Viscoelastic and Dielectric Behavior of Polyisoprene
Monofunctionally Head-Modified with Associative Metal-Carboxylate Group

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For moderately entangled high-cis polyisoprene (molecular weight = 30.5 × 10^3) head-modified with an associative metal-carboxylate (salt) group, PI30-COOM with M = Li, Na, and K, linear viscoelastic and dielectric measurements were conducted to examine an effect(s) of the head-to-head association on the chain dynamics. The PI30-COOM chains had type-A dipoles so that their large-scale dynamics was reflected in both viscoelastic and dielectric data at low angular frequencies. The salt groups associate and dissociate (without ionization) with a rate that changes with the temperature T, as known for ionomers having non-polar backbones. Correspondingly, PI30-COOM exhibited failure of the time-temperature superposition for both viscoelastic and dielectric data. This failure was characterized through comparison with non-associative reference homo-PI, the PI30 unimer (a precursor of PI30-COOM), (PI30)2 dimer, and (PI30)6 star-type hexamer. It turned out that the viscoelastic data of PI30-COOLi at low and intermediate T (−20 ° and 20 °C), respectively, were close to those of the star-hexamer and dimer data in the iso-frictional state, and a further increase of T resulted in deviation from the dimer data toward the unimer data. This “crossover” was observed also for PI30-COONa and PI30-COOK but at lower T, which possibly reflected a barrier for the dissociation of the COOM groups lowering in the order of COOLi > COONa > COOK. The dielectric data of PI30-COOM showed a qualitatively similar crossover but at higher T compared to the viscoelastic crossover. This difference between the viscoelastic and dielectric behavior was discussed in relation to the dynamic tube dilation mechanism and also to the motional coupling (conformational transfer) among the PI30-COOM chains coexisting in different association forms.

Key Words: Head-associating chain / Metal-carboxylate group / Viscoelastic and dielectric relaxation / Dynamic tube dilation / Motional coupling

1. INTRODUCTION

Dynamics of associative polymers has been an active research subject in the field of polymer rheology. For example, for ionomer chains having salt groups (such as -SO3Na) along their backbone, viscoelastic terminal relaxation is much slower than the intrinsic relaxation of the backbone because of long-lived association of those groups. The salt group, behaving as a sticker, jumps out its associated domain but mostly returns to the same domain, so that it can migrate into the other domain only after many trials of the jump. For this reason, dissociation/re-organization of the sticker domain corresponding to this migration is much slower than each jump, thereby significantly retarding the terminal relaxation of the ionomers compared to the intrinsic relaxation of the backbone (unless the sticker jumps very frequently at high temperatures). This behavior of the ionomer is well described by sticky chain models. A similar situation is noted also for solutions of telechelic polymers having non-soluble groups at both ends of the chain, for example, aqueous solutions of hydrophobically modified ethoxylate urethane (HEUR). The end alkyl groups of HEUR are insoluble in water and thus behave as the stickers associated in their domain, and the sticker migration from one domain to the others (occurring after many trials explained above) governs the terminal relaxation of the solution.

In the above examples of ionomers and HEUR solutions, the chains have two or more stickers in each backbone to form a transient network, so that the terminal relaxation of the system as a whole is unavoidably governed by the sticker dissociation. In contrast, for chains having just one sticker per backbone, no network is formed and the terminal relaxation can occur even before the sticker dissociation. This situation has been examined for high-cis polyisoprene (PI) monofunctionally modified with a COOH group at the chain
The PI dimer, formed by head-to-head hydrogen bonding of two PI unimers, can still relax completely through its motion even before the sticker dissociation, and viscoelastic experiments for PI-COOH revealed an effect of the sticker association/dissociation on the chain dynamics\(^ {13, 14}\). This effect was detected in dielectric experiments as well, because PI has the so-called type-A dipole parallel along the chain backbone and its end-to-end fluctuation is dielectrically active\(^ {14, 15}\). These experiments revealed that PI-COOH chains in the unimer and dimer forms were motionally coupled through their exchange of the conformation. Namely, a decay of the orientational anisotropy and memory of a dimer (reflected in the viscoelastic and dielectric data) is partly compensated on creation of a dimer through association of two unimers, and vice versa, which results in the mutually correlated dynamics of the unimer and dimer, i.e., the motional coupling. Indeed, models formulating this coupling well describe the viscoelastic and dielectric data of PI-COOH\(^ {13-17}\).

