's probability of intramolecular reaction λ is the sum of the contribution from every graft copolymer in the system, it satisfies

$$\lambda = \sum_{ij}\lambda_{ij} \tag{6-17}$$

Equation 6-16 shall always hold no matter how the species's intrinsic probability of intramolecular reaction of the chain segment is modelled.

6.2.2 Kinetic formulation

Intramolecular reactions do not contribute to the growth of the molecular weight of the system. Intramolecular reactions have to be discounted in the kinetic equations that describe the development of polymer species in the grafting process. The kinetic equations in the presence of intramolecular reactions have the general form

$$\frac{d\overline{C}_{ij}}{dE} = P_{ij}^{g} - P_{ij}^{c} \tag{6-18}$$

$$E = -\ln(1 - f_A^w) \tag{6-19}$$

which is the same as in the case of no intramolecular reaction (see chapter 5).

As was emphasized in the section on background literature, the important physics is the presence of spatial correlation among different coordination balls because of differences in volume exclusion among polymer species. The collisions given for intramolecular reaction cannot be given for intermolecular reaction at the same time, two graft copolymers having high probability of intramolecular reaction must have less probability to react with each than that of two graft copolymers having low probability of intramolecular reaction. The polymer species in the system have to distribute among themselves under the restraints of constant density and volume exclusion. Such spatial correlation needs to be considered in the kinetic description.

The probabilities for the generation and consumption of individual species including the probability of intramolecular reaction are formulated as

$$P_{ij}^{g} = \frac{1}{2x}\sum_{k=0}^{i}\sum_{l=0}^{j}\begin{bmatrix} k(j-l)(1-\lambda_{kl}^{A})(1-\lambda_{(i-k)(j-l)}^{B})\beta + \\ l(i-k)(1-\lambda_{kl}^{B})(1-\lambda_{(i-k)(j-l)}^{A})\beta \end{bmatrix}\overline{C}_{kl}\,\overline{C}_{(i-k)(j-l)} \tag{6-20}$$

$$P_{ij}^{c} = \frac{1}{x}\left[i\overline{C}_{ij}(1-\lambda_{ij}^{A})x + j\overline{C}_{ij}(1-\lambda_{ij}^{B})\right] \tag{6-21}$$

where

$$\beta = \frac{1}{\sum_{pq}(1-\lambda^{A}_{pq})p\overline{C}_{pq}} = \frac{1}{\sum_{pq}(1-\lambda^{B}_{pq})q\overline{C}_{pq}/x} = \frac{1}{1-\lambda} \tag{6-22}$$

β is a normalization factor reflecting the disturbance of species's distribution away from the otherwise complete randomness. The spatial correlation is thus included in equation 6-20 and equation 6-21. The kinetic expression is self-consistent only after we have incorporated the spatial correlation through such a normalization procedure. It is self-consistent that there is no difference no matter which way we look at the probability of intermolecular reaction between two polymer species. It is consistent that the change of total polymer concentration after summing for the concentration of each polymer species reduces to equation 6-33, which is arrived directly from the definition of the system's probability of intramolecular reactions. While the expressions of equations 6-20 to 6-22 holds true for the defined grafting system, implementing such a normalization procedure (which reflects the redistribution of polymer species) into the theory is necessary for other systems as well.

6.2.3 Weight average molecular weight (WAMW) and gel point

With equations 6-18 to 6-22, we complete the description of the grafting process taking into account the presence of intramolecular reactions. From a control point of view, we need to know the effect of intramolecular reactions on the change of gel point as well as the system's molecular weight averages, particularly the weight-average molecular weight (WAMW). This requires often a numerical simulation since the expression for the probability of intramolecular reaction of a polymer species is often nonlinear with the change of chain characteristics. One has to set the numbers of equations in the numerical simulation. Most of all, one needs expressions for equations 6-14 and 6-15. Such expressions, however, are not currently available.

In order to be able to look at the effect of intramolecular reaction on the gel point and the WAMW of the system, some simplification needs to be made. Let us assume that the probabilities of intramolecular reactions of the graft copolymers come mainly from the first neighbor (somehow similar to the concept of secondary cyclization). Under such simplification, we can introduce a generating function to avoid numerical simulation. Both gel point and molecular weight averages can be extracted from the generating function.

Let us define the generating function as:

$$G(A,B,E)=\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}A^{i}B^{j}\overline{C}_{ij}(E) \tag{6-23}$$

where $\overline{C}_{ij}(E)$ is the reduced concentration as was defined in chapter 5. By multiplying equation 6-18 with A^iB^j and summing all the i and j, we can convert equation 6-19 into a nonlinear first order partial differential equation:

$$\begin{aligned}&F=G_E+AG_A+\frac{1}{x}BG_B-\frac{2}{\Theta_B}(AG_A+BG_B-G)-\\&\frac{\beta}{x}\left[\begin{aligned}&AG_ABG_B-(AG_ABG_B+A^2G_A^2-AG_AG)/\Theta_A-\\&(AG_ABG_B+B^2G_B^2-BG_BG)/\Theta_B+(AG_A+BG_B-G)^2/\Theta_A\Theta_B\end{aligned}\right]=0\end{aligned} \tag{6-24}$$

The initial condition for equation 6-24 becomes

$$G(A,B,0)=A+xB \tag{6-25}$$

G_E, G_A, G_B are partial derivatives. We can convert the first order nonlinear partial differential equation into a series of characteristic ordinary differential equations using the method of characteristics. The characteristic ordinary differential equations can not be solved in a compact form. We can, however, obtain the solution in serial form. Before seeking for the serial solution, let us see how the system weight-average molecular weight is extracted from the generating function.

The WAMW is defined by

$$\overline{M}w = \frac{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}(iM_A + jM_B)^2\overline{C}_{ij}}{M_A + xM_B} \tag{6-26}$$

By expanding the square term and recalling the definition of generating function, we have

$$\frac{\overline{M}w}{\overline{M}_w^0} = \frac{\frac{\partial}{\partial A}(AG_A) + 2\frac{M_B}{M_A}G_{AB} + \left(\frac{M_B}{M_A}\right)^2 \frac{\partial}{\partial B}(BG_B)}{1 + x(M_B / M_A)^2} \tag{6-27}$$

in its reduced form at $A=B=1$. We see from equation 6-27 that expressions for AG_A, BG_B instead of G are actually needed to derive expression for the reduced WAMW.

We can write the expressions for AG_A and BG_B into serial forms using Taylor expansion (see appendix B for explanation):

$$AG_A = \zeta\left[1 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^i E^j a_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^i E^j b_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^j E^k c_{ijk}\right] \tag{6-28}$$

$$BG_B = x\eta\left[1 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^i E^j a_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^i E^j b_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^j E^k c_{ijk}\right] \tag{6-29}$$

ζ and η are functions of A, B and E. The other terms in the general Taylor series should not exist for this particular case. Such expressions are obtained from the characteristic equations. The first two coefficients of $\{a_{1j}\}$ and $\{b_{1j}\}$ are found to have values

$$a_{11} = b_{11} = \frac{1}{\Theta_B} \tag{6-30}$$

$$a_{12} = b_{12} = -\frac{1}{2\Theta_B{}^2} + \frac{1+x}{\Theta_B^3} \tag{6-31}$$

The coefficients of the series decrease rapidly with Θ_B. Retaining a few terms is often enough for representing the whole series when Θ_B is large. The reduced WAMW is related further to ζ_A, ζ_B, η_A, η_B at $A = B = 1$. We also have

$$\zeta\big|_{A=B=1} = \eta\big|_{A=B=1} = 1 \tag{6-32}$$

We see from equation 6-32 that only terms with coefficients $\{a_{1j}\}$ and $\{b_{1j}\}$ are actually needed for calculating WAMW.

In order to obtain the coefficients as well as ζ_A, ζ_B, η_A, η_B at $A = B = 1$, we need to get the expression of β in relation to E. Although the functional form of $\beta(E)$ is contained in the characteristic equations, it can be derived separately. From the consideration of reduced total molar concentration, we have in the case of grafting reaction with intramolecular reaction

$$\frac{d\overline{C}_T}{dE} = -(1-\lambda) \tag{6-33}$$

where $\overline{C}_T$ the reduced concentration of total graft copolymers. For the consideration of first neighbor contribution only to the intramolecular reaction, one has from equations 6-14 to 6-17

$$\lambda = (1 + x - \overline{C}_T)/\Theta_B \tag{6-34}$$

By substituting equation 6-34 into equation 6-33 and solving with initial condition $\overline{C}_T(0) = 1 + x$, we have

$$\overline{C}_T = 1 + x + \Theta_B(e^{-E/\Theta_B} - 1) \tag{6-35}$$

By substituting equation 6-35 into equation 6-34, we have

$$\lambda = 1 - e^{-E/\Theta_B} \tag{6-36}$$

We have from the definition of β

$$\beta = e^{E/\Theta_B} \tag{6-37}$$

The correctness of equations 6-35 and 6-37 can be verified directly from one of the characteristic equations in the appendix (B-13) remember

$$\overline{C}_T = G\big|_{A=B=1} \tag{6-38}$$

With the expression of $\beta(E)$ beforehand, we have at $A = B = \zeta = \eta = 1$

