Dynamics of Lightly Sulfonated Polystyrene Ionomers

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The tracer diffusion coefficients of both ion-containing polymer chains and their associated counterions were measured in lightly sulfonated ionomers as a function of temperature, ion content, and chain length. The data are shown to be in good agreement with relaxation times derived from viscoelastic measurements at high temperatures. The results are interpreted in terms of a reptation model, modified to account for the additional constraints on individual chain motion imposed by the associating ion pairs. [S0031-9007(98)07469-9]

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Ionomers are an extremely versatile class of flexible polymers, with tightly bound ion-counterion pairs randomly distributed along their chains. Ionomers find many uses, including biomimetic materials, golf balls, and batteries. Despite considerable advances [1–3], dynamics in ionomer melts is not well understood. In this Letter we demonstrate how dynamic secondary ion mass spectrometry (DSIMS) can be used to observe chain dynamics, thereby enabling us to develop a general theory of diffusion and viscoelastic relaxation in ionomer melts. This model is an extension of the reptation mechanism proposed by de Gennes [4] for an entangled polymer melt, which is modified when additional constraints on individual chain motion are imposed by the associating ion pairs.

The dynamics of ionomers are controlled by six independent variables: N, the degree of polymerization of the polymer chain; N_e, the degree of polymerization of an entanglement strand; τ_0, the relaxation time of a monomer; N_s, the degree of polymerization between ion pairs (stickers); τ, the lifetime of an ion pair in a multiplet; and p, the fraction of ion pairs in multiplets. The first three parameters are also necessary for dynamics of chains without stickers [5]. Since the energy of association is large compared with kT [2], we expect $p \cong 1$ for ionomers. There are many possible regimes for dynamics, depending on the relative sizes of N, N_e, and N_s [6]. The case of entangle ionomers with many entanglements between stickers ($N > N_s > N_e$) was treated in Ref. [7], with a simple pairwise association model. At the level of scaling, we assume that the formation of multiplets with an aggregation number larger than two (e.g., ten) does not have a profound effect on dynamics, apart from possibly increasing the association energy, reflected in τ.

Here we are concerned with the case of $N > N_e > N_s$. We will see below that this case is, in fact, simpler than the case considered in [7]. Since this case is related to the far simpler case of unentangled ionomers (with $N_e > N > N_s$), we begin with the Rouse theory of motion [8]. Unentangled chains without stickers relax by Rouse motion [5] on a time scale $\mathcal{T}_0 \cong \tau_0 N^2$. The diffusion coefficient of the unentangled chain without stickers is $D_0 \cong R^2/\mathcal{T}_0 \cong b^2/(\tau_0 N)$, since the size of the chain is given by random walk statistics ($R \cong bN^{1/2}$) with b the monomer size. For an unentangled chain with stickers having $N_e > N > N_s$, the longest relaxation time is that of a Rouse chain with stickers [8], $\mathcal{T} \cong \tau(N/N_s)^2$. The diffusion coefficient is then given by $D \cong R^2/\mathcal{T} \cong b^2 N_s^2/(\tau N)$. Comparing the diffusion coefficients of the chains with and without stickers, one finds

$$D/D_0 \cong N_s^2 \tau_0/\tau \qquad N_e > N > N_s\,, \tag{1}$$

from which it is clear that for $\tau > \tau_0 N_s^2$ the stickers retard the diffusion of the chain, and the diffusion gets progressively slower as more stickers are added to the chain (since N_s decreases).

For the case of $N > N_e > N_s$ the chain must relax by reptation [4,5]. Entangled chains without stickers have the longest relaxation time, $\mathcal{T}_0 \cong \tau_e^0 (N/N_e)^3$, where τ_e^0 is the Rouse time of an entanglement strand ($\tau_e^0 \cong \tau_0 N_e^2$). The diffusion coefficient of the entangled chain without stickers is thus $D_0 \cong R^2/\mathcal{T}_0 \cong b^2 N_e/(\tau_0 N^2)$. With stickers, the Rouse time of an entanglement strand is that of a Rouse chain with stickers $\tau_e \cong \tau(N_e/N_s)^2$, making the longest relaxation time and corresponding diffusion coefficient

$$\begin{aligned} &\mathcal{T} \cong \tau_e (N/N_e)^3 \cong \tau N^3/(N_s^2 N_e) \quad \text{and} \\ &D \cong R^2/\mathcal{T} \cong b^2 N_s^2 N_e/(\tau N^2); \qquad N > N_e > N_s\,. \end{aligned} \tag{2}$$

Again comparing the diffusion coefficients of the chains with and without stickers, one finds

$$D/D_0 \cong N_s^2 \tau_0/\tau \qquad N > N_e > N_s\,, \tag{3}$$

which is the same result as for the unentangled case (1).