Here, we note that the PI-COOH chains are exclusively in either unimer or dimer form because the hydrogen bonding of COOH groups is stoichiometric and involves just two groups\(^ {13, 14, 18, 19}\) (as similar to ordinary covalent bonds) and the bonded (COOH)\(_2\) groups are rather nonpolar to exhibit no significant electrostatic attraction. This situation can be tuned for PI-COOM having carboxylate salt of various alkaline metals M at the chain head, because the COOM groups form multiple coordination to form a cluster, for example, (COOLi)\(_4\) tetramer cluster\(^ {19-21}\). In addition, those groups should be considerably polar even in a non-ionized form to exhibit a significant electrostatic attraction, thereby being organized further into an associated domain. Consequently, the PI-COOM chains at equilibrium are expected to be in several different association forms, as schematically illustrated in Fig. 1. The chain may be in the linear unimer form (without ionization in a nonpolar medium of PI backbone), in the linear dimer form, and in the star-like multimer form. It is of interest to examine how this multiplicity in the coexisting association forms, not observed for PI-COOH, affects the dynamics of the PI-COOM chains.

Thus, we have conducted viscoelastic and dielectric measurements for moderately entangled PI30-COOM samples with M = Li, Na, and K. The time-temperature superposition failed for both viscoelastic and dielectric data of bulk PI30-COOM, as naturally expected from a change of the rate of dissociation from the associated COOM domain with \(T\). This failure was further characterized through comparison with non-associative reference homo-PI, the PI30 unimer (a precursor of PI30-COOM)\(^ {13}\), its head-to-head dimer\(^ {13}\), and star-type (PI30)\(_6\) hexamer\(^ {22}\) (cf. Fig. 1), all synthesized in previous studies. It turned out that PI30-COOLi exhibits a crossover of its viscoelastic behavior from the star-like behavior to the dimer-like behavior and further to the unimer-like behavior on an increase of \(T\), as naturally expected from the enhanced dissociation at higher \(T\). A qualitatively similar crossover was noted also for PI30-COONa and PI30-COOK but at lower \(T\), which possibly reflected a difference in the dissociation barrier of the COOM groups. The dielectric data also showed the crossover. However, this dielectric crossover occurs at higher \(T\) compared to the viscoelastic crossover. This article presents these results and discusses the difference of the viscoelastic and dielectric crossover in relation to the entanglement relaxation mechanism (dynamic tube dilation) and also to the motional coupling among the PI30-COOM chains that coexist in different association forms illustrated in Fig. 1.

2. EXPERIMENTAL

2.1 Material

High-cis linear polyisoprene having a carboxylic acid group at the chain head, PI30-COOH with \(M_w = 30.5 \times 10^3\) and \(M_w/M_n = 1.02\), was anionically synthesized in our previous work\(^ {13}\). The PI30-COOM samples of our interest were prepared by allowing the COOH group to react with an equimolar alkaline base, MOH with M = Li, Na, and K. The reaction was conducted at room temperature in a THF solution of PI30-COOH to which a prescribed amount of MOH dissolved in a THF/water mixture was added. The reaction product (PI30-COOM) was dried in vacuum, first at room temperature for 1 day and then at 60 °C for 2-3 days to...
thoroughly remove THF and water. The resulting PI30-COOM samples were subjected to viscoelastic and dielectric tests explained later.

