Molecular motions of polystyrene in concentrated solutions as studied by n.m.r. relaxation and self-diffusion measurements

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In concentrated solutions of polystyrene in C_6D_6 the dependences of the macromolecular self-diffusion coefficients and nuclear relaxation times T_1, T_2 and $T_{2_{\mathrm{eff}}}$ on molar mass, concentration and temperature were measured. The self-diffusion coefficients strongly decrease with increasing polymer concentration. The monomeric friction coefficient and the correlation frequency of segmental motions determined from n.m.r. relaxation times show an identical dependence on concentration, leading to the conclusion that the concentration dependence of the self-diffusion coefficient is determined by a monomeric friction coefficient that is controlled by the strongly concentration-dependent cooperative segmental motion. The onset of tube formation, which is not seen in the self-diffusion experiments, was revealed in the n.m.r. relaxation experiments.

(Keywords: n.m.r. relaxation; self-diffusion; concentrated solution; polystyrene)

INTRODUCTION

In the last two decades n.m.r. spectroscopy has become a powerful technique for polymer research. Detailed information on structure and motion of macromolecules or subunits of macromolecular chains can be obtained from n.m.r. line-shape analysis and the temperature and/or frequency dependence of n.m.r. relaxation times. In addition, translational diffusion processes can be studied well by using the n.m.r. pulsed-field-gradient technique.

The molar-mass–concentration plot of polymer solutions may be conveniently subdivided into different regions. In the dilute region the polymer coils are isolated from one another, so that the response of the spin system in an n.m.r. experiment is liquid-like owing to fast rotational motions of the segments and of the molecules as a whole. The translational motion (diffusion) of the polymer coils is well described by the Kirkwood formula and looks like the motion of hard spheres in a viscous medium[1]. Beyond the overlap concentration

$$c^* \simeq \frac{M}{N_A R_G^3} \tag{1}$$

(where M is the molar mass, R_G the radius of gyration and N_A the Avogadro constant), the coils begin to overlap. In the semidilute region the overlapped coils may be considered to divide into blobs. The blob dimensions are controlled by the correlation length ξ (ref. 2) and outside a blob excluded volume effects and hydrodynamic interactions between segments are screened out. In the semidilute region, where the polymer concentration is still small, the blobs behave as isolated chains where only polymer–solvent interaction takes place. This is seen by n.m.r., for example, where the correlation times of segmental reorientations derived from T_1-measurements are nearly independent of concentration[3]. In this region the self-diffusion coefficient D strongly decreases with increasing concentration, but it is now well established that the segmental mobility or the monomeric friction coefficient remains concentration independent; the concentration dependence is determined only by concentration-dependent blob dimensions[4], in contrast to the results of Wesson *et al.*[5].

With increasing concentration the blob picture breaks down at the concentration c^{***}[4] when the blobs become smaller than the statistical segment length. This is a characteristic of the concentrated region, where polymer–polymer interaction becomes dominant. The segmental motion is increasingly cooperative, it strongly depends on concentration and its temperature and concentration dependence can be described by WLF- or free-volume-type equations[6].

If at a given polymer concentration ϕ_2 (we will use the polymer volume fraction ϕ_2 in this work) a characteristic molar mass $M_{c,\eta}(\phi_2) = M_{c,\eta}(0)/\phi_2$ is exceeded, the shear viscosity behaviour of polymers indicates the formation of entanglements. Now the chain is confined in a tube because the lateral excursions of the chains are encumbered by its complements of neighbouring chains whereas the longitudinal motions are not influenced. The chain may be divided into subchains with end-to-end distance $\boldsymbol{h}$, approximately equal to the tube diameter (see *Figure 1*). For the self-diffusion coefficient of polymer

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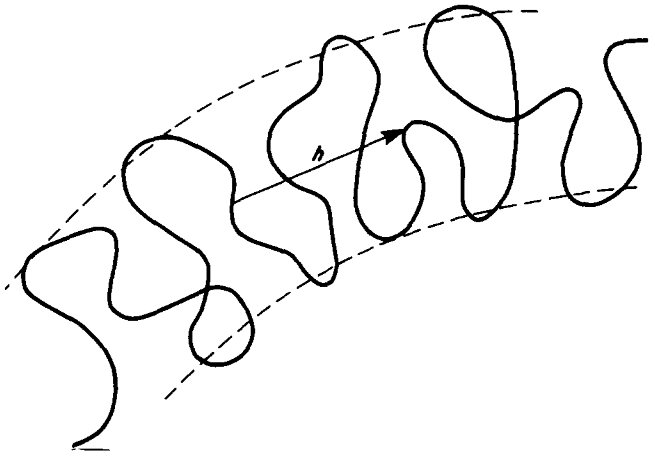

