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Diffusion of styrene–acrylonitrile copolymers

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Tracer diffusion coefficient, D^*, and the Newtonian zero shear-rate viscosity, η_0, were measured for a high molecular weight random copolymer (SAN) of styrene and acrylonitrile. As predicted by the reptation model, D^* was in agreement with the molecular-weight scaling of M_W^{-2} (M_W is the weight average molecular weight of the chain being probed) and was independent of matrix molecular weight. η_0 showed a molecular-weight scaling of $M_W^{3.4}$. While the temperature dependence of these two relaxation processes could be well explained by the free-volume model up to 252 °C, they showed a discrepancy in activation enthalpy, E_a, of about 20%, with a larger value for diffusion.

1. Introduction

The flow properties of polymers have unique features due to chain entanglement which arises from the fact that chains cannot cross each other. Reptation theory has provided a simple and intuitive model of processes which are affected by chain entanglement including diffusion and viscoelastic relaxation. Various experimental results have been compared with the predictions of the theory [1]. A recent observation by Russell *et al.* on short-range diffusion across polymer interfaces [2] that showed that the chain ends slither across the interface first as the reptation picture suggests, is particularly notable. We investigated the temperature and molecular-weight dependence of tracer diffusion, D^*, and zero shear-rate viscosity, η_0, of a random copolymer (SAN) of styrene and acrylonitrile. The results will be discussed in the context of reptation and the free-volume model.

For times $t > \tau_{\text{rep}}$ where τ_{rep} is the reptational relaxation time, the reptation diffusion coefficient, D^*_{rep}, can be written as [3]

$$D^*_{\text{rep}} = \frac{4M_0M_ek_BT}{15\zeta_0M_W^2} \tag{1}$$

or rearranged to give ζ_0

$$\zeta_0 = \frac{4M_0M_ek_BT}{15D^*_{\text{rep}}M_W^2} \tag{2}$$

where M_0 is the monomer molecular weight, M_e is the entanglement molecular weight, ζ_0 is the monomer friction coefficient, M_W is the weight-average molecular weight of tracer chain, and k_BT is Boltzmann's constant times the absolute temperature. Equation 1 would allow the extraction of ζ_0 from the diffusion measurements. On the other hand, ζ_0 can also be obtained from the zero shear-rate viscosity, η_0. η_0 is first measured in the reptation regime, and then reduced to η_0 at M_c ($= \eta_{0,M_c}$) by multiplying the measured η_0 by a factor $(M_c/M_W)^\alpha$, with $\alpha = 3.4$, where M_c is the critical molecular weight for viscous flow at which the crossover from reptation to Rouse behaviour takes place. The Rouse model is then used to give the following relation [4].

$$\zeta_0 = \frac{36\eta_{0,M_c}M_0}{\rho N_{\text{Avo}}M_cC_r} \tag{3}$$

where ρ is the density of the polymer, N_{Avo} is Avogadro's number, and C_r ($= 5.9 \times 10^{-17}$ cm^2 g^{-1} at 25 °C [5]) is square of end-to-end distance divided by molecular weight.

Free-volume theory has been used to explain the temperature dependence of the molecular motions in glass-forming materials at temperatures not far above the glass transition temperature, T_g [6]. In the theory, the free-volume availability is a rate-determining factor, while simple Arrhenius behaviour will eventually dominate at some higher temperatures at which the free volume is no longer the factor limiting polymer-chain mobility. Comparison of Equations 2 and 3 shows that the temperature dependence of D^*/T and η_0^{-1} would be nearly the same through the common factor ζ_0 if the temperature dependence of ρ, C_r, M_e, and M_c were not important [7, 8]. The relations in the form of the Vogel–Fulcher equation can be

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summarized as

$$\begin{cases} \log\dfrac{D^*(T)}{T} = A - \dfrac{B(D^*)}{T - T_\infty} \\ \log\eta_0(T) = A' + \dfrac{B(\eta_0)}{T - T_\infty} \end{cases} \qquad (4)$$

where T_∞ is called the Vogel temperature where the extrapolated free volume vanishes, and $B(D^*)$ and $B(\eta_0)$ are the coefficients representing the temperature dependence of D^*/T and of η_0, respectively. The activation enthalpy is approximately given by Equation 5 and approaches $2.303\,N_{\mathrm{Avo}}\,k_{\mathrm{B}}B$ asymptotically as the temperature increases.