$$\zeta_A = \frac{\tilde{B}(\tilde{L}+\tilde{F}\tilde{K}/\tilde{A})+\tilde{K}(\tilde{E}-\tilde{F}\tilde{B}/\tilde{A})}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{6-39}$$

$$\eta_A = \frac{\tilde{F}\tilde{K}+\tilde{A}\tilde{L}}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{6-40}$$

$$\zeta_B = \frac{\tilde{B}(\tilde{D}+\tilde{F}\tilde{C}/\tilde{A})+\tilde{C}(\tilde{E}-\tilde{F}\tilde{B}/\tilde{A})}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{6-41}$$

$$\eta_B = \frac{\tilde{F}\tilde{C}+\tilde{A}\tilde{D}}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{6-42}$$

where

$$\tilde{A} = 1+\tilde{c}\int_0^E \beta dE - \tilde{b}\int_0^E \beta \sum_{i=1}^{\infty} a_{1i}E^i dE \tag{6-43-a}$$

$$\tilde{B} = \tilde{a}\int_0^E \beta dE + \tilde{b}\int_0^E \beta \sum_{i=1}^{\infty} b_{1i}E^i dE \tag{6-43-b}$$

$$\tilde{C} = \tilde{o}\int_0^E \beta dE \tag{6-43-c}$$

$$\tilde{D} = 1+\tilde{g}\int_0^E \beta dE \tag{6-43-e}$$

$$\tilde{E} = 1+\tilde{n}\int_0^E \beta dE - \tilde{r}\int_0^E \beta \sum_{i=1}^{\infty} b_{1i}E^i dE \tag{6-43-f}$$

$$\tilde{F} = \tilde{q}\int_0^E \beta dE + \tilde{r}\int_0^E \beta \sum_{i=1}^{\infty} a_{1i}E^i dE \qquad \text{(6-43-g)}$$

$$\tilde{K} = 1 + \tilde{d}\int_0^E \beta dE \qquad \text{(6-43-h)}$$

$$\tilde{L} = \tilde{p}\int_0^E \beta dE \qquad \text{(6-43-i)}$$

$$\tilde{a} = 1 - (1+x)/\Theta_B + 2x/\Theta_B^2 \qquad \text{(6-44-a)}$$

$$\tilde{b} = 1 - (3+x)/\Theta_B + 2(1+x)/\Theta_B^2 \qquad \text{(6-44-b)}$$

$$\tilde{c} = \tilde{a} - \tilde{b} \qquad \text{(6-44-c)}$$

$$\tilde{d} = 1/\Theta_B - 2/\Theta_B^2 \qquad \text{(6-44-d)}$$

$$\tilde{g} = 1/\Theta_B - 2x/\Theta_B^2 \qquad \text{(6-44-e)}$$

$$\tilde{n} = 2/\Theta_B - 2x/\Theta_B^2 \qquad \text{(6-44-f)}$$

$$\tilde{o} = x\tilde{d} \qquad \text{(6-44-g)}$$

$$\tilde{p} = \tilde{g}/x \qquad \text{(6-44-h)}$$

$$\tilde{q} = \tilde{a}/x \qquad \text{(6-44-i)}$$

$$\tilde{r} = \tilde{q} - \tilde{n} \qquad \text{(6-44-j)}$$

$\partial(AG_A)/\partial A$, $\partial(BG_B)/\partial B$, G_{AB} are related to ζ_A, ζ_B, η_A, η_B by

$$\frac{\partial}{\partial A}(AG_A) = (1 + \sum_{i=1}^{\infty} a_{1i}E^i)\zeta_A + \eta_A \sum_{i=1}^{\infty} b_{1i}E^i \qquad \text{(6-45)}$$

$$\frac{\partial}{\partial B}(BG_B) = x(1 + \sum_{i=1}^{\infty} b_{1i}E^i)\eta_B + x\zeta_B \sum_{i=1}^{\infty} a_{1i}E^i \qquad \text{(6-46)}$$

$$G_{AB}=\frac{\partial}{\partial B}(AG_A)=\frac{\partial}{\partial A}(BG_B)$$
$$=(1+\sum_{i=1}^{\infty}a_{1i}E^i)\zeta_B+\eta_B\sum_{i=1}^{\infty}b_{1i}E^i=x(1+\sum_{i=1}^{\infty}b_{1i}E^i)\eta_A+x\zeta_A\sum_{i=1}^{\infty}a_{1i}E^i \qquad (6\text{-}47)$$

at $A=B=\zeta=\eta=1$. The reduced WAMW of equation 6-27 is calculated with the results of equations 6-39, 6-40, 6-41, 6-42, 6-43, 6-44, 6-45, 6-46, 6-47. There is a common denominator associated with the WAMW. This leads to the condition for the critical point of gelation

$$\tilde{A}\tilde{E}-\tilde{F}\tilde{B}=0 \qquad (6\text{-}48)$$

We have thus obtained the expressions for the gel point, the system's WAMW and the probability of intramolecular reaction at any instant of grafting conversion. The statistically equivalent number Θ_B of chain B, free and confined in the local environment of the simplest graft copolymer, is the model parameter. It is a function of chain characteristics and dilution. The results reduce to the situation of grafting with no intramolecular reaction when Θ_B (or Θ_A) goes to infinity.

6.2.4 Effects of chain characteristics and dilution on the model parameter

Before looking at the effect of intramolecular reaction on the WAMW and the grafting conversion at the gel point, we need to estimate the range of Θ_B (or Θ_A) value. Θ_B is related to chain characteristics and dilution by (from equation 6-7 and equation 6-11)

$$\Theta_B=\frac{xN_{ball}N_aN_bn_{iso}(1-\varphi_s)}{(N_A+N_Bx)\sum_{k=1}^{n_{iso}}\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}P^k_{a_ib_j}} \qquad (6\text{-}48)$$

For chains of gaussian distribution, we have

$$P^k_{a_ib_j}\approx\left(\frac{3}{2\pi N^k_{a_ib_j}l^2}\right)^{3/2}V_{ball} \qquad (6\text{-}49)$$

Where $N^k_{a_ib_j}$ are the numbers of statistical equivalent units between the two reactive groups a_i and b_j for k isomer, l is the length of the statistically equivalent unit, V_{ball} is the volume of the coordination sphere. The exponential term is omitted since it is very close to one for large $N_{a_ib_j}$. Let the radius of the coordination sphere $R_{spherel}$ be expressed by

$$R_{spherel}=kl \tag{6-50}$$

The volume of the coordination sphere becomes

$$V_{sphere}=\frac{4}{3}\pi k^3 l^3 \tag{6-51}$$

By substituting equation 6-51 into equation 6-49, we have

$$P^k_{a_ib_j} \approx 1.38k^3 (N^k_{a_ib_j})^{-3/2} \tag{6-52}$$

We see from equation 6-52 that the effect of chain flexibility is reflected in k. k equals to one for random flight chain, normally k is less than one. It is related to the fixed bond angle and rotational potential barrier (no consideration of steric interactions resulting in the interdependence of rotations about neighboring bonds) by [Benoit, 1947; Kuhn, 1943; Freed, 1987]

$$k=\frac{1+\cos\theta-\langle\cos\psi\rangle}{1-\cos\theta+\langle\cos\psi\rangle} \tag{6-53}$$

where θ is the fixed bond angle, ψ is the rotational angle, and the azimuthal averages $<\cos\psi>$ are defined by

$$<\cos\psi>=\frac{\int_{-\pi}^{\pi}\cos\psi\exp[-w(\psi)/(kT)]d\psi}{\int_{-\pi}^{\pi}\exp[-w(\psi)/(kT)]d\psi} \tag{6-54}$$

The summation in equation 6-48 is over all the reactive groups and all the isomers that can be constructed of a simple graft copolymer. Block and symmetric four-arm star copolymers are two extreme cases. Their structures are sketched in Figure 6-5.

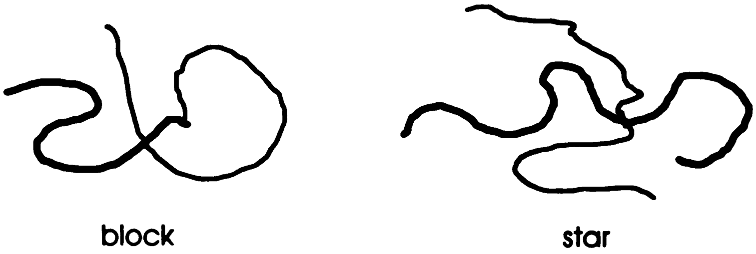

Figure 6-5 Sketches of block and star linkage

The statistically equivalent numbers of structural units satisfy

$$N_{a_ib_j} = k(iv_a + jv_b) \tag{6-55}$$

In case of block linkage, the double summation of equation 6-48 becomes

$$\sum_{i=1}^{N_a}\sum_{j=1}^{N_b} P_{a_ib_j}^{block} = 1.38k^{1.5}v_a^{-1.5}\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\left(i+\frac{v_b}{v_a}j\right)^{-1.5} \tag{6-56}$$

In case of symmetric star linkage, the double summation of equation 6-48 becomes

$$\sum_{i=1}^{N_a}\sum_{j=1}^{N_b} P_{a_ib_j}^{block} = 5.52k^{1.5}v_a^{-1.5}\sum_{i=1}^{N_a/2}\sum_{j=1}^{N_b/2}\left(i+\frac{v_b}{v_a}j\right)^{-1.5} \tag{6-57}$$