Figure 1 A subchain of a macromolecule in the tube

molecules in the concentrated entangled region the reptation model[7] gives

$$D \propto \frac{a^2}{M^2\zeta_0} \propto \frac{1}{\phi_2 M^2 \zeta_0} \qquad (2)$$

where a is the primitive path step (approximately the tube diameter). Entanglement models and plateau modulus data give the proportionality $a \propto \phi_2^{-1}$ (ref. 8). Now D is determined by two concentration-dependent quantities. The monomeric friction coefficient ζ_0 describes the mobility of the segments, and the concentration dependence of the geometry of the system, the tube diameter, enters in equation (2) as ϕ_2^{-1}.

The well-known dependence $D \sim M^{-2}$ is observed in the non-entangled semidilute solutions as well as in good solvents and in entangled solutions; consequently the self-diffusion proceeds by reptation in both cases, and the concentration and molar mass dependence of D is not influenced by entanglement effects.

However, n.m.r. relaxation properties are influenced by constraints of chain motion. The tube prevents free rotation of the subchains, which leads to an anisotropy of motion. It reorients itself with a time constant no longer than the tube disengagement time T_d. This anisotropy of motion leads in consequence to solid-like contributions to n.m.r. resonance lines and should be detected in n.m.r. experiments. For anisotropic internal motion the second moments of proton resonance lines can be described approximately by the *ad hoc* equation[9]

$$\langle \delta B^2 \rangle = \langle \Delta B_{\mathrm{st}}^2 \rangle + \langle \Delta B^2 \rangle \frac{2}{\pi} \arctan \alpha(\gamma \delta B \tau_c) \qquad (3)$$

where $\langle \Delta B_{\mathrm{st}}^2 \rangle$ means a static contribution to the second moment $\langle \Delta B_0^2 \rangle$, which cannot be averaged out by thermal motions. That part which is influenced by fast quasi-isotropic reorientation processes

$$\langle \Delta B^2 \rangle = \langle \Delta B_0^2 \rangle - \langle \Delta B_{\mathrm{st}}^2 \rangle \qquad (4)$$

is to be obtained separately from the minima in the temperature dependence of the relaxation times T_1 (at $\omega_0 \tau_c \approx 0.5$) or $T_{2_{\mathrm{eff}}}$ (at $\omega_{\mathrm{eff}} \tau_c \simeq 0.5$), respectively, by using the equations (see, for example, ref. 9)

$$T_{1,\mathrm{min}} = \frac{A}{\beta} \frac{1.05 B_0}{\gamma \langle \Delta B^2 \rangle} \qquad (5)$$

$$T_{2_{\mathrm{eff}},\mathrm{min}} = \frac{A}{\beta} \frac{4.08 \bar{B}_1}{\gamma \langle \Delta B^2 \rangle} \qquad (6)$$

$$\omega_{\mathrm{eff}} = 2\gamma \bar{B}_1 = \frac{\pi}{2\tau} \qquad (7)$$

where γ is the gyromagnetic ratio. τ used as a measure for the effective magnetic field means the distance between r.f. pulses in a $T_{2_{\mathrm{eff}}}$-experiment, by which very slow processes can be observed.

The factor A in equations (5) and (6) takes into account the deviation of the fast segmental reorientation process of the polymer (sub-) chains from the isotropic case and β means the parameter of a possible distribution of rotational correlation times τ_c with $0 < \beta < 1$ (ref. 9). $A > 1$ takes into consideration the fact that, for example in dilute solutions, proton relaxation is caused by three-bond conformational transitions (with correlation time τ_{cd}) as well as by overall tumbling motions (with correlation time τ_{co})[3]. From a comparison of experimental results with those predicted by theory for isotropic rotational diffusion ($\tau_{\mathrm{cd}} \gg \tau_{\mathrm{co}}$), A can be estimated to be $A \approx 1.5$.

While dilute and semidilute polymer solutions and melts are extensively studied with n.m.r. techniques, the data on concentrated polymer solutions are still limited. In the present paper we report investigations of dynamic processes in concentrated polymer solutions whereby the interest is directed to the translational and rotational motion of the polymers and their segments, and especially the validity of equation (2), and to the beginning of tube formation (onset of entanglements). Recently, similar investigations on solutions of poly(ethylene oxide) and a scaling treatment were reported by Sundukov *et al.*[10].