$$E_a = 2.303\,N_{\mathrm{Avo}}\,k_{\mathrm{B}}B\left(\frac{T}{T - T_\infty}\right)^2 \qquad (5)$$

2. Experimental procedure

The materials used consist of SAN of various molecular weights with two different AN contents (~ 23 and 27 wt %), as well as deuterated (d-) SAN of two different molecular weights with approximately 23 wt % AN content in which the styrene units were perdeuterated. The AN contents, weight-average molecular weights, and polydispersity indices for various SANs used in this study are summarized in Table I. Protonated SANs were commercial materials supplied by Monsanto, and d-SANs were synthesized by free-radical polymerization. The procedure for synthesizing d-SAN is as follows. Acrylonitrile (18.6 wt %) and perdeuterated styrene (60.3 wt %) monomers were mixed with methyl ethyl ketone solvent (20.0 wt %) in the presence of 0.1 wt % *t*-butyl peroctoate as an initiator and 1 wt % terpinolene as a chain-transfer agent. The content of terpinolene was changed to control the molecular weight. The reaction was carried out under vacuum at 110°C for 2 h. After reaction, the polymers were again dissolved in methyl ethyl ketone and precipitated by adding methanol. These were then filtered and dried overnight in a vacuum oven at 80 °C.

For diffusion measurements, a base layer of SAN (> 1000 nm thick) was first prepared by spin casting the solution of polymer (using methyl isobutyl ketone as a solvent) on to a silicon wafer. The tracer layer of d-SAN of about 20 nm thickness was spun cast on to a glass slide, and floated on the surface of deionized water. It was picked up on the base layer, dried to remove excess water, and then annealed at the desired temperature in the range 153–193 °C for various times to allow the diffusion distance w ($= (4D^*t)^{1/2}$) to be approximately 250 nm. The details of this procedure may be found elsewhere [9, 10]. Diffusion coefficients have been determined using forward-recoil spectrometry (FRES) which measures the number of deuterium and hydrogen nuclei with different energies which have been recoiled by incident He^{2+} nuclei from particular depths within the sample. The resulting yield versus energy spectrum was converted into concentration versus depth profile using a simulation program [11].

TABLE I Acrylonitrile content, weight-average molecular weight, and polydispersity indices of protonated and deuterated poly(styrene-co-acrylonitrile) (SAN and d-SAN, respectively)

	AN wt %	M_{w} ($\times 10^5$) g mol^{-1}	$M_{\mathrm{w}}/M_{\mathrm{n}}$
SAN-AB	24.2	1.6	2.1
SAN-CD	24.1	1.1	1.9
RMSAN-23	22.9	1.8	2.4
RMSAN-23-2	21.4	1.8	2.4
RMSAN-23-3	22.8	1.4	2.4
RMSAN-27	27.2	2.4	3.0
d-SAN-EF	22.6	1.8	2.2
d-SAN-GH	22.4	1.1	2.0

The concentration profile for diffusion of monodisperse chains [12] is

$$\phi(x) = \frac{1}{2}\left\{\operatorname{erf}\left[\frac{h - x}{(4D^*t)^{1/2}}\right] + \operatorname{erf}\left[\frac{h + x}{(4D^*t)^{1/2}}\right]\right\} \qquad (6)$$

where x is the distance from the surface, and h is the initial thickness of the tracer film. However, the polymers used in this study had rather broad molecular-weight distributions with polydispersity indices of about 2. As Mills *et al.* [13] showed, the diffusion profile can be calculated assuming that the molecular-weight distribution of the tracer chains obeys a Flory–Schultz distribution [6] and that all chains diffuse by reptation

$$\phi(x) = \frac{1}{2}\sum_i w_i\left\{\operatorname{erf}\left[\frac{h - x}{(4D_i^*t)^{1/2}}\right] + \operatorname{erf}\left[\frac{h + x}{(4D_i^*t)^{1/2}}\right]\right\} \qquad (7)$$

