Dynamics in Miscible Polymer Blends and Associative Polymers

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In the research field of molecular rheology, one of the most challenging tasks is to understand multi-chain interactions, including topological interactions, frictional interactions, and chain associations. Our research in the past ten years have been placed on polymer dynamics under the multi-chain interactions, in particular the topological and frictional interactions between miscible components having large dynamic asymmetry, and physical associations including ionic interactions and hydrogen-bondings.

Key Words: Dynamics / Miscible polymer blends / Associative polymers

1. INTRODUCTION

The ultimate goal of molecular rheology is to understand macroscopic rheological properties from molecular level. Toward this end, there are several important milestones. The Rouse’s bead-spring theory is the first molecular theory. It simplified a multi-chain problem into a single-chain problem, by regarding the surrounding chains as a uniform frictional medium. Nevertheless, the Rouse model cannot predict the dynamic features of long chains, in particular the rubbery plateau and delayed terminal relaxation. This problem was solved theoretically by Doi and Edward[1]. They again simplified the multi-chain problem into a single-chain problem, by regarding surrounding chains as a fixed tube that restricts the motion of a focused chain. As a result, the focused chain is forced to move along the contour of the tube, through one-dimensional diffusion defined as reptation by de Gennes[2].

After the development of the Rouse and tube theories, several molecular theories were developed for associative polymer systems through considering an association point as a sticky point, e.g. the sticky-Rouse theory by Baxandall[3] and sticky-Reptation theory by Leibler, Rubinstein, and Colby[4]. These molecular theories inherited the single-chain treatment, and thus are applicable when the associative network has been well developed, so that each chain attached physically to the network relaxes in a similar manner.

Obviously, the single-chain treatment greatly simplifies predictions of dynamic behavior of non-entangled and entangled, non-sticky and sticky systems. Nevertheless, when quantitative prediction is of importance, we should look back into the detailed dynamic aspects owing to multi-chain interactions.

For example, almost all modifications of the original tube model for the non-sticky systems have been placed on incorporating multi-chain interactions, including the constraint release, double reptation, tube dilation mechanisms and so on[5-8]. The newly developed molecular theories can predict quantitatively dynamics of non-sticky systems having polydispersity in chain size. Nevertheless, our understanding is less comprehensive on frictional distribution that manifests when two distinct components are mixed at the molecular level, e.g. in miscible polymer blends or disordered block copolymers.

For the sticky system, the single chain approach should fail near the gelation point, where the system is a mixture of non-associative chains, chains associated to sol, and possibly also chains associated to gel. These chains exhibit distinct dynamics. Rubinstein and Semenov developed a mean-field theory to predict dynamic changes of associative polymers along with the sol-to-gel transition[9]. Nevertheless, to our best knowledge, there is no experimental approach to test quantitatively this important theory until our recent approach[10-12].

Our research in the past ten years’ was taken with respect to the multi-chain interactions of polymer-related systems, particularly in miscible polymer blends and associative polymers. This short review summarizes our progresses in
understanding these interactions.

2. DYNAMICS OF MISCIBLE POLYMER SYSTEM

2.1 Overview

Polymer pairs usually show immiscibility owing to small mixing entropy and unfavorable energetic interaction. However, there are several polymer pairs having negligible or favorable interaction within certain composition and temperature ranges, allowing them to be miscible at the molecular level.

Over a long period, miscible polymer blends have been regarded as a frictional uniform system to exhibit a single $T_g$ and uniform segmental mobility. As a result, the chain dynamics is expected to be similar to that of binary blends, i.e., blends of chemically identical components of different MW.

Nevertheless, it is gradually understood that miscible polymer blends are microscopically heterogeneous owing to the self-concentration. Namely, since the same segments are connected in a chain, a given segment, say A, is in a dynamic environment locally condensed in A. Similarly, B segment feels a dynamic environment locally condensed in B. As a result, dynamics of either A or B tends to bias toward its bulk behavior, and the dynamic contrast of A and B magnifies if they have large contrast in their bulk $T_g$.