EXPERIMENTAL

The n.m.r. relaxation data were obtained by means of an *FT*-spectrometer of type FKS 178 (Zentrum für wissenschaftlichen Gerätebau of the Academy of Sciences of G.D.R.) at a proton resonance frequency of 60 MHz. The electronic assembly is characterized by a $\pi/2$ pulse-width of 1 μs and a dead time of 6–7 μs. Well-known pulse sequences were used for measuring T_1 and $T_{2_{\mathrm{eff}}}$ (cf. for example, ref. 11). The n.m.r. pulsed-field-gradient experiments using the method of stimulated echo[12] were made with a custom-built spectrometer, FEGRIS[13], which also has a resonance frequency of 60 MHz. The measurements of the lowest self-diffusion coefficients had to be done very carefully since the large field gradients may influence the r.f. pulses, and also mechanical vibrations and shocks may cause additional displacements, both leading to an overestimation of D (ref. 13). The typical experimental error in D in this work is ±20%. Monodisperse polystyrenes were standards purchased from Knauer GmbH (West Berlin). Perdeuterated benzene was supplied by Isocommerz GmbH, Leibzig, and IBJ Swierk (Poland).

The samples were prepared by weighing them in n.m.r. glass tubes directly and sealing in vacuum at liquidnitrogen temperatures. Care was taken to minimize the empty volume in the glass tubes. Concentrations are given as volume fractions of polymer in the solution.

RESULTS AND DISCUSSION

Concentration dependence

First, as an example, the temperature dependence of the self-diffusion coefficients of different solutions of a polystyrene standard with $M_w = 19\,000$ in C_6D_6 is shown in *Figure 2*. The values strongly depend on concentration, as demonstrated in *Figure 3*, where DN^2 is drawn *versus* concentration for three polystyrene standards at a temperature of 473 K. The data give one master curve, confirming the dependence $D \propto M^{-2}$ within experimental error. According to equation (2) it is to be expected that in this concentration region the self-diffusion coefficient is inversely proportional to the monomeric density (or the polymer volume fraction) and to the monomeric friction coefficient. $D\phi_2$ (the full curve in *Figure 3*) should have the concentration dependence of the monomeric friction coefficient. In contrast to the semidilute region ζ_0 is now strongly concentration dependent. The onset of the concentration dependence in the concentrated region is already seen in *Figure 2* of ref. 4, where for $c > c^{***} \approx 0.3$ the experimental data begin to deviate from the curve calculated with the assumption of a constant monomeric friction coefficient.

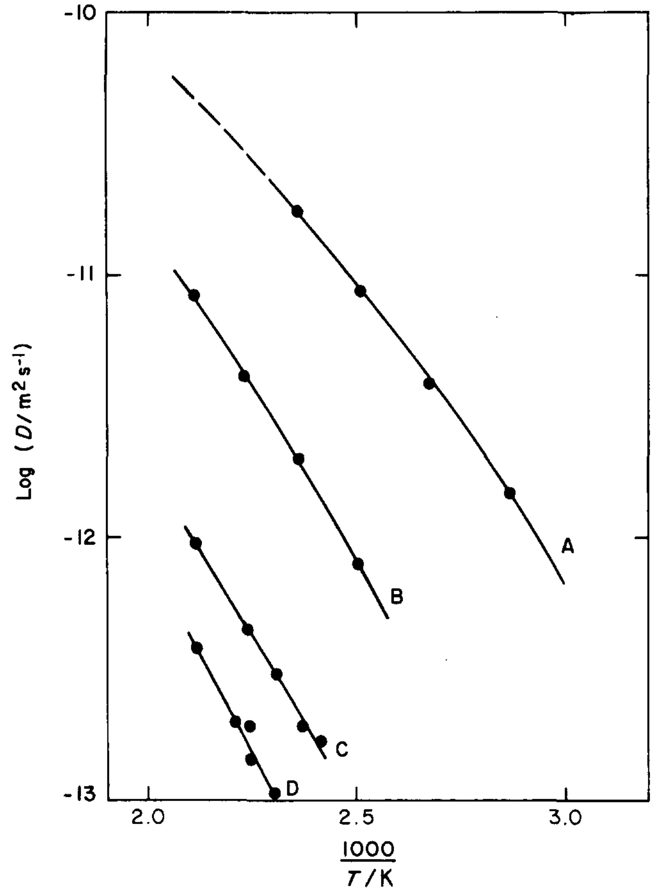

Figure 2 Temperature dependence of the self-diffusion coefficients of polystyrene 19 000 dissolved in C_6D_6 with concentration $\phi_2 = 0.53$ (A), 0.75 (B), 0.86 (C) and 0.94 (D)