where w_i and D_i^* are the weight fraction and tracer diffusion coefficient of species i which has a molecular weight of M_i. Equations 6 and 7 were convolved with a Gaussian with a full width at half maximum of 80 nm to account for the instrumental resolution of FRES. The simulation procedures used to extract D^* for d-SAN at a given weight-average molecular weight are illustrated in Fig. 1. (a) The height of experimental profile at $x = 0$ was fitted to the convoluted monodisperse solution (Equation 6) while matching the area of these two [13]. (b) A better fit is shown using the same D^* as in (a) but employing the polydisperse solution (Equation 7). Diffusion into higher AN-content SANs was also measured. When d-SAN was put on the surface of SAN with 27 wt % AN, the diffusion profile became different from the Fickian one right at the surface due to the surface segregation of d-SAN. (It has been found that d-SAN segregates at the surface when it is mixed with 27 wt % AN content SAN because of its lower surface energy [14, 15].) In this case, the surface portion of the spectrum was disregarded and the diffusion coefficient was extracted using Equation 7 as shown in Fig. 1c.

The melt rheology was measured under sinusoidal oscillatory shear between parallel plates using Rheometrics Mechanical Spectrometer, RMS-805. The measurements were carried out for two molecular weights of SAN over the temperature range, 161–252 °C, and the frequency range, 10^{-2}–10^2 rad s^{-1}

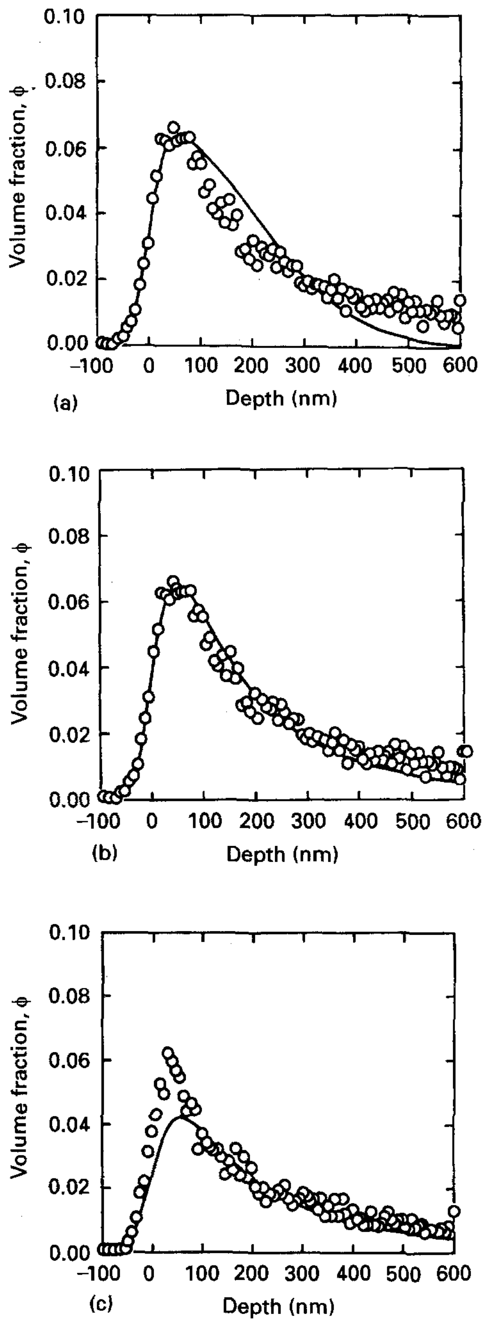

Figure 1 Volume fraction of d-SAN-EF as a function of depth from the surface. (a) The sample using RMSAN-23 as a matrix was annealed for 3 h at 172 °C ($D^* = 1.7 \times 10^{-14}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$). (——) Fit to the data using Equation 6. (b) The same experimental profile as (a) is shown. (——) Fit to the data using Equation 7 considering polydispersity. The same D^* as (a) was used. (c) The sample using RMSAN-27 as a matrix was annealed for 5 h at 172 °C ($D^* = 1.3 \times 10^{-14}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$). (——) Fit to the data using Equation 7 considering polydispersity. The surface portion of the spectrum was disregarded.