To investigate the dynamic role of frictional asymmetry, we chose a model system composed of cis-polyisoprene (PI) and poly (4-tert butyl styrene) (PtBS). This pair of polymers has a very large contrast in the bulk $T_g$: PI and PtBS have $T_g \approx -70 \, ^\circ C$ and $150 \, ^\circ C$, respectively, whereas they are surprisingly miscible owing to a weak attractive interaction as reflected in their $\chi$ parameter slightly smaller than 0 over a wide $T$ range. Owing to the self-concentration, PI and PtBS with low and high bulk $T_g$ usually behave as the fast and slow components, respectively.

To study the dynamics of this system, we designed an experimental protocol as explained in Fig. 1, where the PI and PtBS chains are shown in red and blue colors, respectively. Both PI and PtBS have type-B dipoles (green arrows) that are perpendicular to the chain backbone. Therefore, segmental relaxations of PI and PtBS are dielectrically active. The PI chain also has dipoles parallel along the backbone, the so-called type-A dipoles. Therefore, end-to-end fluctuation of the PI chains can be selectively detected in the dielectric response at long time. Moduli of both components can be detected in the stress relaxation measurement. However, the slower component would govern the stress response particularly at long time where the fast component has relaxed.

In summary, the dielectric and viscoelastic responses at long time scales are mainly contributed by PI and PtBS, respectively, unless the PI chains are significantly longer than the PtBS chains. This feature enables us to examine dynamics of each component through a combination of the dielectric and rheological techniques.

Fig. 1. Experimental design to resolve separately dynamics of the fast PI and slow PtBS components.

![Fig. 1](image1)

![Fig. 2](image2)

Fig. 2 (a) Comparison of viscoelastic storage and loss moduli, $G'$ and $G''$, and dielectric loss $\varepsilon''$ obtained at 30, 60, and 100 $^\circ C$ for a PI20/PtBS16 blend with PI/PtBS composition of 50 wt/50 wt. (b) Time temperature superposition fails significantly for $\varepsilon''$ of PI20 in the blend. Inset of panel (a) shows a molecular picture of this blend. Redrawn, with permission, from *Macromolecules*, 41, 8694 (2008).
2.2 Miscible blends of short PI and PtBS chains

Figure 2 (a) compares the viscoelastic storage and loss moduli, $G'$ and $G''$, and dielectric loss $\varepsilon''$, of a 50 wt/50 wt blend of short PI and PtBS chains that are barely entangled ($M_{PI} = 20 \text{kDa} > M_{e,PI} = 5 \text{kDa}$, $M_{PtBS} = 16 \text{kDa} < M_{e,PtBS} = 38 \text{kDa}$)\(^{20}\). The PI and PtBS components are coded by MW in unit of kDa. The viscoelastic terminal relaxation frequency, as estimated by cross point of $G' \sim \omega^2$ and $G'' \sim \omega$ tails (solid lines), is strongly delayed with respect to the peak frequency of $\varepsilon''$ at low $T = 30 \text{ºC}$ close to the localized $T_g$ of PtBS. A degree of this delay reduces with increasing $T$ from 30 to 100 ºC, and the viscoelastic terminal relaxation frequency finally approaches the peak frequency of $\varepsilon''$ at high $T = 100 \text{ºC}$.

Figure 2 (b) tests the time temperature superposition (tTs) for $\varepsilon''$, where strong failure of tTs is seen; the $\varepsilon''$ peak narrows with increasing $T$, and finally coincides with the $\varepsilon''$ peak of bulk PI (solid curve) at the highest $T = 120 \text{ ºC}^{20, 21}$.