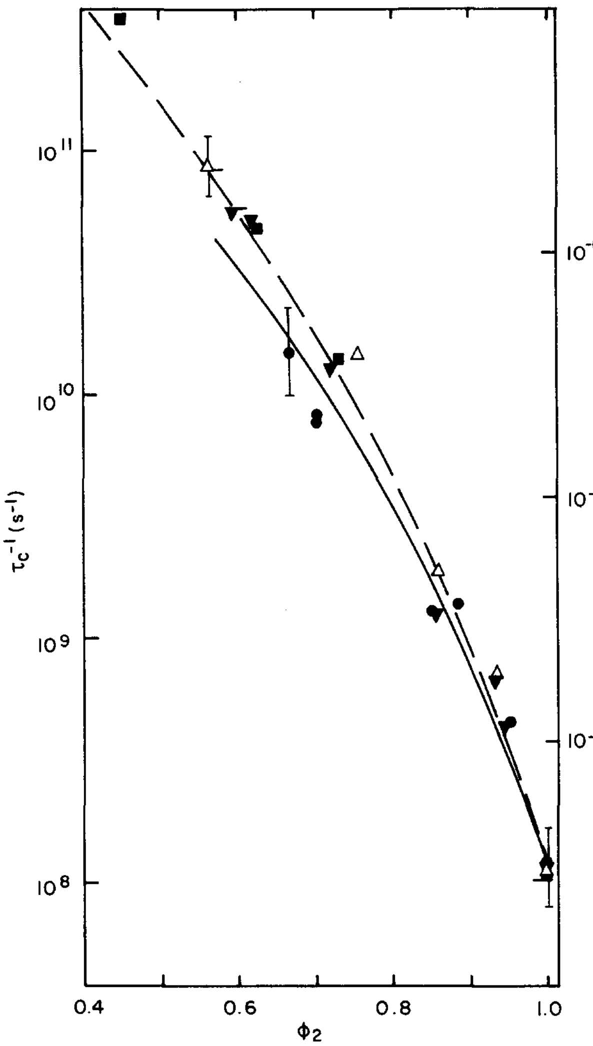

Figure 3 Dependence of DN^2 (right scale) and τ_c^{-1} (left scale, symbol ●) of polystyrene in C_6D_6 at $T = 473$ K on concentration ϕ_2. N is the number of monomeric units in the polystyrene, τ_c the correlation time of segmental motion determined by n.m.r. The full curve is $D\phi_2$ (in arbitrary units) calculated from equation (8) and the parameters given in the text. The molar masses are: (■) 1.1×10^5, (△) 1.9×10^4 and (▼) 1.2×10^4. The data with a 'pip' right are extrapolated via temperature and with a 'pip' left via molar mass

The concentration dependence of $\zeta_0 \propto D\phi_2$ is a typical free-volume curve characteristic for cooperative segmental motions. The broken curve in *Figure 3* was fitted to the experimental data by using the free-volume expression after Fujita[14] for the monomeric friction coefficient

$$D \propto \frac{1}{\phi_2 \zeta_0} \propto \frac{1}{\phi_2} \exp\left(-\frac{B}{f_1\phi_1 + f_2\phi_2}\right) \qquad (8)$$

The fractional free volume f_2 of polystyrene was calculated from $f_2 = 0.025 + 3 \times 10^{-4}\,\mathrm{K}^{-1}$ $(T = 373\,\mathrm{K})$ (ref. 15). The fractional free volume of benzene f_1 and the constant B were obtained by the fitting procedure: $f_1 = 0.128$ and $B = 0.88$ are the results, the value for f_1 being surprisingly small. In the more elaborate free-volume theory of Vrentas and Duda[16], f_1 is greater by a factor of about 3–4 and B is smaller and slightly concentration dependent. Their curves of $\log D$ *versus* ϕ_2 are far too convex and do not fit our data.

From $T_{1,\mathrm{min}}$ values (see *Figure 4*), where $\omega_0\tau_c \approx 0.5$ holds together with the activation energies reported below, we have calculated the correlation frequencies τ_c^{-1} of segmental reorientations at 473 K. Since monomeric