in all cases, and 10^{-3}–10^{2} in some cases. (In the melt rheological experiments, RMSAN-23-2 and RMSAN-23-3 were used as the protonated equivalent of d-SAN-EF and d-SAN-GH, which were the closest samples available.) These data permitted the zero shear viscosity, η_0, the plateau modulus, G_N^0, and the minimum loss tangent, $(\tan\delta)_{\min}$, to be measured. To obtain the best numbers for G_N^0 and $(\tan\delta)_{\min}$, time–temperature superposition of the data was invoked. Superposing the shear modulus versus frequency data using the corresponding shift factor, a_T, worked well over the entire temperature range and resulted in similar values of the shear modulus in the plateau region (G_N^0). From this result we judge that the entanglement molecular weight, M_e, is effectively independent of temperature. It was estimated that G_N^0 is 4×10^5 Pa, from which M_e was calculated to be 9 800 g ($M_e = \rho RT/G_N^0$). (Alternatively, using the equation given by Vinogradov *et al.* [16], $(\tan\delta)_{\min} = 2.5\,(M/M_e)^{-0.8}$, with values for $(\tan\delta)_{\min}$ of 0.375 and 0.412, respectively, for RMSAN-23-2 and RMSAN-23-3, M_e of 16 500 and 14 700 were obtained for these two samples, respectively. Using Hogberg *et al.*'s coefficient of 1.8 [17] rather than 2.5, yielded still higher values of M_e.)

3. Results and discussion

The following two conditions were checked to see whether D^* data are consistent with the molecular weight dependence that reptation theory predicts: (1) D^* is independent of the matrix molecular weight, and (2) D^* scales as $M_{\bar{W}}^{-2}$. As shown in Table II only slightly different diffusion coefficients were obtained for the diffusion of d-SAN into the two matrices of the different molecular weights (SAN-AB and SAN-CD). From the negligible decrease in D^* caused by increasing the matrix molecular weight by 53 000, it could be concluded that the constraint release contribution to D^* is negligible above the molecular weight of SAN-AB. A calculation according to the constraint release theory of Graessley [18] using 3.5 for the number of suitably situated constraints [3, 10] also supports the result that D^* should become nearly independent of matrix molecular weight in the molecular-weight range above $\sim 1.5 \times 10^5$.

Fig. 2a shows the Vogel–Fulcher plot for D^* according to Equation 4 using a T_∞ of 48 °C which was obtained by determining the non-linear least squares fit to the η_0 data (in Fig. 3). All the d-SAN-EF and d-SAN-GH data could be reduced to fit one line by multiplying D^* by M_W^2 (Fig. 2b). Tracer diffusion coefficients of d-SAN into SAN containing 27 wt % AN (RMSAN-27) are also included in Fig. 2a and b. These D^* values were nearly the same as those of the same d-SAN into the SAN with a matched AN content (RMSAN-23). This result shows that, as expected for tracer diffusion coefficient, the unfavourable thermodynamic interaction due to the mismatch in AN content had little or no effect. (SANs with AN contents of 22.5% and 27.2% were shown to approach phase separation at 163 °C [15]). The Vogel–Fulcher plot of the η_0 data is also shown in Fig. 3. The sets of η_0 data for different molecular weights in Fig. 3a were well superimposed by multiplying η_0 by $M_{\bar{W}}^{3.4}$ and this result is shown in Fig. 3b. Figs 2 and 3 illustrate that the temperature dependence of both D^* and η_0 followed the Vogel–Fulcher equation (not showing Arrhenius behaviour) over the entire temperature range, consistent with the free-volume theory. The viscosity data were also plotted as an Arrhenius plot ($\log \eta_0$ versus $1/T$; Fig. 3c): the activation enthalpy (proportional to the slope of the curve) is clearly a strong

TABLE II Diffusion coefficients

Temperature (°C)	Diffusion coefficients ($cm^2 s^{-1}$)			
	EFAB[a]	EFCD[b]	GHAB[c]	GHCD[d]
177	3.2×10^{-14}	3.9×10^{-14}	7.3×10^{-14}	8.0×10^{-14}
194	1.8×10^{-13}	2.2×10^{-13}		

[a] EFAB: Tracer diffusion of d-SAN-EF into SAN-AB matrix.
[b] EFCD: Tracer diffusion of d-SAN-EF into SAN-CD matrix.
[c] GHAB: Tracer diffusion of d-SAN-GH into SAN-AB matrix.
[d] GHCD: Tracer diffusion of d-SAN-GH into SAN-CD matrix.