A combination of Figs. 2 (a) and (b) suggests a molecular picture shown in the inset of Fig. 2 (a), where PtBS chains (in blue) are not strongly overlapped in the space. When motion of the PtBS chains is quenched at low $T = 30 \text{ ºC}$ close to the localized $T_g$ of PtBS, PI chains (in red) in a region locally condensed in PtBS would feel stronger friction than other PI chains out of this region, leading to the frictional non-uniformity for the PI chains. This non-uniformity smears with reduction of the dynamic contrast between PI and PtBS upon increasing $T$ away from the localized $T_g$ of PtBS. At sufficiently high $T = 120 \text{ ºC}$, the PI and PtBS chains become equally fast in motion and thus PI exhibits the same relaxation mode distribution as its bulk (solid curve in Fig. 2 (b)).

2.3 Miscible blends of long PI and PtBS chains

Dynamics of the entangled PI and PtBS chains was examined through the same experimental protocol\(^{22}\). Figure 3 shows $G'$ and $G''$, and $\varepsilon''$ for the well-entangled PI and PtBS chains having MW $\gg M_e$ ($M_{PI} = 99 \text{kDa} \gg M_{e,PI}$, $M_{PtBS} = 348 \text{kDa} \gg M_{e,PtBS}$)\(^{23}\).

Linear viscoelasticity changes significantly with temperature. Double plateau behavior is observed at $T = 100 \text{ ºC}$, where the frequency for the decay of the high-$\omega$ plateau coincides with the peak frequency of $\varepsilon''$, indicating that the decay is owing to the disentanglement of PI. Meanwhile, the relaxation behavior of low-$\omega$ plateau is very similar to that of the semidilute PtBS solution of the same PtBS content (not shown here)\(^{22}\), indicating that the relaxed PI chains behave as a diluent for the PtBS chains that are mutually entangled in space.

In contrast, the high frequency plateau is not seen at frequency higher than the $\varepsilon''$ peak at 30 ºC. Instead, a Rouse-type region characterized by $G' \sim G'' \sim \omega^{\frac{1}{2}}$ is seen (blue dashed line)\(^{22}\). This result strongly suggests that PI and PtBS...
are equilibrated in a coupling way. Namely, the full equilibration of PI to a length scale cannot be realized until the equilibration has been achieved for the coexisting PtBS segment to the same length scale. Then, the equilibration of the entanglement segment is governed by that of the slower PtBS component.

This mechanism can be better understood through a rough estimation. In Fig. 3, the arrow indicates a characteristic frequency $\omega_c$, expected for equilibration at the entanglement length (where $G' \sim G'' = kT$ per entanglement). This frequency is not too much faster than the frequency of $\varepsilon''$ peak at 30 °C, meaning that the PI chains relax immediately after the full equilibration is achieved for both PI and PtBS over the entanglement length. The small delay of the disentanglement of PI with respect to the equilibration of entanglement of PtBS should account for the vanish of high frequency plateau.

Detailed analysis shows that the strong frictional contrast between PtBS and PI plays a central role in the mechanism explained above\textsuperscript{20}. Since the frictional coefficient per segment of PtBS is much larger than that of PI, i.e., $\zeta_{\text{PtBS}} \gg \zeta_{\text{PI}}$, the reptation time $\sim \zeta_{\text{PI}} N^2 / N_e$ for PI is not too much larger than the entanglement time $\sim \zeta_{\text{PtBS}} N_e^2$ for PtBS, even if the number of segments per chain $N$ of PI is much larger than that per entanglement $N_e$.

### 2.4 Disordered PI-PtBS block copolymer

Since PI and PtBS have such a large frictional contrast at low $T$, one natural question is: how does dynamic behavior change if they are connected in a diblock copolymer? Figure 4 shows (a) $\varepsilon''$ and a change of dielectric constant from its static value $\Delta \varepsilon'$ and (b) $G'$ and $G''$ plotted against $\omega$ of a PI-PtBS diblock copolymer (with $M_{\text{PI}} = 53$ kDa and $M_{\text{PtBS}} = 42$ kDa for the PI and PtBS blocks, respectively) in the disordered state at $T = 20 ^\circ$C, where the frictional contrast is high\textsuperscript{20}. In Panel (a), we find $\Delta \varepsilon'$ is much broader than that expected for one block of linear chain with no frictional contrast (green filled symbols). Instead, both $\varepsilon''$ and $\Delta \varepsilon'$ are similar to those of star-shaped PI (blue curves) with arm size the same as the size of the PI block. This behavior can be explained if we consider the great frictional contrast therein. The highly mobile PI block is tethered by the immobilized PtBS block, and thus it is forced to relax akin to a star arm with one tethered end.

