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Simulation study on molecular relaxation in ionomer melts☆

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Abstract

Relaxation behavior of ionomer molecule in melt state was investigated by Brownian simulation where motion of a bead-rod chain representing a linear ionomer molecule was calculated in two-dimension. Entanglement between the other molecules was assumed by a repulsive interaction between the chain and randomly located entanglement points. Effect of ion aggregates was also introduced by an attractive interaction between the chain and attractive sites randomly dispersed in the simulation box. Relaxation spectra of end-to-end motion and local bond orientation were obtained in equilibrium calculation for various chain lengths. The effect of the attractive site was discussed on the spectrum. It was found that on the end-to-end motion, the longer the chain was, the more discrepant the spectrum was, while on the bond orientation, the shorter it was, the more discrepant the spectrum was. On the basis of these results, a picture to describe the experimental phenomena was proposed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Brownian dynamics; Ionomer melts; Relaxation functions

1. Introduction

Ionomers are group of polymers which have acid residual groups partially neutralized by metal ions [1]. Because of their distinguishable characters from ordinary polymeric materials, e.g. tensile strength, sealing and peeling properties, and maximum elongational ratio, they have been extensively applied to industry, such as equipment for sports, food packages, etc. The mechanical superiority has been considered to cause by ion aggregates (or also called as ion clusters). Longworth and Vaughan [2] proposed a model where the metal ions and counter-ions bind to the polymer aggregate and create local clustering structure. The cluster has been considered as physical crosslink and thus it causes higher tensile strength. Most of the mechanical properties in fact depend on amount of ionic contents; the more the ionic contents exist the stronger the tensile strength becomes, for example.

The products made of ionomers are processed in melt state similar to the ordinary polymeric materials. Effect of the ion aggregates on the melt rheology, however, has not been understood well. It has been reported that curves of dynamical shear modulus for various ionic content can be superimposed on each other [3–6]. This suggests that the ion aggregate changes friction of local dynamics of polymers just like temperature. On the other hand, it has been also reported that behavior of transient uniaxial elongational viscosity strongly depends on the ionic content [5,7]. This could be interpreted that the ion aggregate plays a role such like crosslink, similar to that in the solid state.

To understand the mechanism of the above two seemingly incompatible phenomena, molecular simulation was used in this study. Through the molecular motion and relaxation behavior, rheology of ionomers will be discussed.

2. Model

Because typical commercialized ionomers have enough molecular weight, model of this study is based on a coarse-grained model incorporating the entanglement effect [8]. Fig. 1 shows a typical snapshot. Ionomer molecule is represented by a bead-rod chain where the average rod length, a, corresponds to the Kuhn length. Position of the bead in the chain, $\mathbf{r}$, obeys Langevin type equation of motion

$$\zeta \dot{\mathbf{r}} = -\nabla U + \mathbf{f} \tag{1}$$

where ζ is a friction coefficient. Contribution of the other

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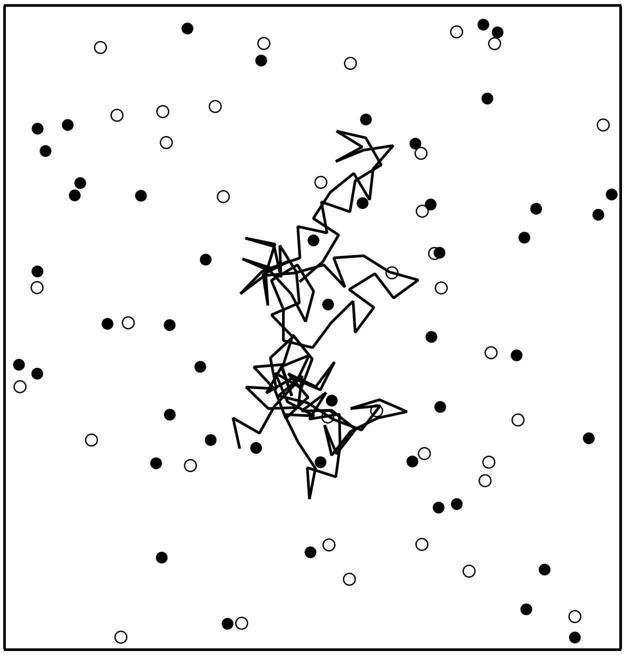

Fig. 1. A typical snapshot. Lines stand for an ionomer molecule, open circle is the attractive cite corresponding to the ion aggregate, and closed circle is the entanglement point. Chain length is 120.

molecules is incorporated by the potential field U and the random force $\mathbf{f}$.