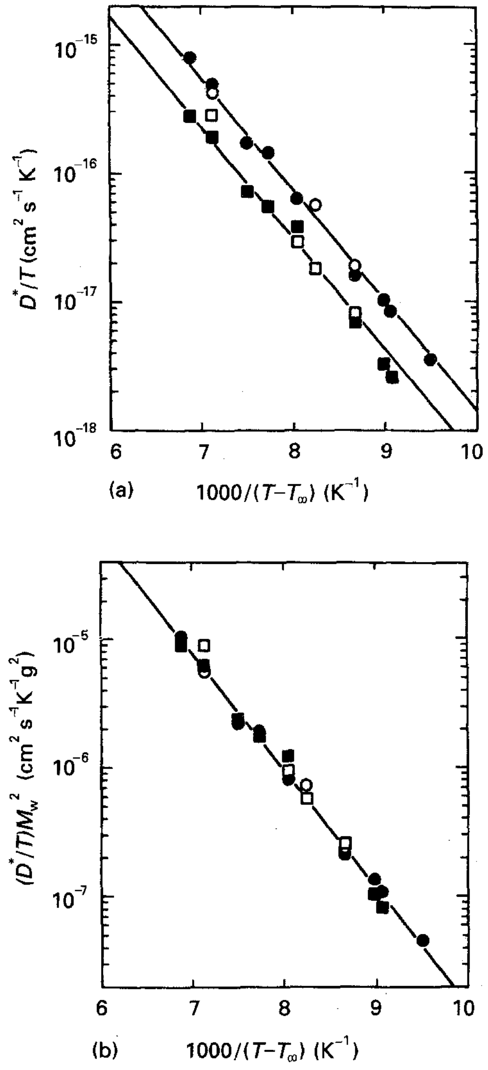

Figure 2 Temperature dependence of tracer diffusion coefficients, D^*. (a) Log (D^*/T) as a function of $1/(T - T_\infty)$ (Vogel–Fulcher plot according to Equation 4) was plotted for d-SAN-EF in (■) RMSAN-23 matrix and (□), RMSAN-27 matrix and for d-SAN-GH in (●) RMSAN-23 matrix and (○) RMSAN-27 matrix. The value used for T_∞ was 48 °C. (b) All the d-SAN-EF and d-SAN-GH data were reduced to fit one line by multiplying D^*/T by M_W^2. For key, see (a). The values of $B(D^*)$ and A in Equation 4 were found to be 910 and $1.26 - 2\log M_W$, respectively.

function of temperature even well above 200 °C. This result is in disagreement with a previous report by Mendelson [19] that the temperature dependence of the melt viscosity on SAN could be described by an Arrhenius equation above 191 °C with a constant activation energy of 25.5 kcal mol^{-1}. From the above plots of D^* and η_0, the monomer friction coefficient, ζ_0, could be calculated according to Equations 1 and 2. Equation 2 shows that ζ_0 should scale as $M_c^{2.4}$. While M_c for SAN is not known, M_c is usually between $2M_e$ and $3M_e$ [6]. The ζ_0 values from η_0 were plotted in Fig. 4 for (a) $M_c = 2M_e$ and (b) $M_c = 3M_e$. The magnitudes of ζ_0 obtained from D^* and from η_0 are in reasonable agreement, supporting previous reports in the literature [1, 4, 7, 8, 20, 21]. The interesting finding in this study is that the slope B in the Vogel–Fulcher equation (Equation 4) seems to be different ($B(D^*) = 910$ K and $B(\eta_0) = 737$ K). In Fig. 5 the apparent activation enthalpy, E_a, from Equation 5 was also plotted; the dotted line represents the E_a of 25.5 kcal mol^{-1} from Mendelson [19]. Diffusion has an E_a that is consistently 20% larger than that of viscosity. The parameters C_r, ρ, M_e, and M_c appear separately in either Equation 2 or 3. If one or several of these were temperature dependent, it might account for the difference in the temperature dependence of ζ_0 extracted from D^*/T and η_0. However, we can show that the possible temperature dependence of C_r or ρ could not help rationalize the difference in B. For example, if we allow C_r (i.e. the square of chain dimension) to increase linearly by 20% from 25 °C to 225 °C, the increase in $B(\eta_0)$ is calculated to be only about 8 K. If we take the expansion of the specific volume into account so that ρ decreases as the temperature increases, a similarly small influence is calculated, but in this case the discrepancy is increased. Bartels *et al.* [22] have shown for polybutadiene that the temperature dependence of G_N^0 may be written in terms of $\rho(T)$ and $C_r(T)$, and these could cause a difference in E_a by 2.0 kcal mol^{-1} which roughly corresponds to 25 K in B scale (in this case η_0 had a higher E_a). However, our data on shear modulus versus frequency showed that G_N^0 was nearly the same over all temperatures. Glass transition temperatures were also measured for d-SAN on which D^* measurements were made, and for protonated SAN on which η_0 measurements were made. Again there was almost no difference (~ 112 °C for both). The remaining possibility for D^*/T and η_0^{-1} not sharing the same activation enthalpy may be that diffusion and viscosity have monomer friction coefficients with different temperature dependence. As far as we know, the similar temperature dependence in the rheological and diffusion measurements has been studied only for a few