We also used previously synthesized PI30 unimer (precursor of PI30-COOH) and its head-to-head covalently bonded (PI30)$_2$ dimer, having $M_w = 30.5 \times 10^3$ and $61.0 \times 10^3$, respectively, and $M_w/M_n = 1.02$ for both, as non-associative reference materials for PI30-COOM. A six-arm star-branched PI synthesized previously, was (PI30)$_6$ hexamer with $M_w = 30.6 \times 10^3$ and $M_w/M_n = 1.04$, was also utilized as a non-associative reference. The arm of this hexamer is practically identical to the linear PI30 unimer.

### 2.2 Measurements

For the bulk PI30-COOM samples with $M = \text{Li}$, Na, and K, dynamic viscoelastic measurements were conducted with a laboratory rheometer (ARES-G2; TA Instruments) at several temperatures $T \geq -20^\circ\text{C}$. The strain amplitude was kept small ($\leq 0.1$) so as to ensure the linearity of the measured storage and loss moduli, $G'$ and $G''$. The samples were also subjected to dynamic dielectric measurements conducted with an impedance analyzer/dielectric interface system (ModuLab XM MTS; Solartron Analytical) at several $T \geq 0^\circ\text{C}$. A home-made dielectric cell (in a parallel plate configuration) was mounted in the rheometer chamber to achieve thorough temperature control as in the viscoelastic measurements. The applied electric field was kept weak ($= 30 \text{ V/mm}$) to ensure the linearity of the dynamic dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ measured for those samples.

For the non-associative PI30 unimer and (PI30)$_2$ dimer in respective bulk state, the viscoelastic and dielectric data have been obtained in our previous study. We utilized those data as the reference data for the PI30-COOM samples. The viscoelastic data of the (PI30)$_6$ hexamer reported previously were also utilized as the reference data. However, for this hexamer, no dielectric measurement was made in the previous study. Thus, its $\varepsilon'$ and $\varepsilon''$ were measured in this study in the way explained above. The viscoelastic and dielectric data of these non-associative homo-PI excellently obeyed the time-temperature superposition with the shift factor $a_{t_1}^{[\text{PI}]}$ specified as

$$\log a_{t_1}^{[\text{PI}]} = -\frac{4.13(T - T_0^{[\text{PI}]})}{150 + T - T_0^{[\text{PI}]}} \text{ with } T_0^{[\text{PI}]} = 40^\circ\text{C} \tag{1}$$

Those reference data are later presented as master curves and compared with the data of PI30-COOM in the iso-frictional state for PI segments.

### 2.3 Analysis of dielectric data

Comments need to be added for the dielectric data of PI30-COOM and the reference homo-PI. As an example, Fig. 2 shows raw data obtained for the PI30-COOLi sample at 60 °C. The dielectric relaxation reflecting the end-to-end fluctuation of the PI30-COOLi chain is clearly observed at intermediate to high angular frequencies, $\omega = 10^2 \text{ to } 10^4 \text{ s}^{-1}$, whereas a direct current (dc) contribution governs the $\varepsilon''$ data at low $\omega < 10^1 \text{ s}^{-1}$ (cf. solid line in the bottom panel). The $\omega$-independence of the $\varepsilon'$ data at low $\omega$ indicates that the electrode polarization, giving increases of both $\varepsilon'$ and $\varepsilon''$ on a decrease of $\omega$, is negligible in the range of $\omega$ examined. In addition, the $\varepsilon''$ data for the dominant part of relaxation is hardly affected by the dc contribution, suggesting that the COOLi group hardly ionized during this relaxation.

For discussion of such dielectric data, we subtract the dc contribution from the raw $\varepsilon''$ data to evaluate the dielectric loss due only to the large scale dynamics of the PI30-COOLi chain. Furthermore, we focus on a “decrease” of the dynamic dielectric constant $\Delta\varepsilon''(\omega) = \varepsilon'(0) - \varepsilon'(\omega)$ (rather than $\varepsilon'(\omega)$ itself) because the phenomenological expressions of $\Delta\varepsilon'(\omega)$ and $\varepsilon'(\omega)$ in terms of the (un-normalized) dielectric relaxation function $\Psi(t)$, shown in eqs 2a and 2b, are formally identical to the well-known expressions of $G'(\omega)$ and $G''(\omega)$ in terms of the relaxation modulus $G(t)$.