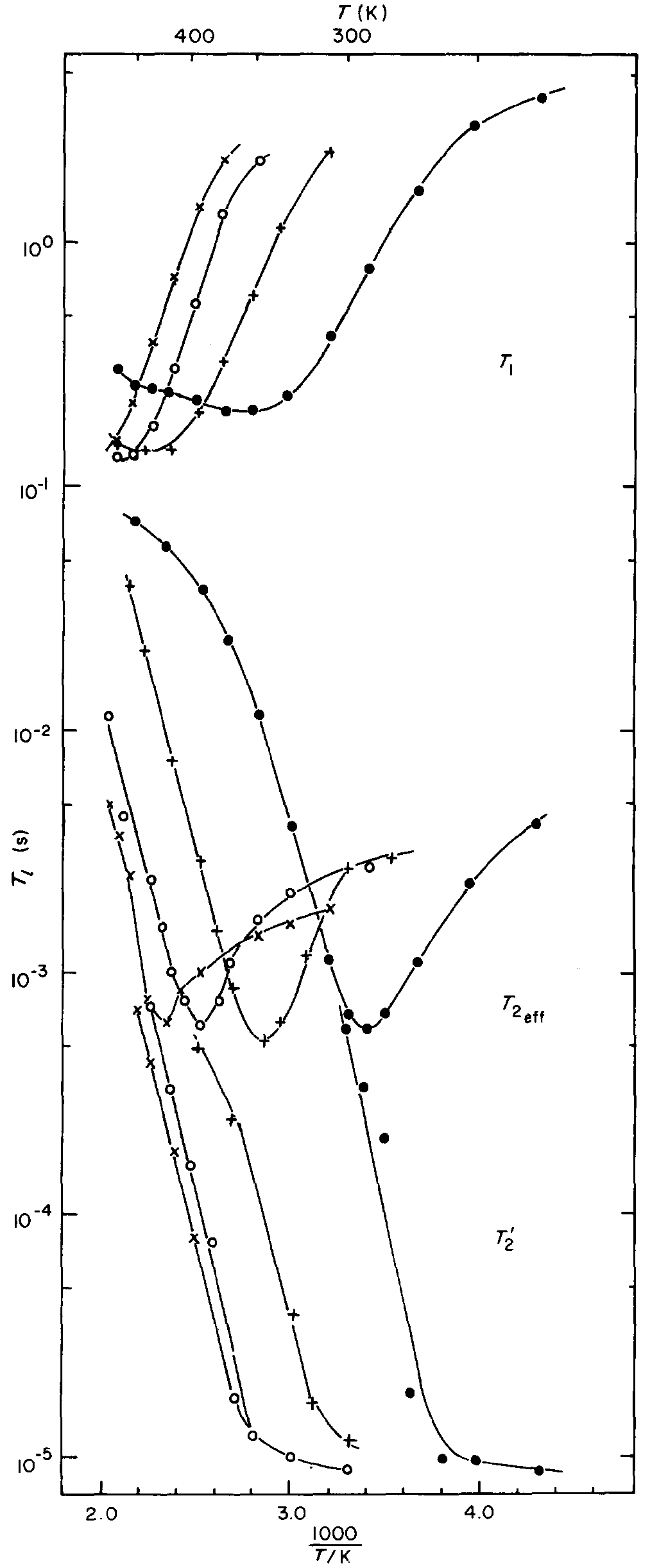

Figure 4 Temperature dependence of relaxation times T_1, $T_{2_{\text{eff}}}$ and T_2' of polystyrene 6.1×10^5 dissolved in C_6D_6 with different concentrations: (●) 0.67, (+) 0.83, (○) 0.94 and (×) 1.0

friction is strongly connected with the segmental motion, one should expect the same concentration dependence of both quantities. The correlation frequencies of segmental reorientations, also shown in *Figure 3*, indeed have an identical concentration dependence to the monomeric friction coefficient (as $D\phi_2$).

From D and τ_c the root-mean-square displacement of a segment during τ_c can be estimated from

$$\langle r^2 \rangle = D_{\text{seg}} 6 \tau_c \tag{9}$$

with

$$D_{\text{seg}} = \frac{3DN^2}{N_e} \tag{10}$$

D_{seg} is the self-diffusion coefficient of a segment, N_e the number of monomeric units between entanglements. For $\langle r^2 \rangle^{1/2}$ we obtain *ca.* 15 Å, i.e. during the correlation time τ_c of segmental reorientation a segment moves a distance of about its own length (which is about 20 Å for polystyrene). This value is smaller than the tube diameter but greater than the correlation length ξ calculated for this concentration region[4].

Figure 4 shows the effect of polymer concentration on the temperature dependence of relaxation times T_1, $T_{2_{\text{eff}}}$ and T_2'. T_2' is calculated from the width of the resonance line at half height and T_1 and $T_{2_{\text{eff}}}$ are time constants for the magnetization decay from 1 to 1/e. With increasing concentration the $T_{1,\text{min}}$-values decrease and the minima are shifted to higher temperatures. This can be explained by stronger polymer–polymer interactions and increasing cooperative motions, as typical for glass transitions. The 'plateau'-values of T_2' in the low-temperature region became smaller with increasing polymer concentration, indicating larger values of the second moment. The results are in good agreement with those of earlier investigations[17,18].