The lifetime of a sticker in the associated state τ is related to the association energy E, as $\tau \cong \tau_0 \exp(E/kT)$, where it is important to note that τ_0 is the time scale for monomer motion in the chain without stickers. Therefore, τ_0 has a complicated Williams-Landel-Ferry (WLF) temperature dependence [9], and the temperature dependence of τ is the product of this implicit WLF dependence of the bare polymer and the Arrhenius temperature dependence from the association energy. Such considerations lead to a quite general scaling law for the diffusion coefficient of an ionomer compared with that of the same chain without stickers

$$D/D_0 \cong N_s^2 \exp(-E/kT)\,. \tag{4}$$

This law should be quite general for associating systems in the melt, provided that $E > 2kT \ln N_s$, meaning that the sticker lifetime is longer than the Rouse time of a chain between stickers ($\tau > \tau_0 N_s^2$), which is the case of interest, where the stickers retard diffusion. We use (4) here to estimate the association energy E from our experimental data.

To model the diffusion of counterions, we assume that ion pairs in the multiplet state exchange counterions on time scale τ_x. Unfortunately, a detailed quantum mechanical calculation of this exchange time is not available, so we do not *a priori* know τ_x. In the slow exchange limit ($\tau_x > \tau$) the counterions simply diffuse with the chain. However, we expect exchange to be considerably faster than this, due to the quadrapolar and higher order nature of the multiplet interactions [2]. The ion pair does not dissociate in the low dielectric constant medium surrounding the multiplets (consisting primarily of bare polymer strands of length N_s). However, the effective dielectric constant *within the multiplet* should be significantly higher, allowing for rapid exchange of counterions between ion pairs in the multiplet.

In the limit of fast exchange ($\tau_x < \tau$) with many stickers between entanglements ($N_e > N_s$), the diffusion of counterions is simply controlled by random hopping between multiplets while attached to the chain in the form of an ion pair. Each hop moves the counterion in a random direction, an average distance $bN_s^{1/3}$ (the average distance between multiplets) on time scale τ. The counterion diffusion coefficient is thus

$$D_{\text{ion}} \cong b^2 N_s^{2/3}/\tau; \qquad \tau_x < \tau \quad \text{and} \quad N_e > N_s\,. \tag{5}$$

Our ionomers are monodisperse ($M_w/M_n < 1.07$) lightly sulfonated polystyrene, completely neutralized with Na or Rb (PSSx-Na or PSSx-Rb), and their perdeuterated analogs (dPSSx-Na or dPSSx-Rb). The symbol x denotes the mole percentage of sulfonation in the ionomers and ranged from 0.85% to 5.3%. The polymers, their respective molecular weights, and glass transitions are listed in Table I. Details regarding the synthesis of these polymers are given in [10]. The sulfur content was determined by Dietert sulfur analysis, and the glass transition temperatures were determined by differential scanning calorimetry (DSC).

Samples were prepared for the tracer diffusion experiments by spin casting a thick layer (about 2000 Å) of PSSx-Na from toluene solution onto native oxide covered Si wafers. In order to ensure tracer levels of diffusant polymer, a thin second layer (about 150 Å), composed of 20 wt. % of dPSSx-Na and 30 wt. % of PSSx-Na was spun cast on a glass slide and floated from water onto the pure PSSx-Na layer. The degree of sulfonation x of the deuterated tracer and hydrogenated matrix polymers were matched as closely as possible (see Table I). All samples were annealed under vacuum (10^{-4} Torr) at temperatures ranging from 130 to 190 °C for various times ranging from 10 min to 24 h. The concentration profiles were measured using DSIMS, which yields concentration vs depth profiles for a number of ionic fragments sputtered from the sample. Details of the DSIMS analysis can be found in [11].

Figure 1 shows the measured diffusion coefficients as a function of the number of stickers per chain, N/N_s. The inset shows DSIMS spectra obtained for the three dPSS samples allowed to diffuse for 30 min at 160 °C into the PSS matrix of the closest molecular weight (Table I). The solid curves in the inset are fits to the solution of the Fickian equation for diffusion of a thin film of thickness h into a semi-infinite medium [12]. Even a small amount of sulfonation, 0.85 mole %, reduces the diffusion coefficient relative to that of polystyrene [13] by an average factor of 30. The reduction is even greater for higher degrees of sulfonation. The error bars shown reflect the 0.5% absolute uncertainty in the degree of sulfonation. The solid line has the slope of -2 predicted by (4), while regression yields $D \sim (N/N_s)^{-1.7\pm0.3}$. The data in Fig. 1 are all for d/h pairs that are closely matched in sulfonation level and chain length, except for the two highest N/N_s samples, which are $\text{PSS}_{4.73}$-Na diffusing into $\text{dPSS}_{5.3}$-Na and $\text{PSS}_{2.84}$-Na diffusing into $\text{dPSS}_{2.8}$-Na. Neither matrix chain length is short enough to interfere with the reptation scaling for diffusion of the longer tracer chains [12].