This formal identity allows us to directly compare $\omega$ dependence of $\Delta\varepsilon'(\omega)$ and $\varepsilon'(\omega)$ with that of $G'(\omega)$ and $G''(\omega)$. This comparison is very useful when the relaxation of entangled polymers is affected by the dynamic tube dilation mechanism:

$$\Delta\varepsilon'(\omega) = \omega \int_0^\infty \Psi(t) \sin \omega t \, dt \tag{2a}$$

$$\varepsilon'(\omega) = \omega \int_0^\infty \Psi(t) \cos \omega t \, dt \tag{2b}$$

In fact, the $\Delta\varepsilon'(\omega)$ and $\varepsilon'(\omega)$ data of the PI30-COOLi sample (after subtraction of the dc contribution from the raw $\varepsilon''$ data) exhibit the $\omega$ dependence similar but not identical to that of the viscoelastic $G'$ and $G''$ data of entangled homopolymers, as shown in Fig. 3. (This difference between the dielectric and viscoelastic data is discussed later in Fig. 11.) Thus, in the remaining part of this article, we focus on the $G'$ and $G''$ data for the PI30-COOM samples and the reference homo-PI and their dielectric data cast in the form of $\Delta\varepsilon'(\omega)$ and $\varepsilon'(\omega)$. 
3. RESULTS AND DISCUSSION

3.1 Viscoelastic Data of PI30-COOM

Figures 4, 5, and 6, respectively, show viscoelastic moduli data of the PI30-COOM samples with \( M = \text{Li, Na, and K} \) measured at several temperatures as indicated (symbols). For the non-associative homo-PI references, PI30 unimer, \((\text{PI})_2\) dimer, and star-type \((\text{PI30})_6\) hexamer, the master curves of the moduli data reduced at \( T_r[\text{PI}] = 40 \degree \text{C} \) are shown with dot-, solid, and dashed curves, respectively. The reduced angular frequency \( \omega_a T_r[\text{PI}] \) for these master curves was evaluated with the shift factor \( aT_r[\text{PI}] \) for homo-PI given by eq 1. The data of the PI30-COOM samples are also plotted against \( \omega_a T_r[\text{PI}] \), so that those data and the reference data are directly compared in the iso-frictional (iso-\( \zeta \)) state for the PI segment. Consequently, any difference in Figs. 4–6 noted between the PI30-COOM samples and the reference homo-PI reflects a difference in the chain dynamics due to the association/dissociation of the COOM groups in those samples.

All PI30-COOM samples and the reference homo-PI examined in Figs. 4–6 are in the moderately entangled state, as judged from their molecular weights (\( \geq 30.5 \times 10^3 \)) considerably larger than the entanglement molecular weight of homo-PI \( M_e[\text{PI}] \approx 5.0 \times 10^3 \). In the entangled state, the chain dynamics over the end-to-end distance and the corresponding terminal relaxation sensitively change with the chain architecture and molecular weight, which allows us to discuss the dynamics of the PI30-COOM chains on the basis of the comparison with the non-associative reference homo-PI.

We first focus on the behavior of PI30-COOLi shown in Fig. 4. At −20 °C, its \( G' \) and \( G'' \) data are very close to the data of the \((\text{PI30})_6\) hexamer in the iso-\( \zeta \) state; see red squares and dashed curve. This result strongly suggests that the PI30-COOLi chains at −20 °C associate mostly into a star-like multimer form and fully relax, before the dissociation occurs detectably, via the entangled star-like mechanism similar to that of the \((\text{PI30})_6\) hexamer, e.g., the arm retraction mechanism in a partially dilated tube considered in the current tube model \(27, 28\). In relation to this result, we remember that the COOLi salt group is reported to form tetra- and/or hexa-functional coordination bonds between Li and O \(19, 21\). Because the terminal relaxation behavior of entangled star-PI is insensitive to the number \( n \) of the arms per chain if \( n \geq 4 \) \(30, 31\), we cannot evaluate \( n \) for PI30-COOLi accurately despite the agreement of the data of the PI30-COOLi sample and the \((\text{PI30})_6\) hexamer. Nevertheless, this agreement unequivocally suggests that the dissociation of the COOLi salt groups is much slower than the star-like motion of the associated PI30-COOLi multimer at −20 °C thereby allowing those chains to
behave as the star chain.