Here the reactive groups are taken to be even. The uneven situation shall be very close to the even case for large numbers of N_a and N_b. It is assumed here that the gaussian distribution of two structural units is not affected by the presence of two extra branches as was mentioned earlier. We see from equation 6-56 and equation 6-57 that the summations in the two extreme cases differ by a factor of nearly four fold. It is, therefore, necessary to do a detailed calculation to get the average from all isomers. Let $\overline{S}(N_a, N_b, v_b / v_a)$ be the average of the double summation taken over all the isomers. We have

$$\overline{S}(N_a, N_b, v_b / v_a) = \frac{1}{n_{iso}}\sum_{k=1}^{n_{iso}}\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\left(i+\frac{v_b}{v_a}j\right)_k^{-1.5} \tag{6-58}$$

By counting the numbers of isomers, we have

$$n_{iso} = (N_a / 2 + 1)(N_b / 2 + 1) \tag{6-59}$$

for even numbers of N_a , N_b. Equation 6-48 becomes

$$\Theta_B = \frac{xN_{ball}(1-\phi_s)v_a^{0.5}}{1.38k^{1.5}(\frac{1}{N_b} + x\frac{v_b}{v_a}\frac{1}{N_a})\bar{S}(N_a, N_b, v_b / v_a)} \tag{6-60}$$

6.3 DISCUSSION

6.3.1 Order of magnitude of Θ_B

The system's WAMW and gel point are related to the model parameter Θ_B. Several qualitative conclusions are deduced about the effects of chain characteristics and dilution on Θ_B based on equation 6-60.

(a) Θ_B is directly proportional to dilution in a theta solvent. A good solvent expends the coil and results in smaller k value and therefore higher Θ_B;

(b) Θ_B is very sensitive to the flexibility of the chain, this is shown by the 1.5 powers dependence on k;

(c) Θ_B increases with the numbers of inert units on the chain (v_a), but the influence of inert spacing on Θ_B is much less sensitive than chain flexibility;

(d) the change in molar ratio also affects Θ_B value. Θ_B increases with increasing;

(e) the numbers of reactive groups on chain A and chain B affect Θ_B value.

The numbers of reactive groups on chain A and chain B are perhaps the most important since they connect to the dimensions of chain A and chain B at fixed numbers of inert spacing. Apparently, many factors contribute to Θ_B value. A complete discussion on the various factors and their combinations is cumbersome. The important thing from equation 6-60 is to estimate the order of magnitude of Θ_B given the assumptions made in deriving equation 6-60.

6.3.1.1 Special case: $N_a = N_b$, $v_a = v_b$

Let us look at a special case when the numbers of reactive groups on chain A and chain B are equal, so do the numbers of inert spacing. Let

$$\Theta = \Theta_A + \Theta_B \tag{6-61}$$

One sees from equation 6-11 and equation 6-60 that Θ is independent of x. The meaning of statistically equivalent mean volume is seen more physically in this special case, it is the equivalent volume where the whole simple graft copolymer is contained in it. We can, therefore, choose Θ as the model parameter and see the effect of molar ratio on a common basis.

The mean double summation $\overline{S}(N_a, N_b, v_b / v_a)$ is for the first neighbor contribution only. The contributions from the second neighbor, the third neighbor, so on so forth, can be included by adding additional summations. The asymptotic behavior of the double summation is similar to the single summation (Truesdell summation).

$$S(N) = \sum_{i=1}^{N} i^{-1.5} \tag{6-62}$$

Figure 6-6 shows the fractional increase of $S(N)/S(\infty)$ ($S(\infty)$=2.612) with increasing numbers of reactive groups. Major contribution to $S(N)$ comes from the first 50-150 reactive groups. If the reactive polymers bear that many of reactive groups, then, the first neighbor contribution to intramolecular reaction is indeed a major part. This serves as a justification for the assumption (first neighbor contribution) made in the derivation of the expressions for the system's WAMW and gel point. A particular set of parameters is chosen for an estimation of the change of Θ value with the numbers of reactive groups. The parameters are:

$$v_a = v_b = 10; \varphi_s = 0;\ N_{ball} = 12;\ k = 1.0$$

The selection for the coordination number is 12. No ring size prohibition is made in the calculation of Θ since the smallest ring will contain 20 constitutional units and the next to smallest ring will contain 30 constitutional units for the particular set of parameters. In Dotson's argument, the smallest ring allowed to be considered in the Gaussian approximation is 25 [Dotson et al., 1992].

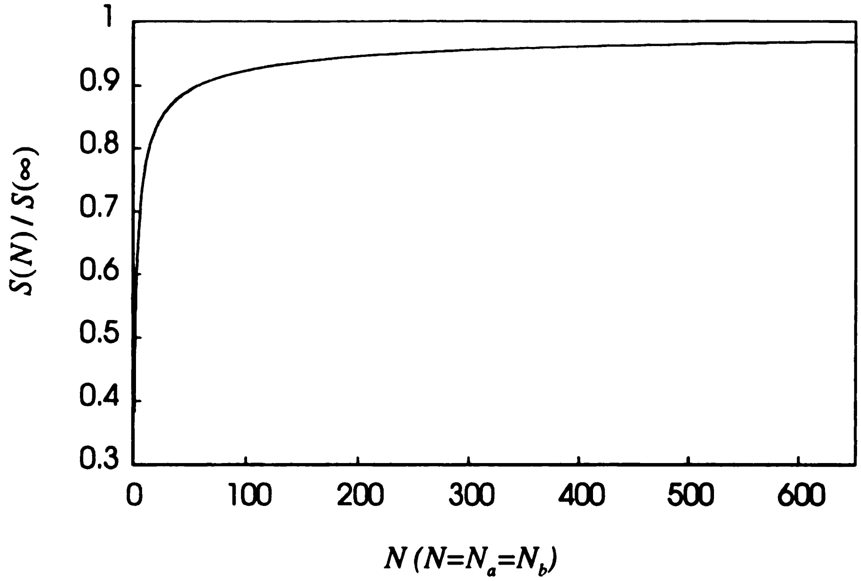

Figure 6-6 Fractional summation $S(N)/S(\infty)$ .vs. the numbers of reactive groups on chain A and B.

Figure 6-7 shows how the average double summation $\overline{S}(N,N,1)$ changes with increasing numbers of reactive groups. It goes through a maximum and then levels off slowly with N. The presence of a maximum is due to the internal shifting of weighting towards the block like (instead of star like) of the graft copolymers. Such a feature is believed to be the same for different combinations of parameters in the double summation.

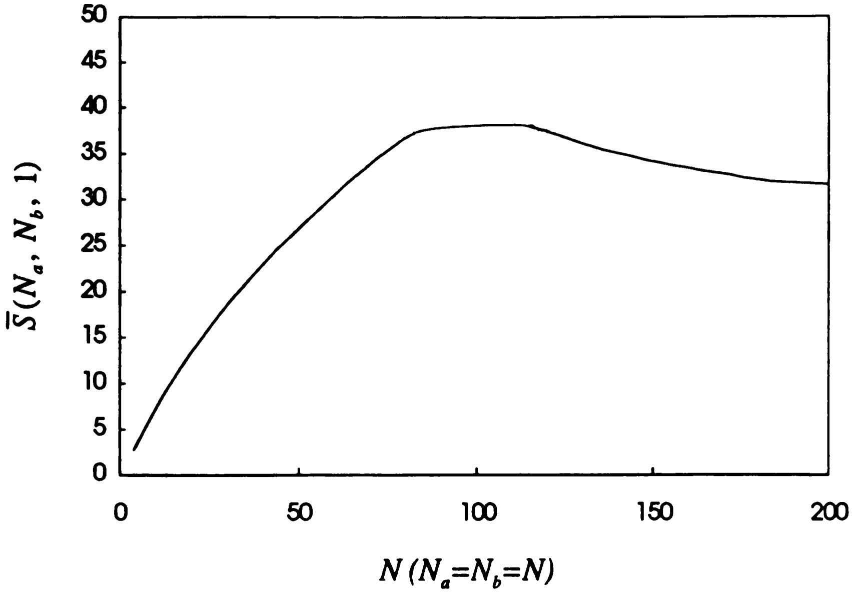

Figure 6-7 Average summation $\bar{S}(N_a, N_b, 1)$ .vs. numbers of reactive groups on chain A and B.

Figure 6-8 shows the change of Θ with N (reactive groups on chain A or chain B) of the random flight chain in the absence of solvent. Θ increases with N. Therefore the probability of intramolecular reaction decreases with increasing numbers of reactive groups on the chains. Θ falls in the range of 50-160 for the numbers of N selected, it falls to the range of 250-800 if we correct for the effect of fixed bond angle, say, 120° with free rotation. For a more accurate estimation of Θ we need to consider the steric interactions resulting in the interdependence of rotations about neighboring bonds. Flory has given an accurate calculation of the reduced mean square end-to-end distance ($<r>^2/ nl^2$) for several polymers in the unperturbed state following his complete theory of chain configuration [Flory,1969], i.e., 6 for polyethylene, 8 for syndiotactic poly(methyl methacrylate) (PMMA) and 10 for isotactic PMMA in the asymptotic limit of coarse-grained gaussian chain [Flory, 1975], with the corresponding k of 1/6, 1/8 and 1/10. Θ increases to 370-2350 if we choose k of 1/6. It drops back in the range of 40-235 for a ten-fold dilution in solution grafting reaction and 20-120 for a twenty-fold dilution (the equivalent number fraction can be considered to be equal to volume fraction in the mean field approach as a first order approximation). Above arguments are based purely on the assumptions of long chain gaussian distribution. Such an analysis is good at least for estimating the order of magnitude of Θ. In a broader sense, we select Θ in the range of 10-100 for a discussion of its effect on the WAMW and gel point. It is very important to point out that the mean probability of intramolecular reaction decreases with chain length.