The Gaussian random force $\mathbf{f}$ standing for the thermal fluctuation obeys

$$\langle \mathbf{f} \rangle = 0, \qquad \langle \mathbf{f}(t)\cdot\mathbf{f}(t') \rangle = 4kT\zeta\sigma(t-t') \tag{2}$$

The potential is written by

$$U = U_{\mathrm{spr}} + U_{\mathrm{ent}} + U_{\mathrm{ion}} \tag{3}$$

where U_{spr} is intra-molecular interaction to connect the beads, U_{ent} is repulsive interaction between the chain and the entanglement points, and U_{ion} is for interaction between the chain and the ion aggregates.

The intra-molecular interaction U_{spr} is given by

$$U_{\mathrm{spr}} = \frac{kT}{2l^2\varsigma^2}\sum_i (u_i - l)^2 \tag{4}$$

where kT is thermal energy, u_i is bond length, and ς is spring constant chosen to keep the bond length fluctuation within 5% of its initial value l.

The entanglement effect is assumed to be repulsive interaction between the chain and the obstacles (entanglement points) randomly located in the simulation box [8,9]

$$U_{\mathrm{ent}} = kT\sigma^6\left(\sum_\alpha\sum_i r_{i\alpha}^{-6} + \sum_\alpha\sum_i b_{i\alpha}\right) \tag{5}$$

where $r_{i\alpha}$ is distance between bead i and obstacle α, and $b_{i\alpha}$ is length of shorter axis of an ellipse whose foci are located at both ends of the bond i and whose curve passes the center of obstacle α. σ determines the size of the obstacles and is fixed at $\sigma = 0.25a$. This potential prohibits the chain motion crossing over the obstacles so that it corresponds to the topological constraint due to the entanglement. It has been reported that polymer dynamics calculated by this method are consistent with the experimental results [8,9]. A few additional comments seem worth concerning this potential. First, to mimic the entanglement constraint by the above potential, this simulation is basically restricted in 2D. Thus self-entanglement of the chain is neglected. Second, this model can involve the constraint release concept by switching the interaction on and off with a certain lifetime standing for the relaxation time of the medium. For the sake of simplicity, however, in this study, the interaction is always switched on.

The ion aggregates are represented by randomly distributed attractive sites. The interaction between the chain and the site, U_{ion}, is assumed to be the following

$$U_{\mathrm{ion}} = \begin{cases} \varepsilon kT(r_{i\beta}^2 - 1), & r_{i\beta} \le a \\ 0, & r_{i\beta} > a \end{cases} \tag{6}$$

where $r_{i\beta}$ is the distance between bead i and site β, and ε is a parameter to determine the depth of the potential well. Here, we assume a short range interaction because the ion aggregate consists of the acid groups along the polymer and counter metal ions, so that the long range interaction is considered to be shielded. The depth of the potential well is also an open problem. Takahashi et al. [5] reported that for an ethylene-based ionomer melt neutralized by a zinc salt, activation energy for flow was 27.1 kcal/mol K, while it was 18.6 kcal/mol K for the neat base polymer. The rate of increase induced by the ionic interaction is less than 50%, therefore, this suggests that the interaction is phenomenologically rather brittle. In this simulation, ε is fixed at 4, though further discussion should be required.