Figure 5 gives the temperature dependence of $T_{2_{\text{eff}}}$ as a function of frequency, cf. equations (5) and (6), allowing a direct estimate of the activation energy to be 65 kJ mol^{-1}, as typical for Arrhenius-like processes at the high-temperature side of a WLF representation. Under the influence of the solvent molecules, the free volume in the system where polymer–polymer interactions dominate is enlarged and the cooperative regions are of the order of a few monomeric units only. For the purpose of comparing the activation energies of τ_c with those of self-diffusion measurements, however, we used, in general, E_a-values obtained from the high-temperature side of T_1, which are of the same order.

The dependence of the apparent activation energies derived from the temperature dependence of the self-diffusion coefficients (see *Figure 2*) and the T_1- and $T_{2_{\text{eff}}}$-values (*Figure 4*) for temperatures between 423 and 473 K on concentration is shown in *Figure 6*. The values from relaxation data resemble the self-diffusion data, indicating the same underlying process. Because of the relatively low molar masses of the samples we do not reach the limit for $M \rightarrow \infty$ of about 170 kJ mol^{-1} for self-diffusion in the melt.

Molar mass dependence

As mentioned in the Introduction, self-diffusion experiments do not reveal the onset of tube formation at $M_{c,\eta}(\phi_2)$ because the diffusion is still strongly controlled by the concentration dependence of ζ_0. The onset of anisotropic motion within a tube should be observable by n.m.r. relaxation experiments. In *Figure 7* the temperature dependence of the relaxation times is given for polystyrene solutions of different molar masses at

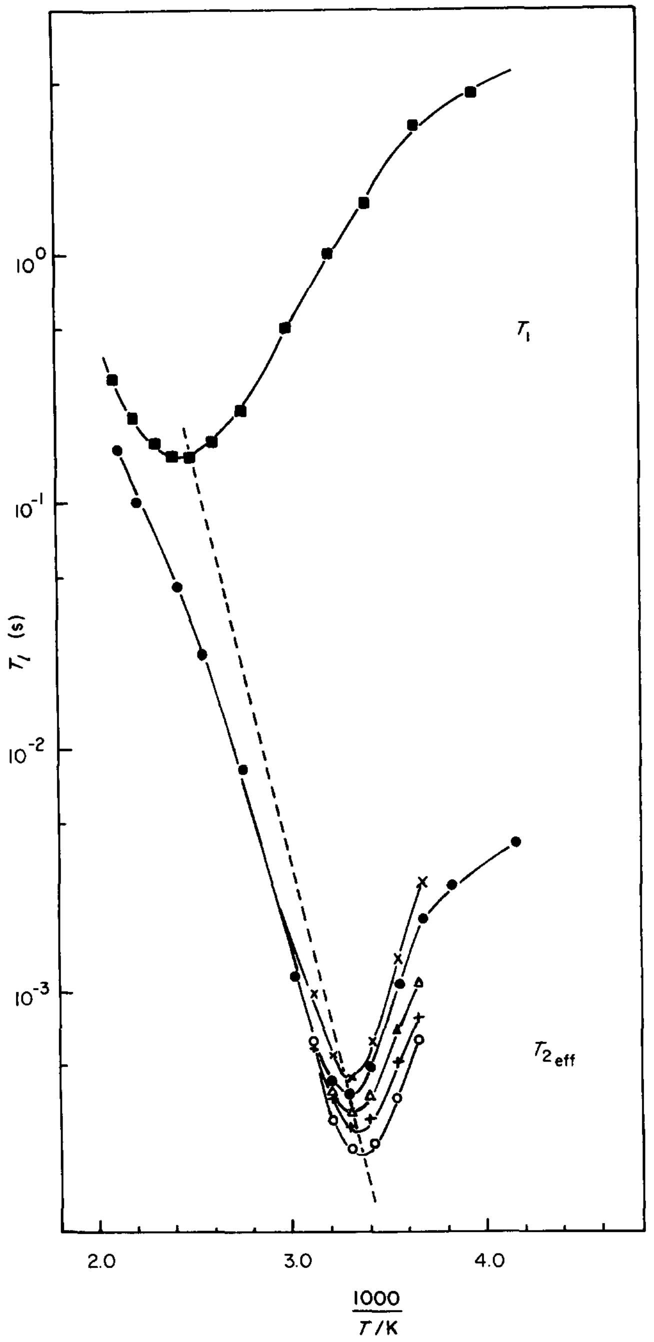

Figure 5 Temperature dependence of T_1 and $T_{2\rm eff}$ for different effective magnetic fields, characterized by τ = (○) 9, (+) 7.8, (△) 6, (●) 5 and (×) 4 μx. System polystyrene/C_6D_6, $\phi_2=0.7$, $M=6.1\times10^5$