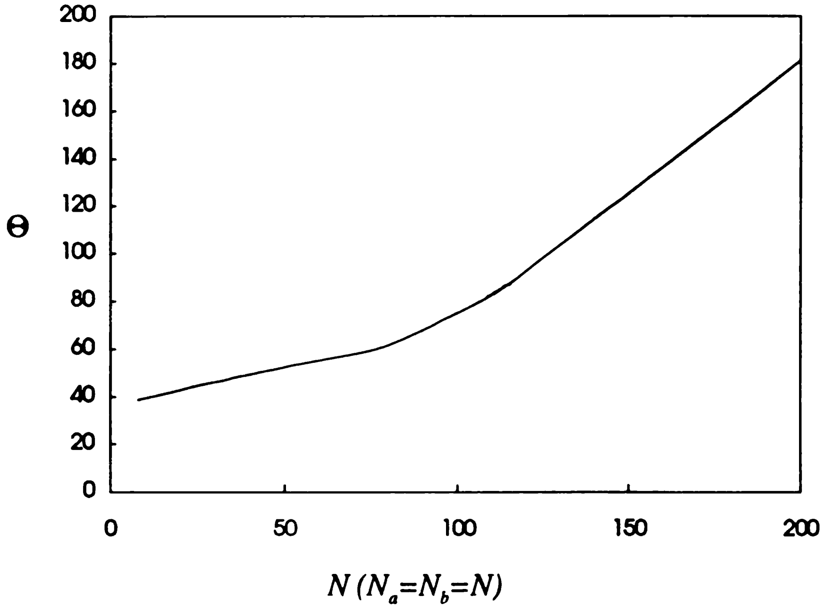

Figure 6-8 Model parameter Θ in relation to the numbers of reactive groups on chain A and B

It was shown in a chapter 5 that the growth of WAMW of the grafting reaction process is the fastest with grafting conversion when there are equal moles of A and B (grafting conversion is based on A when B is to be modified by A). By increasing the molar ratio x, we slow down the growth of weight average molecular weight and the onset of gelation. Θ_B increases with x at fixed Θ value. We choose x values of 1 and 2 for a discussion.

6.3.2 System's probability of intramolecular reaction

The extent of intramolecular reaction in the grafting system is looked also with a special case as was selected above. Figure 6-9 shows that the system's probability of intramolecular reactions increases exponentially with grafting conversion and it decreases with increase of *x*. The curves stop at the gel point. Such self-accelerating characteristics for intramolecular reactions is expected intuitively.

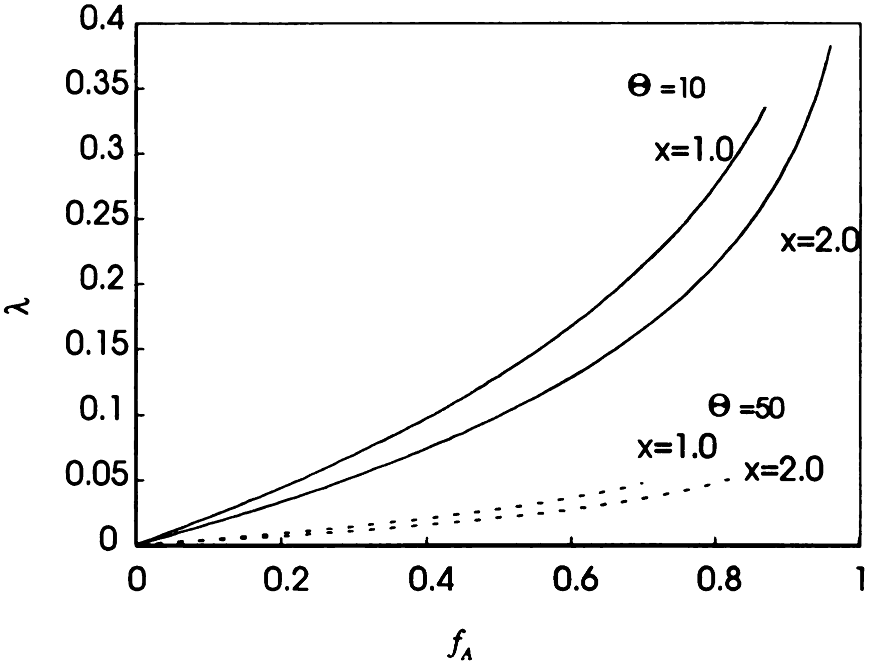

Figure 6-9 System's probability of intramolecular reaction in relation to grafting conversion of polymer A and molar ratio.

6.3.2 Gel point and system's weight-average molecular weight (WAMW)

The expressions for the gel point (equation 6-47) and the WAMW (equation 6-26) contain serial terms with coefficients $\{a_{1i}\}$, $\{b_{1i}\}$. The calculations were made in which terms with coefficients $\{a_{1i}\}$, $\{b_{1i}\}$ were dropped except for those with coefficients a_{11}, a_{12}, b_{11}, b_{12}. This is a good approximation for the range of Θ_B, E, and x values chosen in the calculations.

Table 6-1 Effect of Θ on the Critical Grafting Conversion at Two Molar Ratios

f_A^{cri}	$\Theta=\infty$	Θ=50	Θ=20	Θ=10
x=1.0	0.63	0.67	0.73	0.82
x=2.0	0.76	0.80	0.85	0.93

$N_A = N_B$

Table 6-2 Probability of Intramolecular Reaction λ at f_A^{cri}

λ	$\Theta=\infty$	Θ=50	Θ=20	Θ=10
x=1.0	0.0	0.039	0.123	0.290
x=2.0	0.0	0.047	0.132	0.328

$N_A = N_B$

Tables 6-1, 6-2 list the grafting conversion and the system's probability of intramolecular reaction at gel point. We see that the critical grafting conversion is fairly sensitive to intramolecular reaction even though the system's probability of intramolecular reaction is relatively small at the gel point. We are more concerned with the sensitivity of intramolecular reaction in delaying the take off of the system's WAMW for the purpose of grafting reaction. Figures 6-10, 6-11 show the effect of Θ on the reduced WAMW at two molar ratios of the two reactive polymers (x). The plots are for the relatively small values of reduced WAMW since our grafting system starts with long chain polymers. The effect of intramolecular reaction gradually shows up with grafting conversion. At fixed grafting conversion, the WAMW can be much different once it is in the region of take off. For example, a few percentage changes in grafting conversion means substantially different WAMW with or without the presence of intramolecular reaction at a Θ value of 50 when the desirable reduced WAMW is 4.0.

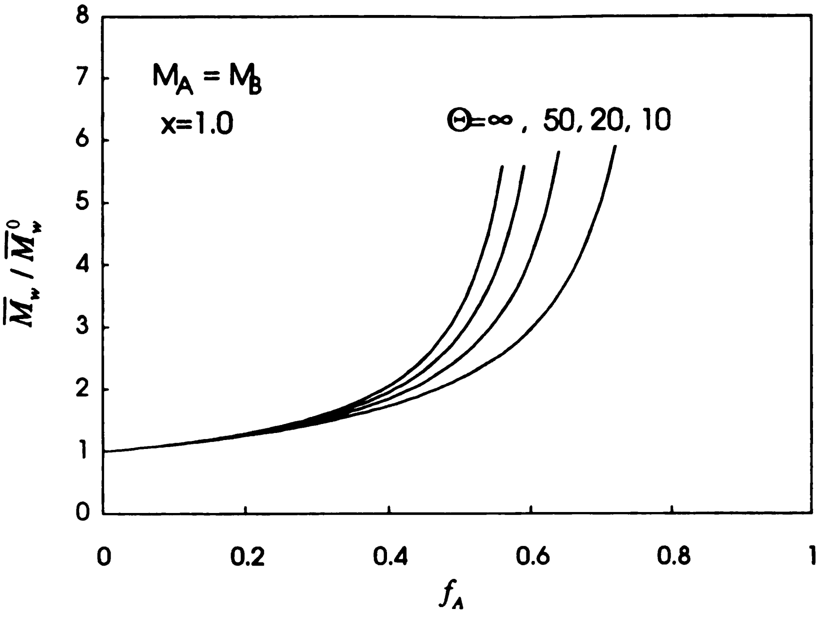

Figure 6-10 Reduced WAMW in relation to grafting conversion at different Θ with equal molar amount A and B.