We chose average bond length a as unit length, $\tilde{t} = \zeta a^2/4kT$ as unit time, and kT as unit energy. It would be noteworthy that the unit time corresponds to Rouse time for $N = 1$ case. Numerical integration was performed by Euler scheme with $\Delta t = 0.001\tilde{t}$. Periodic boundary of 40×40 was employed. The entanglement points and the attractive sites were dispersed randomly with number density of 0.1 for each. This corresponds to average pore size of 2.7 [8]. Simulations under equilibrium were performed much longer than the largest relaxation time for 10 different initial configurations. Results reported in this paper were obtained by taking time and ensemble averages in this respect.

3. Results and discussion

3.1. Local relaxation

To monitor relaxation at bond orientation level, we calculated a relaxation function $\mu(t)$, which corresponds to shear

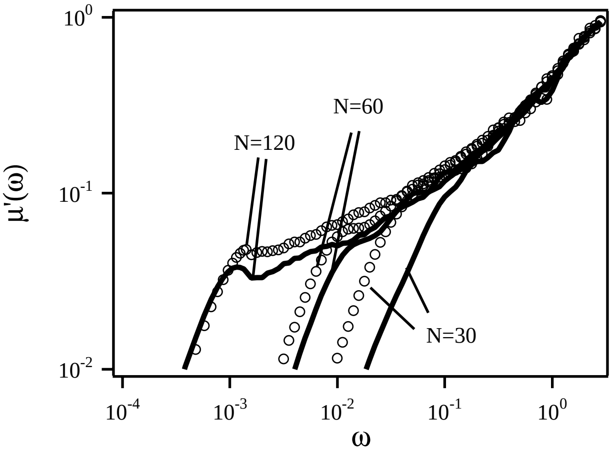

Fig. 2. Bond relaxation spectrum for various chain lengths. Solid lines are for the calculation without the attractive cite. Open circles are the results with the attractive cites. Chain length is indicated in the figure.

stress relaxation

$$\mu(t) = \frac{\langle \sigma_{xy}(t+t')\sigma_{xy}(t') \rangle_{t'}}{\left\langle \sigma_{xy}^2 \right\rangle_{t'}} \tag{7}$$

where $\langle \cdot \rangle_{t'}$ means time and ensemble average as mentioned in the previous section. $\sigma_{xy}(t)$ corresponds to off-diagonal component of the stress tensor and was obtained by

$$\sigma_{xy}(t) \propto \langle F_x(t) u_y(t) \rangle \tag{8}$$

where **F** is tension of each bond and **u** is the bond vector. For the sake of direct comparison with the experimental results, $\mu(t)$ was converted into $\mu^*(\omega)$ by

$$\mu^*(\omega) = \mathrm{i}\omega \int_0^\infty \mu(t) \exp(\mathrm{i}\omega t)\, \mathrm{d}t \tag{9}$$

Fig. 2 shows $\mu'(\omega)$ which is real part of $\mu^*(\omega)$ corresponding to the storage modulus. In the long time region, it is observed that the relaxation is slowed down by the ion aggregates. The rate of slowing down decreases with increase of the chain length. This phenomenon is reasonable considering the local motion of the chain. The characteristic time for the detachment of a bead from an attractive site can be described by

$$\tau_l \simeq \tilde{t} \exp\left(\frac{\varepsilon kT}{kT} \right) \tag{10}$$

The characteristic time is independent of the chain length so that it becomes relatively smaller for the longer chains.

3.2. Global relaxation

Relaxation function of end-to-end vector, **P**, was obtained by

$$\Phi(t) = \frac{\langle \mathbf{P}(t+t') \cdot \mathbf{P}(t') \rangle_{t'}}{\langle \mathbf{P}(t')^2 \rangle_{t'}} \tag{11}$$

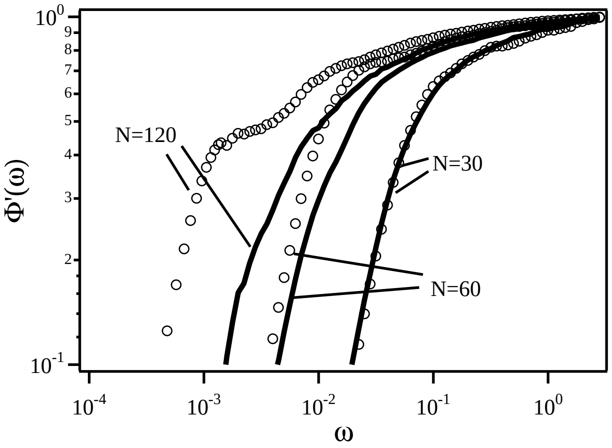

Fig. 3. Similar to Fig. 2 for the end-to-end relaxation spectrum.