On an increase of $T > -20 \, ^\circ C$, the relaxation of PI30-COOLi becomes faster than that of the (PI30)$_6$ hexamer in the iso-ζ state, suggesting that the dissociation of the COOLi group is enhanced to affect the motion of the PI30-COOLi chains. Specifically, the PI30-COOLi relaxation becomes close to that of the (PI30)$_2$ dimer at 20 °C (cf. purple triangles and solid curves in Fig. 4), and a further increase of $T$ leads PI30-COOLi to relax considerably faster than the dimer (cf. pink asterisk). This temperature effect on the PI30-COOLi relaxation in the iso-ζ state suggests that the PI30-COOLi chains effectively associate in several different forms at high $T$ ($> -20 \, ^\circ C$). Further detail of the chain dynamics in these coexisting association forms is later discussed in relation to the dielectric data.

Now, we turn our attention to the relaxation of the PI30-COONa and PI30-COOK samples seen in Figs. 5 and 6. These samples exhibit a crossover, i.e., the acceleration of relaxation in the iso-ζ state with increasing $T$, qualitatively similar to that for the PI30-COOLi sample. However, we also note quantitative differences. For example, at $-20 \, ^\circ C$, the relaxation of PI30-COOK is close to that of the (PI30)$_6$ dimer, not of the (PI30)$_6$ hexamer (as noted for PI30-COOLi); cf. red squares and solid curve in Fig. 6. In addition, at 20 °C, the relaxation of PI30-COONa and PI30-COOK is considerably faster than that of the (PI30)$_6$ dimer, which differs from the behavior of PI30-COOLi; cf. purple triangles and solid curve in Figs. 4-6.

These quantitative differences among the PI30-COOM samples can be related to a difference in the barrier for (non-ionic) dissociation of the COOM groups from their associated domain: This barrier should have lowered in the order of COOLi > COONa > COOK to enhance the relaxation of PI30-COOM chains in this order, as observed in Figs. 4-6. This speculation is consistent with the infrared absorption data in literature indicating that the COONa group is less deformable (and more stabilized) compared to the COOK group possibly due to a smaller ionic radius and a higher areal charge density of Na$^+$ cation compared to K$^+$ cation.

3.2 Dielectric Data of PI30-COOM

Figures 7, 8, and 9, respectively, show dielectric data of the PI30-COOM samples with M = Li, Na, and K (symbols). The curves indicate the data of the non-associative homo-PI references, PI30 unimer, (PI30)$_6$ dimer, and star-type (PI30)$_6$ hexamer, summarized as the master curves reduced at $T_{r, [PI]}^{[PI]} = 40 \, ^\circ C$. The reduced angular frequency $\omega_{r, [PI]}^{[PI]}$ for these curves was evaluated with the shift factor $a_{r, [PI]}^{[PI]}$ for homo-PI.
Changes of the segmental friction with \( T \) have been compensated in \( \langle \tau_\varepsilon \rangle_{\text{iso-}\zeta} \) and \( \langle \tau_G \rangle_{\text{iso-}\zeta} \) so that these \( \langle \varepsilon \rangle_{\text{iso-}\zeta} \) of homo-PI are independent of \( T \). In contrast, for PI30-COOM, \( \langle \varepsilon \rangle_{\text{iso-}\zeta} \) decreases with increasing \( T \) because the association/dissociation equilibrium is shifted toward the dissociation side to accelerate the relaxation of the system as a whole. Clearly this decrease is more significant for the viscoelastic \( \langle \tau_G \rangle_{\text{iso-}\zeta} \) than for the dielectric \( \langle \tau_\varepsilon \rangle_{\text{iso-}\zeta} \) (compare green triangles in the bottom and top panels, for example), which confirms the differences between the viscoelastic data (Figs. 4-6) and dielectric data (Figs. 7-9) mentioned earlier.