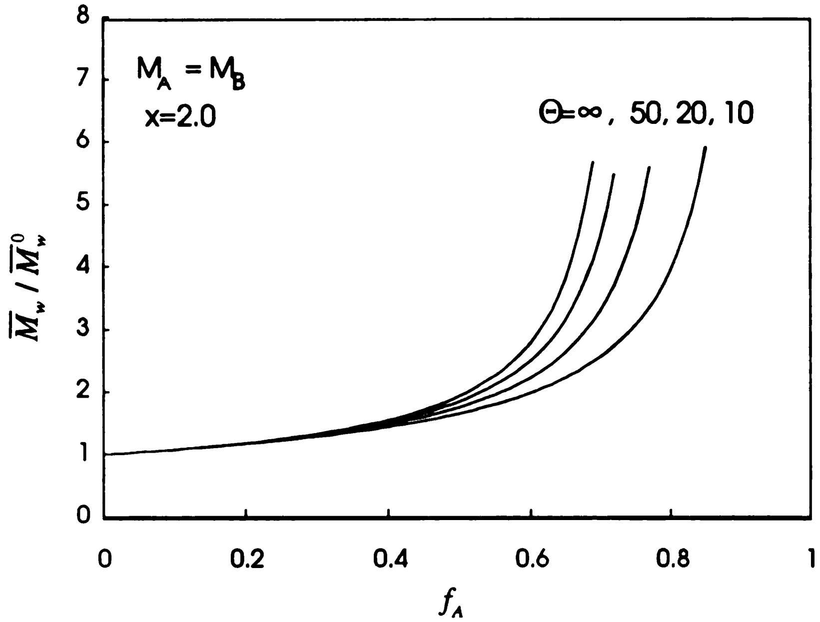

Figure 6-11 Reduced WAMW in relation to grafting conversion at different Θ with *x* of 2.0.

6.4 EFFECT OF POLYDISPERSITY

Effect of polydispersity on the system's probability of intramolecular reaction and the grafting process can be readily extended into the kinetic formulation. However, the gel point and molecular weight averages can not be calculated easily since the change of the probability of intramolecular reaction with length of the chain segment of a graft copolymer is not linear. Implementing the effect of polydispersity directly means the presence of more than first order partial differential equation of the generating equation (equation 6-24), a vast increase in the complexity of the generating equation. No direct numerical simulation was attempted, however we can still tell the importance of polydispersity in terms of intramolecular reaction by comparing to the case of monodisperse reactive polymers at the same number-average molecular weights of polydisperse reactive polymers. Under such consideration, the presence of polydispersity is to reduce the extent of intramolecular reaction at the same percentage conversion of a refrence reactive polymer, since increasing the chain length results in lower probability of intramolecular reaction (see Figure 6-8). Selective grafting conversion of higher molecular weight reactive polymers also results in less extent of intramolecular reactions. Since gel point and weight-average molecular weight of the grafting system are most sensitive to the polymer species of high molecular weight, polydispersity, therefore, will reduce the effect of intramolecular reaction on the change of the gel point and weight-average molecular weight of the grafting reaction system if we compare to the assumed monodisperse polymers having the number-average molecular weights of the polydisperse reactive polymers.

6.5 EFFECT OF INTRAMOLECULAR REACTION IN CA-SMA GRAFTING SYSTEM

There are on the number-average 85 hydroxyls on the CA backbone and 90 anhydrides on the SMA232 backbone. On the average there is one hydroxyl per two modified anhydroglucose units of CA and one anhydride unit per 13 styrenic units. In order to estimate the order of Θ_{sma}, we can do a rough estimation starting with polystyrene chain, that is the modified anhydride glucose units, the anhydride unit are treated as styrenic unit. The parameters of equation 6-60 are:

$$N_{OH}=85,\ N_{ma}=90,\ v_{OH}=2,\ v_{MA}=14,\ x=2.95,\ \varphi_s=0.9,\ Z_{ball}=12,\ k=1/10$$

The selection for x is with equal amount of CA and SMA. The value of k is based on the calculation by Yoon et al. [1975] where the reduced mean square end-to-end distance ($<r>^2/nl^2$) for atactic polystyrene was reported to be 10.0. With the exclusion of small ring of less than 20 constitutional units (the smallest ring will consists of 21 constitutional units in the calculation), Θ_{sma} is found to be 74.6. Therefore the probability of intramolecular reaction is very small and its influence on the grafting process is minor based on the discussion of section 6-3. The consideration of nonuniform distribution of constitutional units bearing reactive groups on the chain backbone will decrease Θ_{sma} since the ring closure probability is a concave function of the numbers of statistically equivalent structure units of the coarse-grained gaussian chain, but this effect is expected to be minor since the ring closure probability decreases smoothly with the numbers of statistically equivalent units when that number is large. The more rigid chain of CA and SMA (the presence of SMA decrease the chain flexibility as is evidenced by increased Tg in the presence of MA) as compared to polystyrene will increase the estimated Θ_{sma} value, so will the unfavorable interaction between CA and SMA. The effect of polydispersity will reduce the extent of intramolecular reactions as was discussed qualitatively in section 6-4. The consideration of all these factors can lead only to the conclusion that the probability and the extent of intramolecular reaction are minor at a polymer concentration of 10 wt% for the purpose of grafting reaction in this particular CA-SMA grafting system.

6.6 SUMMARY

The kinetic formulation in chapter 5 has been extended to include intramolecular reactions for the grafting reaction system of reactive polymers A and B bearing large numbers of reactive groups. The importance of spatial correlation among chain species because of differences in volume exclusion is recognized and properly incorporated into the kinetic theory. Difference in the excluded volume among polymer species creates the overall redistribution away from the state of complete randomness. Such redistribution can be taken care of by introducing a normalization procedure in the kinetic formulation. The kinetic formulation is self-consistent with such normalization procedure when one considers the presence of intramolecular reaction. A general procedure was provided to look into the effect of intramolecular reaction in slowing down the growth of system's weight average molecular weight and the onset of gelation.. While the grafting system is good for the issues at hand, the importance for the consideration of spatial correlation among polymer species because of volume exclusion is believed to be universal in other polymerization systems for the correct formulation of the theory no matter how small the excluded volume effect is.

A mean probability of intramolecular reaction is taken over all the isomers of the graft copolymer in the kinetic formulation. The buildup of the complexity of the structure of graft copolymers calls for a distinction for the probability of intramolecular of different graft copolymers. A generating function is introduced to derive the expressions for the system's probability of intramolecular reaction, WAMW, and gel point in the approximation of only the first neighbor contribution to the probability of intramolecular reaction. Exact expressions for the system's weight-average molecular weight and gel point are obtained

A semi-quantitative discussion was made on the model parameter Θ in relation to chain characteristics and dilution under the assumption of gaussian distribution. Θ is defined as the numbers of chain A and chain B (including chain A and chain B of the graft copolymer) in the statistically equivalent mean volume of a simple graft copolymer. It is shown that Θ can have a broad range depending on chain characteristics and dilution. Increasing the numbers of reactive group on the chain results in increased Θ, therefore of reduced system's probability of intramolecular reactions.

The effects of intramolecular reaction on the system's weight average molecular weight and gel point were discussed in terms of model parameter Θ. It is found that the gel point is fairly sensitive to intramolecular reaction even though the system's probability of intramolecular reaction is relatively small at the gel point. The sensitivity of system's weight average molecular weight can be either sensitive or not depending on the value of the system's WAMW sought in the practical situation. In general, the effect of intramolecular reaction cannot be simply neglected in the defined grafting system.

Even though an extension of the kinetic formulation to polydisperse reactive polymers posses no difficult, direct simulation on the effect of intramolecular reaction with polydisperse reactive polymers represents a difficult task. However, we can still tell qualitatively what the presence of polydispersities of the reactive polymers does in enhancing or reducing the extent of intramolecular reaction in the pregel region by comparing to the monodisperse case at the same percentage conversion and number-average molecular weights. Under such comparative basis, the presence of polydispersity lowers the system's probability of intramolecular reaction since the intrinsic probability of intramolecular reaction of a graft copolymer decreases with chain length and the grafting reaction weights toward more grafting conversion of the high molecular weight chain fraction of the reactive polymers.

In case of CA-SMA grafting system, it is concluded that the effect of intramolecular reaction can be neglected.

Chapter 7. CONCLUSIONS AND SUGGESTION FOR FURTHER WORK

7.1 CONCLUSIONS

Grafting reactions between cellulose acetate (CA) and styrene maleic anhydride random copolymers (SMA) were successfully carried out in solution with the aid of a catalyst. The grafting reaction occurs in a non-homogeneous state at a polymer concentration of ~10 wt%. The dilution of unfavorable interaction between CA and SMA is very sensitive to the concentration of polymer solution. Increasing the MA level in SMA reduces the immiscibility between CA and SMA. Analysis of the free energy of mixing by a mean field approach shows qualitatively the order of sensitivity of the concentration of polymers and the MA content of SMAs in changing the unfavorable interaction between CA and SMAs.

The rate of grafting conversion can be described by taking into account the effect of phase separation and the effect of polydispersity of the reactive polymers. While the effect of polydispersity on the rate of SMA grafting conversion can be analyzed exactly, the rate of SMA grafting conversion cannot be described in a simple manner since information on the phase size and phase size distribution is not readily available. The complexity of the grafting process is also shown by the power of dispersion of the graft copolymers whence they were produced during grafting reaction.