$\phi_2=0.7$. If the critical molar mass $M_{c,\eta}(\phi_2)$ is reached, which can be estimated to be 4.7×10^4 for $\phi_2=0.7$ (cf. ref. 19, for example), and exceeded, a distinct increase in the $T_{1,\min}$ and $T_{2_{\rm eff},\min}$ values could be observed, indicating the onset of anisotropic motion of subchains due to the formation of a tube. At the same time the T_2'-values in the high temperature region indicate a second process with a correlation time $\tau_{c_2}\gg\tau_{c_1}$.

Following a proposal recently given in the literature[20], the tube with its associated locally uniaxial constraints may be identified as a superficial analogue to the nematic cage in a liquid crystalline fluid. The motions in the dense polymer fluid are coarsely subdivided into two processes: the intrachain dynamics and whole-chain processes. A more or less isotropic reorientation of the chain segments is only affected by reorientation of the tube axis $\boldsymbol{h}$ by loss of the tube conformation due to reptation or other dynamic processes. So the correlation function of the n.m.r. relaxation may be assumed to consist of two contributions, given by

$$G(\tau)=G_1(\tau)G_2(\tau) \tag{11}$$

with

$$G_1(\tau)=\langle\Delta B^2\rangle\exp\left(-\frac{\tau}{\tau_{c_1}}\right)+\langle\Delta B_{\rm st}^2\rangle \tag{12}$$

$$G_2(\tau)=\exp\left(-\frac{\tau}{\tau_{c_2}}\right) \tag{13}$$

τ_{c_1} is connected with fast segmental reorientation, which may be of a cooperative kind. $\langle\Delta B_{\rm st}^2\rangle$ is caused by the non-zero residual projections of internuclear vectors $\boldsymbol{r}_{jk}$ into the direction of the vector $\boldsymbol{h}$ and τ_{c_2} is responsible for the time dependence of $\boldsymbol{h}$ and corresponds to all other (much slower) processes, leading to final loss of coherence.

With $\tau_{c_2}\rightarrow\infty$ the case of chemical crosslinked systems may be realized, characterized by temperature-independent T_2'-values in the high-temperature region[21,22], a distinct magic-angle-rotation (m.a.r.) effect[23] and a remarkable increase of $T_{2_{\rm eff},\min}$ dependence on crosslinking degree[24].

A m.a.r. effect can also be observed in entangled polymer solutions[25,26] where the rotation frequency ω_r necessary for line-narrowing is experimentally found to increase with molar mass $M>M_{c,\eta}$ (ref. 26). Considering the effectiveness of m.a.r., the inequality

$$\omega_r>\gamma\langle\Delta B_{\rm st}^2\rangle^{\frac{1}{2}} \tag{14}$$

must hold, i.e. the rotational frequency must be larger than the static contribution to the second moment (in frequency units), because the second condition, in some cases responsible for line-narrowing,

$$(\omega_r\tau_{c_2})^2\gg1 \tag{15}$$

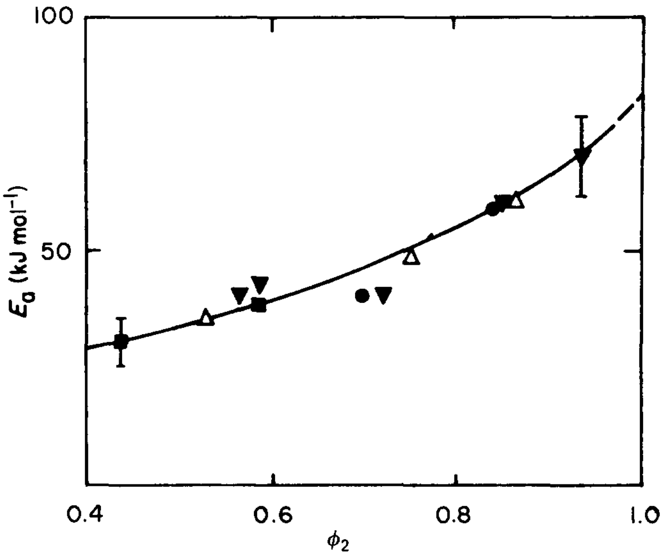

Figure 6 Apparent activation energies E_a of self-diffusion and of the correlation frequency τ_c^{-1} between 423 and 473 K *versus* polymer concentration ϕ_2. Symbols as in *Figure 3*