TABLE I. Lightly sulfonated polystyrenes.

Polymers	$\text{dPSS}_{0.85}$	$\text{dPSS}_{2.8}$	$\text{dPSS}_{5.3}$	$\text{PSS}_{1.18}$	$\text{PSS}_{2.7}$	$\text{PSS}_{2.84}$	$\text{PSS}_{4.73}$	$\text{PSS}_{5.1}$	$\text{PSS}_{5.2}$
Mole % sulfonation	0.85	2.80	5.30	1.18	2.70	2.84	4.73	5.10	5.20
T_g (°C)	107	111	116						
M_w	110 000	110 000	49 500	105 000	105 000	600 000	100 000	105 000	49 200
N_s	120	36	19	85	37	35	21	20	19
N/N_s	8.8	29	25	12	27	160	46	50	25

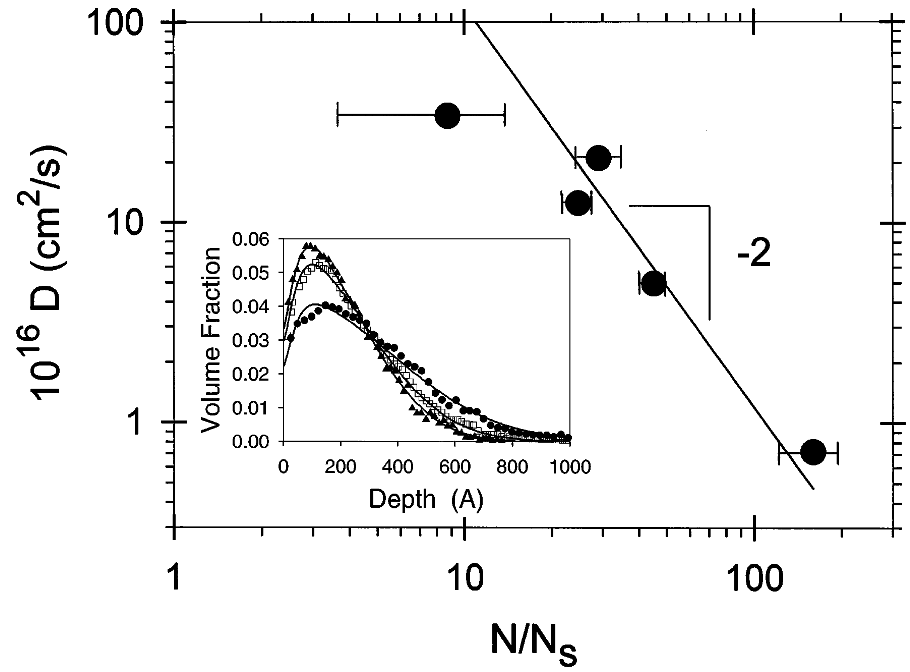

FIG. 1. Diffusion coefficient at 160 °C as a function of the number of stickers per chain. Inset: DSIMS deuterium profiles for dPSS$_{0.85}$-Na (filled circles), dPSS$_{2.8}$-Na (open squares), and dPSS$_{5.3}$-Na (filled triangles) after annealing for 30 min at 160 °C. The solid curves are Fickian fits.

The association energy E of the multiplets can be calculated from (4) using our measured diffusion coefficients and interpolating/extrapolating the data of Green and Kramer [13] for $D_0 \sim N^{-2}$ of polystyrene. In Fig. 2 we plot the association energies as a function of temperature for the three sulfonation levels studied. At high temperatures, E is approximately independent of temperature. E decreases slightly with sulfonation level, but the apparent activation energy for diffusion (from ln D vs $1/T$) actually increases linearly with sulfonation level (0.7 kT/mole %) as reported previously [14]. The activation energies begin to increase with decreasing temperature below T_c, which increases monotonically from 140 to 155 °C with increasing sulfonation level. These results confirm the restricted dynamics model of ionomers, postulated by Eisenberg and co-workers [1]. Above T_c, the decreased mobility in an ionomer melt is due to simple association of ion pairs, or "stickers," on the polymer chains. Below T_c, the increase in the activation energy may indicate a change in multiplet structure, such as an increase in aggregation number. While diffusion is greatly slowed by the presence of the stickers, Fig. 2 clearly shows that the polymer chains still have a measurable center of mass mobility ($D > 0$) for all $T > 130$ °C, and hence have not undergone any glass transition at T_c [1].