Several parameters involved in the rate expression of SMA grafting conversion were studied separately: (a) The stirring intensity indicated by the stirring speed in the range of 200-600 (rpm) has little effect on the rate of grafting reaction. This is explained by the presence of low interfacial tension, high solution viscosity and the dispersion power of graft copolymers for equilibrium phase size. These important factors tend to smear out the effect of mixing intensity. (b) The grafting reaction is very sensitive to the concentration of polymers in solution. The concentration of polymers in solution is rather limited in order to avoid the reduction of compatibilizing ability of the graft copolymers, since the net effect of phase heterogeneity is to reduce the effect chain length of the chain segments of graft copolymers. (c) There is a first order relationship on the intrinsic kinetics between reaction rate and the concentration of catalyst. (d) The grafting reaction is very sensitive to reaction temperature, so does the MA level in SMA. (e) Only small amount of water is allowed in this grafting reaction system in order to avoid excess hydrolysis of CA. The presence of small amount of water promotes grafting reaction.

Tensile properties, moisture adsorption and the dimensional stability of some grafting reaction products were evaluated in the form of cast films. The film alloys show slightly improved tensile strength, appreciably increased tensile modulus and reduced elongation at break in comparison to CA, with/without plasticizer. Such tensile properties, together with reduced moisture adsorption, are good for improving dimensional stability of the grafting products. For example, in the presence of 50 % SMA in the alloys, there is more than 50% reduction on the dimensional change as compared to CA for tests in the form of cast films under various water soaking conditions. The dimensional stability of the film alloys is better or comparable to CTA. There is a good potential to find applications for the grafting reaction products in films, textile fibers and separation membranes.

Phase size and homogeneity in the reaction products need to be controlled for best performance in compatibilized blends and alloys. Controlling phase size and homogeneity depends on the structures of the graft copolymers as well as the amount of graft copolymers in the ternary mixtures. It is found that homogeneous phase structures appears in the grafting reaction product as the grafting conversion of SMA increases. Substantial solubilization of homopolymers into the domains of graft copolymers is found. The formation of complex graft copolymers at high grafting conversion does not lead to the insolubilization of free chains. This desirable property is explained from the grafting conversion of more high molecular weight homopolymers based on the current understanding of solubilization phenomena from block copolymer system, a unique feature for synthesizing the graft copolymers in the defined grafting system. While the driving force for homogeneous solubilization at low graft copolymer content was not clearly understood, the dynamic force could have been important in causing the size distribution of the dispersed phase. The study shows the importance of polydispersity in promoting homogeneous phase size in this grafting reaction system.

For a better understanding of the molecular characteristics of the grafting reaction products from a control point of view, it is important to analyze theoretically the branching process of the CA-SMA grafting reaction system. Such an analysis can be done on a more general basis for the defined system of: (a) two reactive polymers bearing large numbers of reactive groups; and (b) homogeneous, irreversible grafting reaction. A kinetic approach is employed to arrive at various expressions for the molecular characteristics of the grafting process neglecting the presence of intramolecular reaction. Both monodisperse and polydisperse polymers are considered. The discussion made on the monodisperse reactive polymers reveals many important things on the branching process. The two most important findings are: (a) the critical grafting conversion is quite limited and changes with the composition of the two reactive polymers; and (b) the take off of the system's WAMW starts long before the onset of gelation. It, therefore, further limits the extent of grafting conversion. When the two reactive polymers are highly polydispersive, the critical grafting conversion behaves in a complicated manner depending on several factors: PDI, distribution, and composition. Increasing PDI results in lower critical grafting conversion when the polydispersities of two reactive polymers are close to each other. It is found that the presence of high molecular weight tail in the polydisperse reactive polymer reduces the critical grafting conversion of the reactive polymer, an undesirable factor for the purpose of grafting. The practical grafting conversion for a reasonable WAMW can be greatly affected when the PDIs of the reactive polymers become extremely high (much more than 3). The study also shows that simulating the molecular weight distribution of the grafting process with polydisperse reactive polymers is not readily done because of long computational time, even though the concentration of each individual species is obtained analytically.

For the particular case of CA-SMA grafting system, calculation based on the assume homogeneous state indicates that the grafting conversion of SMA is limited to 60±5% at equal amount of CA and SMA, and 70±5% at a quarter amount of SMA in the polymer mixture. The presence of heterogeneity at the early stage of grafting reaction will limit further the grafting conversion of SMA. The theoretical analysis is of great importance because of the difficulty in GPC analysis due to the association of the grafting reaction products in carrier solvents.

Grafting reaction of the defined system starts with long chain reactive polymers. The presence of large numbers of reactive groups on the two reactive polymers calls for an analysis on the extent of intramolecular reaction of the graft copolymers during the course of grafting reaction. In the broad sense, the effect of intramolecular reaction remains to be an old problem that has not been dealt with completely from a theoretical point of view.

A self-consistent kinetic theory is developed to look at the extent of intramolecular reaction in the defined grafting system. The self-consistency is satisfied via a normalization procedure that reflects the hidden redistribution of polymer species away from the complete randomness due to differences in volume exclusion for different polymer species.. A general procedure is provided to look into the effect of intramolecular reaction in slowing down the growth of the system's weight average molecular weight and the onset of gelation. While the grafting system is good for the issues at hand, the consideration of spatial correlation among polymer species because of differences in volume exclusion effect is important, and is believed to be universal in other polymerization systems for the correct formulation of the theory, no matter how small the differences in excluded volume effect is.

A mean probability of intramolecular reaction is taken over all the isomers of the graft copolymer in the kinetic formulation. The buildup of the complexity of the structure of graft copolymers requires distinction for the probabilities of intramolecular reactions of different graft copolymers. A generating function is introduced to derive the expressions for the system's probability of intramolecular reaction, WAMW, and gel point using the approximation of only the first neighbor contribution to the probability of intramolecular reaction. Exact expressions for the system's weight-average molecular weight and gel point are obtained

A semi-quantitative discussion is made on the model parameter Θ in relation to chain characteristics and dilution under the assumption of gaussian distribution. Θ is defined as the numbers of chain A and chain B (including chain A and chain B of the graft copolymer) in the statistically equivalent mean volume of the simplest graft copolymer. It is shown that Θ can have a broad range depending on the chain characteristics and dilution. Increasing the numbers of reactive groups on the chain results in increased Θ, and therefore reduced system's probability of intramolecular reaction.

The effects of intramolecular reactions on the system's weight average molecular weight and gel point are discussed in terms of model parameter Θ. It is found that the gel point is fairly sensitive to the presence of intramolecular reactions even though the system's probability of intramolecular reaction is relatively small at the gel point. The sensitivity of the system's weight average molecular weight depends on the value of the system's WAMW sought in the practical situation. In general, the effect of intramolecular reaction cannot be simply overlooked in the defined grafting system.

Extension of the kinetic formulation to polydisperse reactive polymers poses no difficulty, even thougu a direct simulation of the effect of intramolecular reaction in case of polydisperse reactive polymers represents a difficult task. However, one can still tell qualitatively what the presence of polydispersities of the reactive polymers does in enhancing or reducing the extent of intramolecular reaction in the pregel region by comparing it to the assumed monodisperse case at the same percentage conversion and the same number-average molecular weight. Under such comparative basis, the presence of polydispersity reduces the system's probability of intramolecular reaction since the intrinsic probability of intramolecular reaction of a graft copolymer decreases with chain length and the grafting reaction weights towards more grafting conversion of the high molecular weight chain fraction of the reactive polymers.

For the particular case of CA-SMA grafting system, it is concluded that the effect of intramolecular reaction can be neglected for the purpose of grafting reaction products without crosslinking.

7.2 SUGGESTION FOR FURTHER WORK

There are many potentials to utilize the property of improved dimensional stability (compared to CA, d.s.=2.45) of the new compatibilized blends. It is of practical interest to look at the dimensional stability of grafting reaction products for textile fibers. Further work should include: (a) fiber spinning in acetone-water mixture solvent; and (b) testings of the dimensional stability of the fibers under water soaking condition, particularly at high temperature. The results from the above mentioned tests should then be compared with cellulose triacetate.

APPENDICES

APPENDICES

APPENDIX A: Solution by the method of characteristics

In order to solve the first order nonlinear partial differential equation in case of monodisperse reactive polymers, let us rearrange equation 5-20 into

$$F = G_z + AG_A + \frac{1}{x}BG_B - \frac{1}{x}ABG_AG_B = 0 \tag{A-1}$$

The characteristic equations from equation A-1 become

$$\frac{dA}{ds} = F_{G_A} = A - ABG_B / x \tag{A-2}$$

$$\frac{dB}{ds} = F_{G_B} = (B - ABG_A) / x \tag{A-3}$$

$$\frac{dZ}{ds} = F_{G_Z} = 1 \tag{A-4}$$

$$\frac{dG}{ds} = \sum_{K=A,B,Z} G_K F_{G_K} - ABG_AG_B / x \tag{A-5}$$

$$\frac{dG_A}{ds} = -F_A = -(G_A - BG_AG_B / x) \tag{A-6}$$

$$\frac{dG_B}{ds} = -F_B = -(G_B - AG_AG_B) / x \tag{A-7}$$

$$\frac{dG_Z}{ds} = 0 \tag{A-8}$$

The initial conditions are:

$$\begin{gathered} s = 0,\ Z = 0,\ A = \zeta,\ B = \eta,\ G_A(\zeta,\eta,0) = 1,\ G_B(\zeta,\eta,0) = x, \\ G_Z(\zeta,\eta,0) = \zeta\eta - \zeta - \eta,\ G(\zeta,\eta,0) = \zeta + x\eta \end{gathered} \tag{A-9}$$

We have by solving the characteristic equations

$$G(A,B,Z) = \zeta + x\eta - \zeta\eta Z \tag{A-10}$$

$$A = \zeta EXP[(1-\eta)Z] \tag{A-11}$$

$$B = \eta EXP[(1-\zeta)Z] \tag{A-12}$$

$$G_A = \zeta / A \tag{A-13}$$

$$G_B = x\eta / B \tag{A-14}$$

By taking derivatives of equation A-11 and equation A-12 with A and solving the two resultant equations at $A=B=1$, we have

$$\zeta_A\Big|_{A=B=1} = x/(x-Z^2) \tag{A-15}$$

$$\eta_A\Big|_{A=B=1} = Z/(x-Z^2) \tag{A-16}$$

By taking derivatives of equation A-11 and equation A-12 with B and solving the two resultant equations at $A=B=1$, we have

$$\zeta_B\Big|_{A=B=1} = xZ/(x-Z^2) \tag{A-17}$$

$$\eta_B\Big|_{A=B=1} = x/(x-Z^2) \tag{A-18}$$

The partial derivatives in equation 5-27 contain terms of equations A-15, A-16, A-17, and equation A-18 starting from equation A-13 and equation A-14. Equation 5-28 was obtained by further manipulation.