This result, to our best knowledge, is the first experimental evidence to show that a linear chain could exhibit dynamic feature of a tethered chain owing to the large frictional contrast\textsuperscript{20}. In panel (b), the copolymer chains as a whole exhibit the relaxation behavior very similar to that of a reference PI/PtBS blend, in which the PI and PtBS chains have the same molecular weight as the PI and PtBS blocks of the PI-PtBS copolymer\textsuperscript{20}. This feature is understandable if we consider the dynamic similarity of these two systems. PI is the fast component in both the block copolymer and the reference blend, the relaxed PI blocks/chains serve somehow as the solvent for the unrelaxed PtBS blocks/chains, enabling the latter to relax in a similar way in the copolymer and the reference blend.

### 3. DYNAMICS OF ASSOCIATIVE POLYMER SYSTEM

#### 3.1 Overview

Dynamics of associative polymers strongly relies on the strength, position and density of the associations. Figure 5 compares the energy level of different interactions. Covalent bond is usually ~two orders higher than thermal energy $kT$ at room $T (= 2.5$ kJ/mol, in arrow\textsuperscript{20}). Therefore, the covalent bonds are usually very stable. In contrast, ionic interaction and hydrogen bonding are ~ one order higher than $kT$ at room $T$. Then, the formation and breakup of these interactions could enter the time scale of our observation to exhibit reversibility at sufficiently high $T$\textsuperscript{11, 12}. The reversibility is very important in realizing special functions of associative materials, like shape-memory, ion transport, stimuli-response, and self-healing, as well as in improving processing and recycling abilities of these materials\textsuperscript{11, 12}.

In theory, the ion association and hydrogen bonding are usually treated in different ways depending on their strength. In case if the reversible interaction is only a few $kT$, it can be regarded as a frictional condensed point/region. In contrast, if the interaction energy becomes ~ 10 $kT$ or higher, the

![Fig. 5 Energy levels of different interactions. Redrawn, with permission, from J Rheol, 61, 1099 (2017).](image-url)
interaction can be treated as a sticky point having lifetime much longer than the characteristic time of the segmental motion. In this review, we considered only the latter case.

### 3.2 Sol-to-gel transition

As explained earlier, the sticky Rouse and sticky reptation theories simplify a multi-chain problem into a single-chain problem, and thus they are not applicable near the gelation point where a distribution of number of ions per chain plays a central role. Rubinstein and Semenov developed a mean-field theory based on an assumption that the sol chains/network strands are strongly overlapped. We modified this theory recently through introducing the Ginzburg transition from the mean-field percolation to the critical percolation region. This transition should play an important role near the gel point because the largest sol chains (below the gel point) or network strands (above the gel point) are so sparse there and thus they should finally discard overlapping.

Prediction of storage modulus against frequency based on our reversible-gelation theory is summarized in Fig. 6. Here, the non-entangled precursor chains exhibit Rouse behavior characterized by a power law region $G' \sim \omega^{0.5}$ and the terminal relaxation that follows. The sol chains formed below the gel point exhibit broad power-law-type relaxation characterized by $G' \sim \omega^{0.67}$ in the mean-field region and $G' \sim \omega^{0.5}$ in the critical percolation region. Plateau appears when a degree of gelation is above the gel point, and the plateau increases in amplitude with a densification of the network upon increasing the degree of gelation. Finally, all chains are associated to the network and these chains relax in a sticky-Rouse manner. Namely, the Rouse-type relaxation, characterized by $G' \sim G'' \sim \omega^{1/2}$, persists up to a length scale of the ion-ion distance, followed by a plateau region until the relaxation of length scale larger than the ion-ion distance is activated by the ionic dissociation. If the dissociations of different stickers are independent events, the relaxation activated by the ionic dissociation is again Rouse-type characterized by $G' \sim G'' \sim \omega^{2/3}$. This region is termed as the sticky-Rouse region.