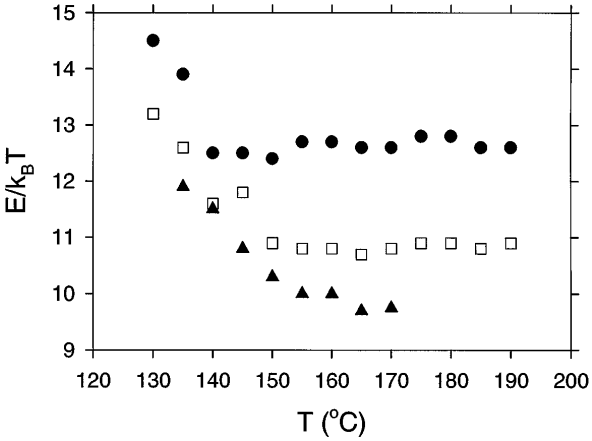

FIG. 2. Temperature dependence of the activation energy calculated from the diffusion data using (4). Sulfonation levels are 0.85 mole % (filled circles), 2.8 mole % (open squares), and 5.3 mole % (filled triangles).

The linear viscoelastic properties of the 0.85 mole % sulfonated polystyrene at 180 °C were studied using torsional oscillatory strain with a Rheometrics RMS-800. A gap height of 0.87 mm was used with 25 mm diameter parallel plates. Small strain amplitudes corresponding to linear viscoelastic response were used throughout. The data obtained after 24 h at 180 °C [15], and acquired in a continuous sweep from high to low frequency, are plotted in Fig. 3. The figure shows two relaxations in the frequency range covered. The reciprocal of the frequency at which the high frequency relaxation occurred is taken as a measure of the average duration of a given ion pair in a multiplet $\tau = 0.03$ s at 180 °C. The reciprocal of the frequency at which the low frequency maximum in the loss modulus occurs is a measure of the terminal relaxation time of the ionomer chains. Assuming the size of the 0.85% sulfonated chains is the same as pure polystyrene with the same degree of polymerization, we calculate the longest relaxation time as $\mathcal{T} = R^2/6D = 25$ s from the measured diffusion coefficient

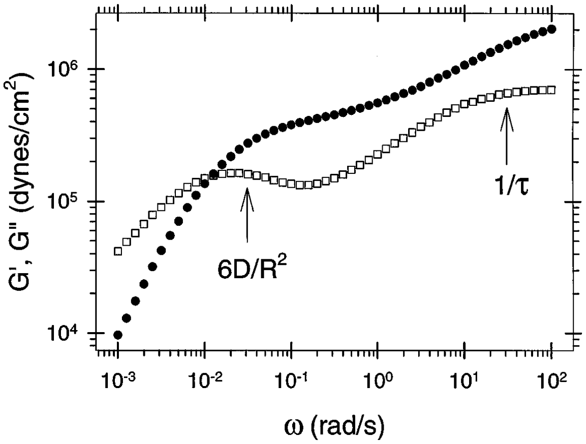

FIG. 3. Frequency dependence of storage modulus G' (filled circles) and loss modulus G'' (open squares) for dPSS$_{0.85}$-Na at 180 °C. The arrows denote reciprocals of time scales, as described in the text.

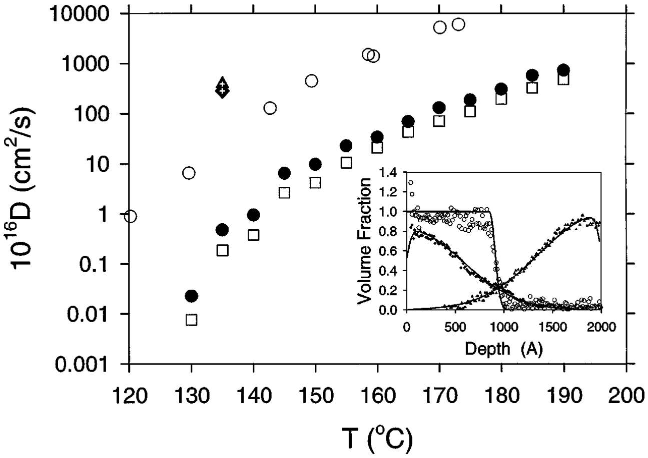

FIG. 4. Temperature dependence of diffusion coefficients for $M = 110\,000$ polymers: polystyrene data of Green and Kramer [13] (open circles), dPSS$_{0.85}$-Na (filled circles), dPSS$_{2.8}$-Na (open squares), Na$^+$ diffusion (triangle with crosshair), and Rb$^+$ diffusion (diamond with crosshair). Inset: DSIMS deuterium (open circles), Na$^+$ (solid diamonds) and Rb$^+$ (solid triangles) profiles of dPSS$_{2.8}$-Na/PSS$_{2.3}$-Rb after annealing for 10 min at 135 °C. Solid curves are the Fickian fits for the counterions and the dPSS$_{2.8}$-Na polymer.