In case of polydisperse polymers, let us rearrange the partial differential equation into

$$G_E = \frac{1}{x}\sum_{m}\sum_{n}\overline{M}_{A_m}\overline{M}_{B_n}A_mB_nG_{A_m}G_{B_n} - \sum_{m}\overline{M}_{A_m}A_mG_{A_m} - \frac{1}{x}\sum_{n}\overline{M}_{B_n}B_nG_{B_n} \tag{A-19}$$

$$(m = i, i', \cdots;\ n = j, j', \cdots)$$

The characteristic equations are:

$$\frac{dA_m}{ds} = A_m\overline{M}_{A_m} - A_m\overline{M}_{A_m}\sum_{n}B_n\overline{M}_{B_n}G_{B_n} / x \tag{A-20}$$

$$\frac{dB_n}{ds} = (B_n\overline{M}_{B_n} - B_n\overline{M}_{B_n}\sum_{m}A_m\overline{M}_{A_m}G_{A_m}) / x \tag{A-21}$$

$$\frac{dE}{ds} = 1 \tag{A-22}$$

$$\frac{dG}{ds} = -(\sum_{m}\sum_{n}\overline{M}_{A_m}\overline{M}_{B_n}A_mB_nG_{A_m}G_{B_n}) / x \tag{A-23}$$

$$\frac{dG_{A_m}}{ds} = -(\overline{M}_{A_m}G_{A_m} - \overline{M}_{A_m}G_{A_m}\sum_{n}B_n\overline{M}_{B_n}G_{B_n} / x) \tag{A-24}$$

$$\frac{dG_{B_n}}{ds} = -(\overline{M}_{B_n}G_{B_n} - \overline{M}_{B_n}G_{B_n}\sum_{m}A_m\overline{M}_{A_m}G_{A_m}) / x \tag{A-25}$$

$$\frac{dG_E}{ds} = 0 \tag{A-26}$$

The initial conditions become

$$\begin{aligned} &s = 0,\ E = 0,\ A_m = \zeta_m,\ B_n = \eta_n,\ G_{A_m} = N^0(\overline{M}_{A_m}),\ G_{B_n} = xN^0(\overline{M}_{B_n}) \\ &G = \sum_{m}\zeta_m N^0(\overline{M}_{A_m}) + x\sum_{n}\eta_n N^0(\overline{M}_{B_n}) \end{aligned} \tag{A-27}$$

$$(m = i, i', \cdots;\ n = j, j', \cdots)$$

By solving equations A-20 to A-26, we have

$$G = \sum_{m}\zeta_m N^0(\overline{M}_{A_m}) + x\sum_{n}\eta_n N^0(\overline{M}_{B_n}) - E\sum_{m}\sum_{n}\zeta_m\eta_n N^0(\overline{M}_{A_m})N^0(\overline{M}_{B_n})\overline{M}_{A_m}\overline{M}_{B_n} \tag{A-28}$$

$$A_m = \zeta_m \exp\left[\overline{M}_{A_m}E(1 - \sum_{n}\eta_n N^0(\overline{M}_{B_n})\overline{M}_{B_n})\right] \tag{A-29}$$

$$B_n = \eta_n \exp\left[\frac{\overline{M}_{B_n} E}{x}\left(1 - \sum_m \zeta_m N^0(\overline{M}_{A_m})\overline{M}_{A_m}\right)\right] \qquad \text{(A-30)}$$

$$G_{A_m} = \zeta_m N^0(\overline{M}_{A_m}) / A_m \qquad \text{(A-31)}$$

$$G_{B_n} = x\eta_n N^0(\overline{M}_{B_n}) / B_n \qquad \text{(A-32)}$$

Likewise from equation A-29 and equation A-30 we have

$$\sum_m N^0(\overline{M}_{A_m})\overline{M}_{A_m} \frac{\partial \zeta_m}{\partial A_m} = \frac{N^0(\overline{M}_{A_m})\overline{M}_{A_m}}{1 - E^2 PDI_A PDI_B / x} \qquad \text{(A-33)}$$

$$\sum_n N^0(\overline{M}_{B_n})\overline{M}_{B_n} \frac{\partial \eta_n}{\partial A_m} = \frac{N^0(\overline{M}_{A_m})\overline{M}_{A_m} PDI_B E}{x - E^2 PDI_A PDI_B} \qquad \text{(A-34)}$$

$$\sum_m N^0(\overline{M}_{A_m})\overline{M}_{A_m} \frac{\partial \zeta_m}{\partial B_n} = \frac{N^0(\overline{M}_{B_n})\overline{M}_{B_n} PDI_A E}{1 - E^2 PDI_A PDI_B / x} \qquad \text{(A-35)}$$

$$\sum_n N^0(\overline{M}_{B_n})\overline{M}_{B_n} \frac{\partial \eta_n}{\partial B_n} = \frac{N^0(\overline{M}_{B_n})\overline{M}_{B_n}}{1 - E^2 PDI_A PDI_B / x} \qquad \text{(A-36)}$$

$$\begin{pmatrix} m = i, i', \cdots;\ n = j, j', \cdots \\ m' = i, i', \cdots;\ n' = j, j', \cdots \end{pmatrix}$$

At $A_m = B_n = 1$, where PDI_A and PDI_B are the polydispersity index of A and B. Equation 5-53 is equivalent to

$$\overline{M}_w = \begin{pmatrix} \sum_m M_{A_m}^2 G_{A_m} + \sum_m M_{A_m} \frac{\partial}{\partial A_m}\left(\sum_{m'} M_{A_{m'}} G_{A_{m'}}\right) + 2\sum_m M_{A_m} \frac{\partial}{\partial A_m}\left(\sum_n M_{B_n} G_{B_n}\right) \\ + \sum_n M_{B_n} \frac{\partial}{\partial B_n}\left(\sum_{n'} M_{B_{n'}} G_{B_{n'}}\right) + \sum_n M_{B_n}^2 G_{B_n} \end{pmatrix} \Big/ \left(\sum_m M_{A_m} G_{A_m} + \sum_n M_{B_n} G_{B_n}\right)$$

(A-37)

The partial derivatives in equation A-37 were taken from equations A-31 and equation A-32. By substituting terms of equations A-33, A-34, A-35 and A-36 into equation A-37 and further manipulations, we arrived at the result of equation 5-54. It is just to mention here that Z-average molecular weight can also be derived by the same procedures.

APPENDIX B: Serial solution of the characteristic equations considering intramolecular reaction

The characteristic equations of equation 6-24 are:

$$\frac{dA}{dS} = F_{G_A} = A - 2A/\Theta_B - \begin{bmatrix} ABG_B - ABG_B/\Theta_B - (ABG_B + 2A^2G_A - AG)/\Theta_A \\ +2A(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix} \beta/x \tag{B-1}$$

$$\frac{dB}{dS} = F_{G_B} = B/x - 2B/\Theta_B - \begin{bmatrix} ABG_A - ABG_A/\Theta_A - (ABG_A + 2B^2G_B - BG)/\Theta_B + \\ 2B(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix} \beta/x \tag{B-2}$$

$$\frac{dE}{ds} = F_{G_E} = 1 \tag{B-3}$$

$$\frac{dG_A}{ds} = -(F_A + G_AF_G) = -G_AF_G - \left\{ G_A - 2G_A/\Theta_B - \begin{bmatrix} BG_BG_A(1-1/\Theta_B) - (BG_BG_A + 2AG_A^2 - \\ G_AG)/\Theta_A + 2G_A(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix} \beta/x \right\} \tag{B-4}$$

$$\frac{dG_B}{ds} = -(F_B + G_BF_G) = -G_BF_G - \left\{ G_B/x - 2G_B/\Theta_B - \begin{bmatrix} AG_BG_A(1-1/\Theta_A) - (AG_AG_B + 2BG_B^2 \\ -G_BG)/\Theta_B + 2G_B(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix} \beta/x \right\} \tag{B-5}$$

$$\frac{dG_E}{ds} = -(F_E + G_EF_G) = -G_EF_G + d\beta/dE \begin{bmatrix} ABG_AG_B - (ABG_AG_B + A^2G_A^2 - AG_AG)/\Theta_A \\ -(ABG_AG_B + B^2G_B^2 - BG_BG)/\Theta_B \\ +(AG_A + BG_B - G)^2/\Theta_A\Theta_B \end{bmatrix} /x \tag{B-6}$$

$$\frac{dG}{ds} = \sum_{i=A,B,E} G_iF_{G_i} = -2G/\Theta_B - \left\{ \begin{matrix} ABG_AG_B(1-1/\Theta_A - 1/\Theta_B) - (A^2G_A^2/\Theta_A + B^2G_B^2/\Theta_B) + \\ \left[(AG_A + BG_B)^2 - G^2\right]/\Theta_A\Theta_B \end{matrix} \right\} \beta/x \tag{B-7}$$

where

$$F_G = 2/\Theta_B - \left[AG_A/\Theta_A + BG_B/\Theta_B - 2(AG_A + BG_B - G)/\Theta_A\Theta_B\right]\beta/x \qquad \text{(B-8)}$$