We checked the validity of this theory in several model systems having association energy of $\sim 10 kT$ or higher, including the sulfonated polystyrene, the multiple hydrogen bonding system based on the 2-ureido-4[1H]-pyrimidinone (UPy) groups.

Figure 7 compares the (peudo-) master curves of sulfonated polystyrene samples of different ion contents (symbols), and predictions of the reversible gelation model (curves). Quantitative agreement is achieved, and the Ginzburg transition from power $G' \sim \omega$ to $G' \sim \omega^{2/3}$ is clearly seen for a sample close to the gel point (green symbols), which highlights an importance of our theoretical incorporation of the Ginzburg transition.

### 3.3 Association energy

One of the greatest challenges in studying the linear viscoelasticity (LVE) of the associative polymers is the failure of tTs. For example, it is clear in Fig. 7 that the tTs holds approximately for the samples below the gel point (i.e., symbols at the right side of the green symbols), because all sol chains therein relax through the thermal motion of the same activation energy. Nevertheless, for the samples above the gel point (i.e. symbols at the left side of the green curve), tTs fails significantly at the valley of $G''$ where the stress relaxation is contributed from both the thermal motion of the Rouse

Fig. 6 Prediction of a change of storage modulus with increasing degree of gelation by the reversible gelation model. Redrawn, with permission, from Macromolecules, 48, 1221 (2015).

Fig. 7 Comparison of linear viscoelastic moduli (symbols) of sulfonated polystyrene with sodium as counterion and those predicted by the reversible gelation model (curves). Redrawn, with permission, from Macromolecules, 49, 3936 (2016).
segments and the sticker dissociation that are associated to different activation energies.

The failure of tTs in turn enables us to determine an association energy \( E_a \). To this end, we designed an experimental protocol through synthesizing associative polymer samples slightly above the gel point. For these samples, the stress relaxation contributed from the Rouse-type motion and sticker dissociation are not well separated and can be detected in a single frequency sweep measurement.

In Fig. 8, we test tTs for a representative Upy-based associative polymer sample slightly above the gel point. In Figs. 8 (a) and (b), we superpose the high-\( \omega \) Rouse part and low-\( \omega \) decrosslinking part of moduli, respectively. The resulting shift factors \( \alpha_\tau /\alpha_T \) reflect the temperature dependence of the Rouse time per segment \( \tau_\text{R} \) and that of the lifetime of ion association \( \tau_s \), respectively. Considering that these two time scales are related by the association energy \( E_a \) as \( \tau_s /\tau_\text{R} = \exp(E_a/kT) \), we plot \( \ln(\alpha_\tau /\alpha_T) \) against \( 1/T \) to determine \( E_a = 33 \text{ kJ/mol} \), as shown in the inset of panel (b)\(^{27,28}\).

It should be noted that \( E_a \) thus-determined (from a temperature dependence of \( \tau_s /\tau_\text{R} \)) is different from the apparent \( E_a \) calculated directly from a temperature dependence of the viscosity (that is governed by \( \tau_s \)) that has been extensively reported in literatures. The latter \( E_a \) is an overevaluation of the association energy because the activation energy for the thermal motion of the Rouse segments has also been counted.