$D = 3.05 \times 10^{-14}$ cm^2/s at 180 °C. The reciprocal of this relaxation time is shown as the arrow in Fig. 3, and agrees nicely with the low frequency maximum in the loss modulus.

In order to determine the diffusion rate of the counterions, bilayer samples were made by spinning a 1172 Å bottom layer of PSS$_{2.3}$-Rb onto native oxide silicon and floating on top a 598 Å layer of dPSS$_{2.8}$-Na. The samples were annealed at 135 °C for 10 min and profiled with DSIMS to determine deuterium, Na$^+$ and Rb$^+$ concentration profiles, shown in the inset of Fig. 4. As expected, no center of mass diffusion of the polymer chains (within the resolution of DSIMS, 80 Å) has occurred during the 10 min annealing interval at 135 °C. However, a measurable amount of counterion diffusion has occurred in this time. The diffusion coefficients of Na$^+$ and Rb$^+$, which were obtained from the Fickian solid curve fits, are 2.8×10^{-14} cm^2/s and 3.9×10^{-14} cm^2/s, respectively. Figure 4 shows that the diffusion coefficients of the counterions are approximately 3 orders of magnitude larger than those of the polymer chains. However, they are still very slow when compared to those of free ions in water (order of 10^{-5} cm^2/s). No counterion diffusion was observed in extensive anneals at room temperature (far below the T_g of the polymers). Since the ions are mobile only above the polymer glass transition, ion diffusion must occur by chain motion and exchange of ion pairs within multiplets. Figure 3 suggests that the lifetime of an ion pair in a multiplet is $\tau = 0.03$ s at 180 °C. The lifetime at 135 °C can be calculated from the ratio of diffusion coefficients: $\tau(135\,°\mathrm{C}) = \tau(180\,°\mathrm{C})D(180\,°\mathrm{C})/D(135\,°\mathrm{C}) = 30$ s. Using (5) with $b = 10$ Å, we estimate $D_{\mathrm{ion}} = 1 \times 10^{-14}$ cm^2/s, which is of the same order of magnitude as the experimental values.

In conclusion, we have shown that a scaling theory of reptating polymers with stickers can be used to model the rheology and diffusion of ionomers. Counterions diffuse by moving with the polymer chain from one multiplet to another, with stickers exchanging counterions within the multiplet. Ionomer diffusion is greatly slowed by the stickers, but there is no glass transition of the multiplet phase [1].

[1] A. Eisenberg and J.-S. Kim, *Introduction to Ionomers* (Wiley, New York, 1998), and references therein.
[2] A. N. Semenov *et al.*, in *Ionomers, Characterization, Theory and Applications,* edited by S. Schlick (CRC Press, Boca Raton, FL, 1996).
[3] R. A. Register and R. K. Prud'homme, in *Ionomers,* edited by M. R. Tant (Blackie Academic, London, 1997), p. 208.
[4] P. G. deGennes, J. Chem. Phys. **55**, 572 (1971).
[5] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
[6] L. Leibler (private communication).
[7] L. Leibler *et al.,* Macromolecules **24**, 4701 (1991).
[8] L. G. Baxandall, Macromolecules **22**, 1982 (1989).
[9] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
[10] R. D. Lundberg and H. S. Makowski, J. Polym. Sci., Polym. Phys. Ed. **18**, 1821 (1980).
[11] S. A. Schwarz *et al.,* Mol. Phys. **76**, 937 (1992).
[12] P. F. Green and E. J. Kramer, Macromolecules **19**, 1108 (1986).
[13] P. F. Green and E. J. Kramer, J. Mater. Res. **1**, 202 (1986).
[14] A. Munari *et al.,* J. Appl. Polym. Sci. **50**, 159 (1993).
[15] The storage and loss moduli increased slowly but systematically with time over four days (at least), presumably because water is slowly removed from the sample; see S. Bhargave and S. L. Cooper, Macromolecules **31**, 508 (1998).