Equation B-6 is not needed in the solution since G_E does not appear in the rest of equations. By dividing equations B-1, B-2, B-4, B-5, B-7 by equation B-3, we have

$$\frac{d\ln A}{dE} = 1 - 2/\Theta_B - \begin{bmatrix} BG_B - BG_B/\Theta_B - (BG_B + 2AG_A - G)/\Theta_A \\ +2(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix}\beta/x \qquad \text{(B-9)}$$

$$\frac{d\ln B}{dE} = 1/x - 2/\Theta_B - \begin{bmatrix} AG_A(1 - 1/\Theta_A) - (AG_A + 2BG_B - G)/\Theta_B \\ +2(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix}\beta/x \qquad \text{(B-10)}$$

$$\frac{d\ln G_A}{dE} = -\left\{1 - 2/\Theta_B - \begin{bmatrix} BG_B(1 - 1/\Theta_B) - (BG_B + 2AG_A - G)/\Theta_A \\ +2(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix}\beta/x\right\} - F_G \qquad \text{(B-11)}$$

$$\frac{d\ln G_B}{dE} = -\left\{1/x - 2/\Theta_B - \begin{bmatrix} AG_A(1 - 1/\Theta_A) - (AG_A + 2BG_B - G)/\Theta_B \\ +2(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix}\beta/x\right\} - F_G \qquad \text{(B-12)}$$

$$\frac{dG}{dE} = -2G/\Theta_B - \begin{Bmatrix} ABG_AG_B(1 - 1/\Theta_A - 1/\Theta_B) - (A^2G_A^2/\Theta_A + B^2G_B^2/\Theta_B) + \\ \left[(AG_A + BG_B)^2 - G^2\right]/\Theta_A\Theta_B \end{Bmatrix}\beta/x \qquad \text{(B-13)}$$

The initial conditions are:

$$E=0;\ A=\zeta\ ,\ B=\eta\ , G_A=1,\ G_B=x,\ G=\zeta+x\eta \qquad \text{(B-14)}$$

No analytical solution is obtained for G. We have from equations B-9, B-11

$$\frac{d\ln(AG_A)}{dE} = -F_G \qquad \text{(B-15)}$$

We have from equations B-10, B-12

$$\frac{d\ln(BG_B)}{dE} = -F_G \qquad \text{(B-16)}$$

We can see from the inspection of equations B-13, B-15 and B-16 that G, AG_A and BG_B are functions of E, ζ, η. Integrating equations B-15, B-16 gives

$$\frac{AG_A}{\zeta} = \frac{BG_B}{x\eta} = f(E,\zeta,\eta) \tag{B-17}$$

By integrating equations B-9, B-10, B-15, we have

$$\ln\frac{A}{\zeta} = (1-\frac{2}{\Theta_B})E - \int_0^E \left\{ \begin{bmatrix} BG_B - BG_B/\Theta_B - (BG_B + 2AG_A - G)/\Theta_A + \\ 2(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix} \beta / x \right\} dE \tag{B-18}$$

$$\ln\frac{B}{\eta} = (\frac{1}{x}-\frac{2}{\Theta_B})E - \int_0^E \left\{ \begin{bmatrix} AG_A - AG_A/\Theta_A - (AG_A + 2BG_B - G)/\Theta_B + \\ 2(AG_A + BG_B - G)/\Theta_B\Theta_A \end{bmatrix} \beta / x \right\} dE \tag{B-19}$$

$$\ln\frac{AG_A}{\zeta} = \frac{2E}{\Theta_B} - \int_0^E \{[AG_A/\Theta_A + BG_B/\Theta_B - 2(AG_A + BG_B - G)/\Theta_B\Theta_A]\beta / x\} dE \tag{B-20}$$

We have from the definition of the generating function

$$AG_A\big|_{A=B=1} \equiv 1 \tag{B-21}$$

$$BG_B\big|_{A=B=1} \equiv 1 \tag{B-22}$$

From equation 6-37, we have

$$\beta = e^{E/\Theta_B} \tag{B-23}$$

From equations B-18, B-19, we have

$$\zeta\big|_{A=B=1} = 1 \tag{B-24}$$

$$\eta\big|_{A=B=1} = 1 \tag{B-25}$$

With the requirements of equations B-14, B-21, B-22, B-24, B-25, $f(E,\zeta,\eta)$ of equation B-17 satisfies

$$f(0,\zeta,\eta) = 1 \tag{B-26}$$

$$f(E,1,1) = 1 \tag{B-27}$$

We must have for the Taylor expansion of $f(E,\zeta,\eta)$

$$f(E,\zeta,\eta) = 1 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^i E^j a_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^i E^j b_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^j E^k c_{ijk} \tag{B-28}$$

By substituting equation B-28 into equation B-17, we have

$$AG_A = \zeta\left[\begin{array}{l} 1 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^i E^j a_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^i E^j b_{ij} \\ + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^j E^k c_{ijk} \end{array}\right] \tag{B-29}$$

$$BG_B = x\eta\left[\begin{array}{l} 1 + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^i E^j a_{ij} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^i E^j b_{ij} \\ + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^j E^k c_{ijk} \end{array}\right] \tag{B-30}$$

The system's WAMW is related to $\partial(AG_A)/\partial A$, G_{AB} and $\partial(BG_B)/\partial B$ at $\zeta=\eta=1$. The terms with coefficients c_{ijk} are not needed for getting the system's WAMW, only terms with coefficients a_{1i}, b_{1i} $(i=1,2,\cdots)$ appear in the expression for the molecular weight average. $\partial(AG_A)/\partial A$, G_{AB} and $\partial(BG_B)/\partial B$ are related further to ζ_A, ζ_B, η_A, η_B at $\zeta=\eta=1$. The coefficients of a_{1i}, b_{1i} $(i=1,2,\cdots)$ and ζ_A, ζ_B, η_A, η_B at $\zeta=\eta=1$ were obtained simultaneously by taking partial derivatives of equations B-18, B-19, B-20 with A and B where we have already substituted equations B-29, B-30 into them. ζ and η are independent variables that were taken out of the integrals before we took the partial derivatives. We need also to substitute the results of $G_A=1$, $G_B=x$ at $\zeta=\eta=1$. From the partial derivatives of equations A-18, A-19, we obtained the expressions for ζ_A, η_A and ζ_B η_B. By substituting these expressions into the partial derivative of equation B-20, we have

$$\sum_{i=1}^{\infty} g_i E^i = 0 \qquad (\text{from } \frac{\partial}{\partial A}) \qquad \text{(B-31)}$$

$$\sum_{i=1}^{\infty} h_i E^i = 0 \qquad (\text{from } \frac{\partial}{\partial B}) \qquad \text{(B-32)}$$

We recovered the coefficients of a_{1i}, b_{1i} $(i = 1,2,\cdots)$ by setting $g_i = h_i = 0$ $(i = 1,2,\cdots)$, in return, ζ_A, η_A and ζ_B η_B. were obtained. Coefficients of a_{11}, a_{12}, b_{11}, b_{12} were shown in equations 6-22, 6-23. The expressions for ζ_A, η_A and ζ_B η_B. were shown in equations 6-31, 6-34. In order to get the results of equations B-31, B-32, we need to expand the results of several integrals from the partial derivatives of equations B-18, B-19, B-20 into serial forms. These are:

$$\int_0^E \beta dE = \sum_{i=1}^{\infty} \frac{1}{i!}\left(\frac{1}{\Theta_B}\right)^{i-1} E^i \qquad \text{(B-33)}$$

$$\sum_{i=1}^{\infty} \int_0^E a_{1i} E^i \beta dE = \sum_{i}^{\infty} \sum_{j=1}^{\infty} \frac{a_{1i}\Theta_B^{1-j}}{(i+j)(j-1)!} E^{i+j} \qquad \text{(B-34)}$$

$$\sum_{i=1}^{\infty} \int_0^E b_{1i} E^i \beta dE = \sum_{i}^{\infty} \sum_{j=1}^{\infty} \frac{b_{1i}\Theta_B^{1-j}}{(i+j)(j-1)!} E^{i+j} \qquad \text{(B-35)}$$

Detailed manipulations are tedious but straight forward, it is, therefore, not included here.

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