In Fig. 9, we plot \( E_a \) calculated by our protocol (based on \( T \) dependence of \( \tau_s /\tau_\text{R} \)) against \( E_a \) calculated directly from analysis of the LVE master curves with the reversible gelation model (c.f. curves in Fig. 7) for the sulfonated PS with Na, K, Rb, Cs as counterions and Upy-based polymers. The analysis of the master curves gives directly \( \tau_s \) and \( \tau_\text{R} \), and accordingly \( E_a \) at the reference temperature \( T_r \). Good agreement can be achieved for \( E_a \) evaluated from these two methods, lending support to our protocol\(^{12,28}\).

### 3.4 Model telechelic ionomers with distribution of number of ions at chain ends

All ionomers explained above are characterized by low content of ion groups that are well separated along a polymer chain. As a result, the association energy and accordingly the lifetime of ion associations are relatively uniform. For application, it is usually necessary to broaden the distribution of association energy to realize multi-time-scale dissipation. This strategy is widely employed in natural materials and living organism\(^{29}\), as well as in commercial associative polymers, to achieve high strength and toughness simultaneously. For example, the well-known commercial ionomer Surlyn...
contains more than one type of counterions (such as Na, K, and Zn), endowing it with high toughness and impact resistance in varied weather conditions\(^\text{30}\).

To tailor the association energy, one possible pathway is through utilizing connecting ionic groups. Since the connecting ionic groups cannot dissociate independently, their dissociation energy as a whole should be much higher than that of single ion group. This pathway has been explored in our recent study\(^\text{31}\). We synthesized a unique type of telechelic ionomers through two-step copolymerization. Namely, we first polymerized a polystyrene block with a bifunctional agent, and later incorporated small amount of ion-containing monomers at both ends of the central PS block. Since the ion-containing monomers were statistically incorporated at the chain ends, the number of connecting ions at each chain end exhibited certain distribution.

Figure 10 shows evolution of LVE with increasing \(m\), an average number of ions per chain end, where the sol-to-gel transition can be clearly seen (the telechelic ionomers are coded as TPS-\(m\)). However, the relaxation mode distribution above the gel point is quite different from that shown in Fig. 7. The plateau region is followed by a power-law like region rather than the terminal relaxation. This result strongly suggests that the system is still far from full relaxation after the onset of the decrosslinking process.

To simplify the discussion, we classify the chain ends into three types, \(i.e.,\) non-ion, single-ion, and multi-ion ends. The fractions of three types of chain ends change with increasing \(m\), as estimated in the inset of Fig. 10 (b) (based on the assumption of random placements of ions at the chain ends). The gel network should be constructed by chains having both ends sticky. The sticky ends could be either the single-ion or the multi-ion ends. In our opinion, we detected only the dissociation of the single-ion ends in the frequency and temperature ranges of our measurement. Continuous dissociations of the single-ion chain ends would gradually activate the relaxation of sol chains formed by the multiple-ion chain ends, resulting in a power law like region that follows the plateau region. This study suggests a convenience pathway to develop a system with wide distribution of the ion association energy.

### 3.5 Relationship between brittle-ductile transition and gelation

As explained earlier, high toughness of ionomer network is usually realized through broadening the dissociation energy. Nevertheless, ionomer networks based on a single ion pair usually show brittleness upon application of fast elongation. For example, several studies in literatures revealed that ionomers based on a single-ion pair deform elastically before failure at the maximum Hencky strain, \(\varepsilon_H < 2\), upon applying the fast elongation (with Weissenberg number \(W_i > 1\)), where \(\varepsilon_H < 2\) corresponds to a maximum stretch ratio \(\lambda < \exp (2) = 7.4\)\(^\text{32-36}\).

One noteworthy common feature of these studies is that the ionomer samples are all well above the gel point. Considering a network strand containing averagely \(N_s\) Kuhn segments of length \(b\), the strand should have equilibrium length \(N_s^{0.5} b\) and fully stretched length \(N_s b\), leading to a maximum stretch ratio \(\lambda_{\text{max}} \approx N_s^{0.5} b / N_s^{0.5} b = N_s^{0.5}\). This estimation shows that stretchability would increase with increasing \(N_s\) upon decreasing a degree of gelation.