Similar to the bond relaxation, $\Phi(t)$ was converted into $\Phi^*(\omega)$. Fig. 3 shows $\Phi'(\omega)$. Note that $\Phi^*(\omega)$ corresponds to dielectric relaxation spectrum of type-A polymers though it is hard to measure for the ionomer melts.

It is shown that the longer the chain is, the more apparent the effect of the attractive site is. This inverse tendency to the local relaxation can be explained by a simple picture. As shown in Fig. 1, the chain is always trapped by a certain number of the attractive sites. Though the characteristic time of the local detachment is rather small, for overall relaxation, all of the trapped segments should be released. The characteristic time of the detachment of whole of the chain from all of the trapped attractive sites can be written by

$$\tau_g \simeq \tilde{t} \exp(\varepsilon n) \tag{12}$$

where n is the number of trapped segments in the chain. It can be estimated by

$$n \simeq C\mathbf{P}^2 = CNa^2 \tag{13}$$

where C is the number density of the attractive site and N is bead number of the chains. Thus the relaxation time of the overall motion can be written by

$$\tau' = \tau + \tau_g \tag{14}$$

$$\tau' \simeq \tau + \tilde{t} \exp(\varepsilon CNa^2) \tag{15}$$

where τ is the relaxation time of the base polymer. Here, it is shown that relaxation time τ' is dominated by the ionic contribution when N or C is large. Note that Eq. (15) is for 2D case; for 3D, $n \propto N^{3/2}$. Thus in reality, N dependence of τ' is expected to be more evident.

3.3. Comparison with the experiments

It has been reported that the storage moduli of ionomer melts for various neutralization degree can be superimposed horizontally on that of the base polymer [3–6]. This phenomenon is consistent with our observation on the local motion related to the relaxation modulus. The local motion is dominated by one-by-one attachment and detachment process between a chain segment and an attractive site. In this case, the attractive sites only increase the effective friction of the segment motion because the characteristic time of the detachment is relatively small compared with the relaxation time of the whole chain and the attractive sites are regarded as uniformly distributed for long chains.

On the other hand, contribution of the ion aggregates to the non-linear rheology can be explained by the overall motion. It has been reported that strain hardening in transient uniaxial elongational viscosity is significantly intensified by increase of the neutralization degree [5,7]. As the strain hardening is directly related to the overall chain stretching, this phenomena can be described by Eq. (15) where relaxation time of the overall motion is dependent on the concentration of the ion aggregates.

4. Conclusion

Molecular motion in ionomer melts was considered by Brownian simulation incorporating the entanglement effect and interaction between ionomer and ion aggregates. It was found that (i) the local motion corresponding to the stress relaxation is dominated by the one-by-one attachment and detachment process between the chain segment and the ion aggregate so that the effect of the ion aggregates on the relaxation spectrum is rather small especially for long chains, and (ii) the global motion corresponding to the dielectric relaxation is determined by the characteristic time of detachment process of overall chain from all the trapped ion aggregates so that the relaxation time of the global motion such as chain stretching is strongly dependent on molecular weight and concentration of ion aggregates.

Although this picture is consistent with the earlier experimental results, more detailed verification is apparently required on several points. One is the discrepancy between the local relaxation and the global relaxation. Correlation between the relaxations is unclear; in the exceedingly long time region, modulation of the local motion spectrum might be observed consistently with the global motion. Second one is on the molecular weight dependence, which has not been studied well. As strong molecular weight dependence on the global relaxation time is predicted by our model, experimental studies are expected to observe it. Compensative works with experiments are in progress and the results will be reported elsewhere.

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