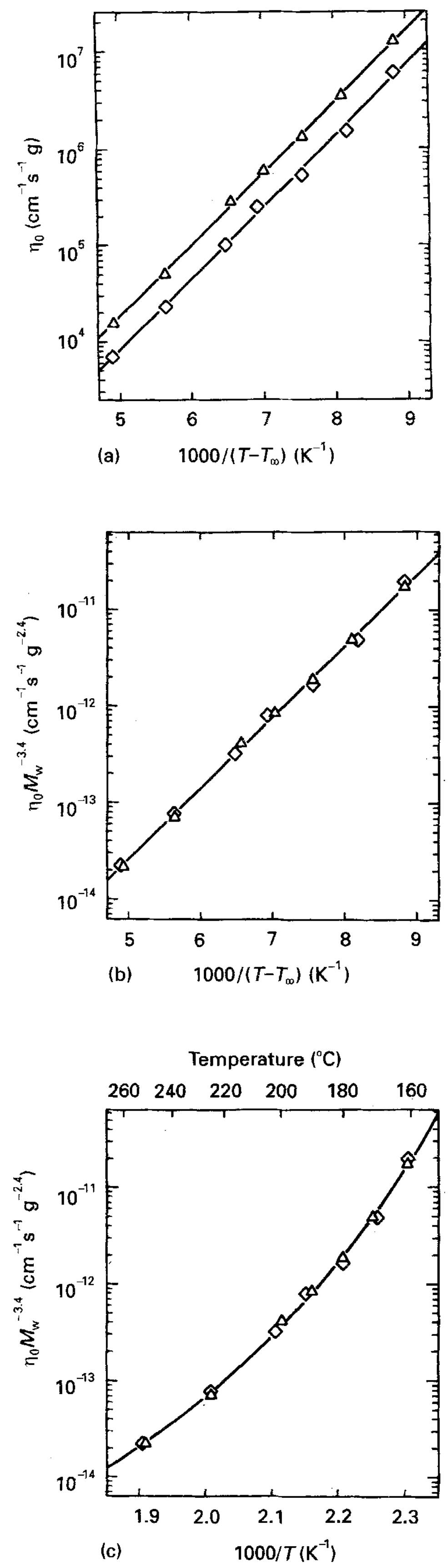

Figure 3 Temperature dependence of zero shear-rate viscosity, η_0, (1 cm^{-1} s^{-1} g = 1 P). (a) Log η_0 as a function of $1/(T - T_\infty)$ (Vogel–Fulcher plot according to Equation 4) was plotted for (△) RMSAN-23-2 and (◇) RMSAN-23-3. (b) RMSAN-23-2 and RMSAN-23-3 data were reduced to fit one line by multiplying η_0 by $M_W^{-3.4}$. For key, see (a). The values of $B(\eta_0)$ and A' in Equation 4 were found to be 737 and $-17.27 + 3.4 \log M_W$, respectively. (c) Log η_0 was plotted as a function of $1/T$ (Arrhenius plot) for (△) RMSAN-23-2 and (◇) RMSAN-23-3.