In our recent study, we studied a relationship between the ductility and degree of gelation of ionomers. Figure 11 compares elongational stress against Hencky strain of three ionomer samples at different ion contents. These ionomer samples were synthesized through copolymerizing sodium 4-vinylbenzenesulfonate hydrate and hexyl methacrylate at a common DP ~ 50. The number associated to the curves are Weissenberg number \(W_i\), defined as a product of the Hencky strain rate and terminal relaxation time. \(W_i > 1\) means that the elongational flow is fast and thus we expect the elastic defor-
The three samples have distinct degrees of gelation: the sample showing in panel (a) is slightly above the gel point, which contains both gel strands and sol chains but the sol chains are the majority. The sample showing in panel (b) has higher degree of gelation, where the gel stands become the majority. The sample showing in panel (c) is a fully gelled sample in which almost all chains are associated to the gel network and a fraction of gel strands ~ 1.

The elongational behavior is quite different for these samples\(^{37}\). In panel (c), the sample shows rubbery elasticity that can well predicted by the neo-Hookean model (solid curve). The macroscopic fracture occurs at Hencky strain lower than \(\ln(\lambda_{\text{max}}) = \ln(N^{0.5})\) (red dashed line). This result means that the sample is very brittle therein. The sample in panel (b) shows similar behavior for \(W_i = 6.3\), but stretchability enhances upon applying slower deformation with \(W_i = 2.1\) (where the largest \(\varepsilon_H\) before the fracture becomes higher than \(\ln(\lambda_{\text{max}})\)), meaning that the sample can adjust the structure better when the elongational flow becomes slower. Finally, high stretchability is achieved for the sample elongated at \(W_i = 1\) and 10 in panel (a). The sample shows the strain hardening at low strain, and the pseudo-yielding behavior at \(\varepsilon_H = \ln(\lambda_{\text{max}})\). After that, the sample can be stretched up to \(\varepsilon_H\) of 5 (close to limit of our equipment) without macroscopic fracture. This value corresponds to stretch ratio \(\lambda = \exp(5) = 148\), meaning that this ionomer is much more ductile than all ionomers so far examined in literature\(^{32-36}\).

4. CONCLUDING REMARKS

To summarize, our past ten years’ research work has been focused on multi-chain interactions in miscible polymer blends and associative polymers. We combined dielectric and rheological measurements to study the component dynamics of the miscible PI/PtBS blends. Three important dynamic features are revealed: (1) the composition fluctuation of the slow component can be quenched with respect to the fast component at a length scale as large as the chain dimension, (b) a localized motional coupling of the two components significantly modifies the relaxation dynamics below the entanglement length, where the fast component is forced to equilibrate together with the slow component, (c) when the two dynamically asymmetric blocks are connected in a disordered diblock copolymer, the slow block would anchor the fast block, to force the latter to relax like a star arm. This result evidences that “free linear chain” can also exhibit tethered chain dynamics.

For associative polymers, we modified the mean-field theory of Rubinstein and Semenov by introducing the Ginzburg transition. The newly developed reversible gelation model can predict well LVE of non-entangled associative polymers during the sol-to-gel transition.

Knowledge of the sol-to-gel transition are of both fundamental and practical importances. For example, we show that (1) analysis of the thermo-rheological complex behavior of the associative polymers slightly above the gel point enables quantitative determination of the association energy, (2) unique sol-to-gel transition behavior shows up via changing an average number of ions at the ends of the telechelic ionomers, and (3) ductility of ionomers can be enhanced via reducing a degree of gelation.

The systems we studied so far are mainly on non-entangled ionomers, while almost all commercial ionomer samples are entangled. Therefore, it is particularly appealing to examine dynamic change associated to the sol-to-gel transition of entangled associative polymers. It is well expected that the interplay between energetic association and topological entanglement would endow the entangled associative system with rich dynamic features, which is considered as an inter-
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