As a most critical test of this difference for the PI30-COOM samples with \( M = \text{Li}, \text{Na}, \text{and K} \), we here focus on a temperature \( T^* \) where the dielectric \( \Delta \varepsilon' \) and \( \varepsilon'' \) data of those samples in the iso-\( \zeta \) state are close to the (PI30)\(_2\) dimer data. Fortunately, we found such temperatures, \( T^*/\degree\text{C} = 60, 40, \) and \( 0 \) for PI30-COOM with \( M = \text{Li}, \text{Na}, \text{and K} \) (as can be noted also from the \( \langle \tau_\varepsilon \rangle_{\text{iso-}\zeta} \) data in Fig. 10a). In Fig. 11a, the dielectric data at those \( T^* \) are normalized by the dielectric relaxation intensity \( \Delta \varepsilon \) and plotted against the reduced frequency \( \omega a_{[\text{PI}]} \) in the iso-\( \zeta \) state; see symbols. The solid curves indicate the data of the (PI30)\(_2\) dimer plotted in the same format. The normalized dielectric data of all PI30-COOM samples are confirmed to almost coincide with the (PI30)\(_2\) dimer data.

From this close coincidence of the dielectric data for the PI30-COOM samples and dimer, one may assume that the PI30-COOM chains at \( T^* \) are exclusively in the dimer form. However, this assumption does not work at all, as evidenced in Fig. 11b where the normalized viscoelastic moduli of the samples, \( G'/G_N \) and \( G''/G_N \) with \( G_N (= 0.48 \text{ MPa})^{14, 29} \) being the entanglement plateau modulus of homo-PI, are plotted against \( \omega a_{[\text{PI}]} \); see symbols. Solid curves show the dimer moduli plotted in the same format\(^{44}\). If the PI30-COOM chain at \( T^* \) were exclusively in the dimer form, their dynamics should have coincided with the dimer dynamics and then their normalized moduli data (symbols) should have agreed with the dimer data (solid curves) However, in reality, the moduli of the PI30-COOM samples in the terminal zone significantly shift toward the higher-\( \omega \) side compared to the dimer moduli, indicating that the terminal viscoelastic relaxation of those samples are faster than that of the dimer relaxation in the iso-\( \zeta \) state (as can be noted also from Fig. 10).

The above observation suggests that the PI30-COOM sample at \( T^* \) is a mixture (blend) of differently associated components, the linear unimer, the linear dimer, and the star-like multimer illustrated in Fig. 1, and the dielectric and viscoelastic data reflect the entanglement relaxation of those
components dynamically correlated through the dynamic tube dilation (DTD) mechanism established for blends of homo-PI. In those homo-PI blends, the viscoelastic relaxation reflects the orientational anisotropy decay of the dilating entanglement segments. The number of those segments per chain, \( N_D \), decreases with time due to DTD, which results in the acceleration of the viscoelastic relaxation. In contrast, the dielectric relaxation detecting the end-to-end fluctuation of the PI chains is basically not relevant to \( N_D \) and thus much less sensitive to DTD. The dielectric data of the PI30-COOM samples at \( T^* \) appear to reflect the end-to-end orientational memory summed up for the coexisting unimer, dimer, and multimer. Then, the dielectric relaxation function \( \Psi(t) \) of these samples corresponding to this sum could agree, coincidentally, with \( \Psi(t) \) of the non-associative dimer, as noted for the dielectric data in Fig. 11a. Even for that case, the DTD

![Fig. 7](image1)

![Fig. 8](image2)

![Fig. 9](image3)

![Fig. 10](image4)

![Fig. 11](image5)
mechanism should accelerate the viscoelastic relaxation of those samples to give rise to the difference between them and the (PI30)2, dimer, as noted in Fig. 11b.