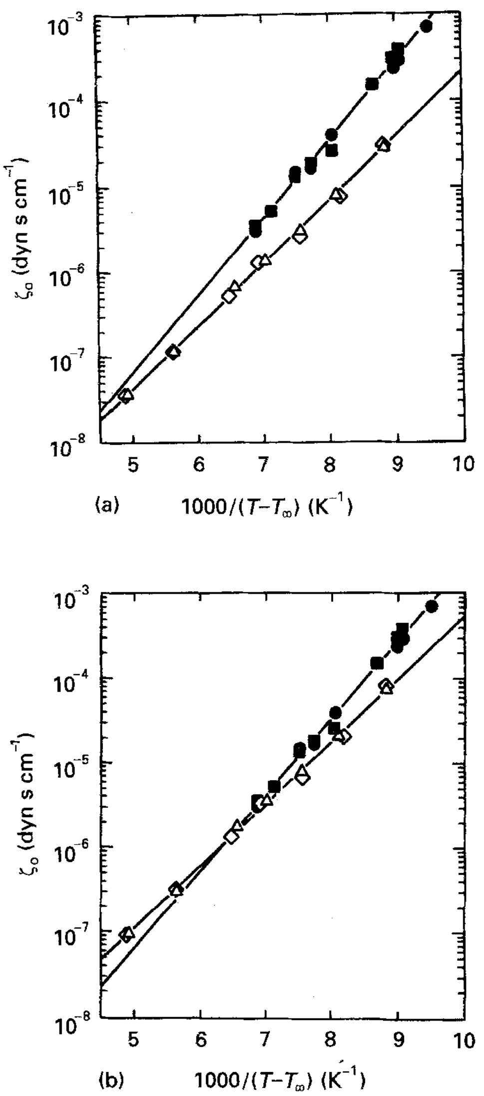

Figure 4 Logarithm of monomer friction coefficient, ζ_0, is plotted as a function of $1/(T - T_\infty)$ (Vogel–Fulcher plot) using (a) $M_c = 20000$ and (b) $M_c = 30000$. ζ_0 was extracted from the diffusion, D^*, and viscosity, η_0, measurements at various temperatures according to Equations 2 and 3, respectively. Solid symbols are from diffusion data (see Fig. 2 for key); open symbols are from viscosity data (see Fig. 3 for key).

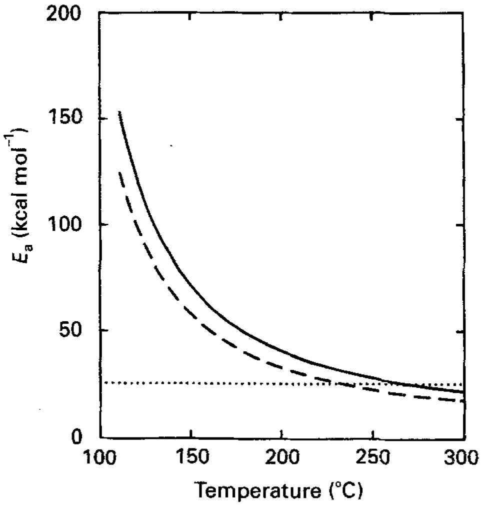

Figure 5 The activation enthalpies for (——) the tracer diffusion coefficients, D^*, and (– – –) the viscosity η_0 as a function of temperature obtained according to Equation 5. (· · ·) $E_a = 25.5$ kcal mol^{-1} [19].

polymers (polyisoprene [7], polystyrene [8], and poly(propylene oxide) [21]). More experimental studies in the other polymer systems, especially in random copolymer systems, seem to be required to judge whether the mismatch that we found is an exceptional case.

4. Conclusion

In well-entangled SAN melts, D^* was effectively independent of molecular weight of the matrix and behaviour consistent with D^* and η_0 scaling as M_W^α, with the exponent α of -2 for D^* and 3.4 for η_0, was observed. The temperature dependence of η_0 and D^* followed the Vogel–Fulcher equation up to 252 °C without manifesting Arrhenius behaviour. This is what would be observed if the free-volume availability is the main factor which determines the activation enthalpy. Stronger temperature dependence of D^* than η_0 was found, which corresponds to about a 20% larger activation enthalpy for diffusion than for viscosity.

Acknowledgements

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