In the high-\(T\) limit, PI30-COOM chains should be in the fully dissociated state and behave as the unimer (though not observed in the range of \(T\) examined in this study). On the other hand, in the low-\(T\) limit, they should behave as the fully associated multimer (which would be the case for PI30-COOOLi at \(-20^\circ\text{C}\), as noted in Figs. 4 and 10). However, at intermediate \(T^*\), the chains can be in various association forms to superficially behave, in total, as the dimer in the dielectric response but not in the viscoelastic response, as noted in Figs. 10 and 11. The unimer, dimer, and multimer co-existing at \(T^*\) should be dynamically correlated not only through the DTD mechanism but also through an exchange of their conformations at association/dissociation equilibrium. The motional coupling among the unimer, dimer, and multimer due to this conformational exchange should have been combined with the DTD mechanism to determine the dielectric and viscoelastic responses of PI30-COOM.

The effect of this motional coupling on the dielectric and viscoelastic responses should be qualitatively similar to but quantitatively different from the effect formulated for the head-carboxylate PI30-COOH chains\(^{15-17}\) that are exclusive-ly in the unimer and dimer forms (not in the star-like multimer form because the hydrogen bonding involves just two COOH groups). It is of interest to extend the model\(^{15-17}\) for PI30-COOH to the conformational exchange among all possible association species in the PI30-COOH sample to formulate the viscoelastic and dielectric relaxation functions affected by the motional coupling of those species. This extension is considered as a challenging but interesting subject of a future study.

4. CONCLUDING REMARKS

For head-associative PI30-COOM (\(M = \text{Li, Na, and K}\)) in a moderately entangled state, linear viscoelastic and dielectric behavior was examined to discuss an effect of the chain association on the chain dynamics. The PI30-COOM chains were in the unimer, dimer, and star-like multimer forms coexisting at equilibrium, and exhibited “multimer-dimer-unimer” crossover of their relaxation behavior with increasing \(T\) because of a shift of the association/dissociation equilibrium toward the dimer and unimer. This crossover, resulting in the failure of the time-temperature superposition, occurred at different \(T\) for PI30-COOM with different \(M\). Specifically, the temperature for the crossover was higher in the order of COOLi > COONa > COOK, possibly due to a difference of the dissociation barrier being higher in this order.

The effect of the chain association on the chain dynamics, underlying this crossover, was examined through comparison with non-associative reference homo-PI, PI30 unimer, (PI30)\(_2\) dimer, and (PI30)\(_6\) hexamer in the iso-frictional (iso-\(\zeta\)) state for the PI segment. It turned out that the viscoelastic relaxation of the PI30-COOM chains was considerably faster compared to the non-associative (PI30)\(_2\), dimer in that state even when their dielectric relaxation was almost identical to the dimer relaxation. This difference between the viscoelastic and dielectric relaxation can be related to different DTD effects on the viscoelastic and dielectric relaxation (stronger effect for the former) as well as to the conformational exchange and the motional coupling among the PI30-COOM chains coexisting in several different association forms.

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34) For the PI30 unimer, the dielectric relaxation is slower than the viscoelastic relaxation by a factor of ~2, because the dielectric and viscoelastic relaxation processes reflect the decay of the orientational memory and anisotropy (first- and second-moment averages of the end-to-end vector of entanglement segments) and are differently affected by the dynamic tube dilation mechanism\(^\text{26,28}\). However, this is not the case for the head-to-head coupled (PI30)\(_2\) dimer, because the dipole is symmetrically once-inverted in the dimer chain and the slowest mode of the chain motion is dielectrically inert\(^\text{26,28}\). Then, the terminal dielectric relaxation of the (PI30)\(_2\) dimer is faster by a factor of ~4 compared to the case of no dipole inversion, and thus by a factor of ~2 compared to the viscoelastic relaxation, as can be noted from comparison of the solid lines in the top and bottom panels of Fig. 10.