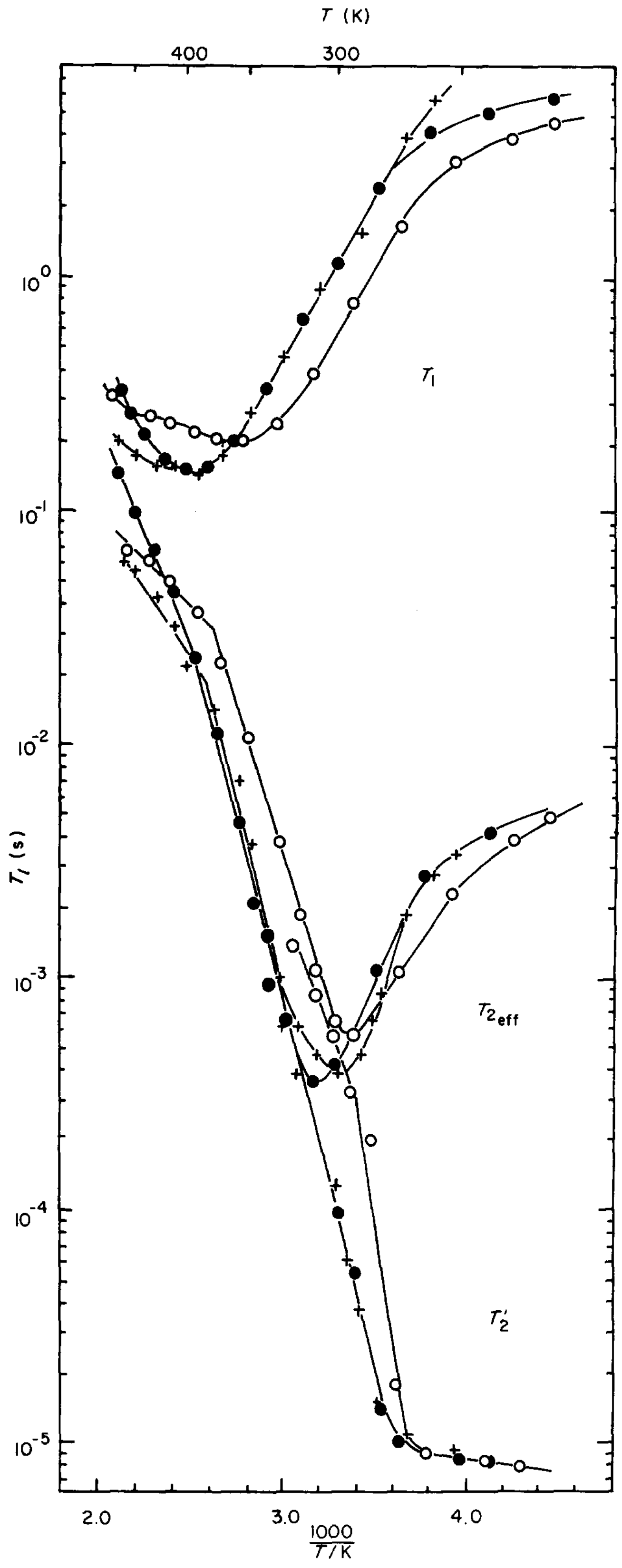

Figure 7 Temperature dependence of relaxation times T_1, $T_{2_{eff}}$ and T'_2 for polystyrene dissolved in C_6D_6 with a concentration of $\phi_2 = 0.7$ for the molar masses: (○) 6.1×10^5, (+) 1.1×10^5 and (●) 1.9×10^4

is not in agreement with experimental results[26]. One has to keep in mind that $T_d \approx \tau_{c_2}$ strongly increases with molar mass, and inequality (15) would imply a rotational frequency ω_r decreasing with increasing molar mass. The equation (14) allows one to estimate the reptation time T_d to be

$$T_d \approx \tau_{c_2} \geqslant (\gamma\langle\Delta B_{st}^2\rangle^{\frac{1}{2}})^{-1} \qquad (16)$$

since τ_{c_2} must be greater than the inverse of the static contribution of the second moment (in frequency units).

It is worth noting that from $T_{2_{eff,min}}$ values of the entangled systems, $\langle\Delta B_{st}^2\rangle$-values can be evaluated for the temperature of the minimum (about 313 K), which are of the same order as in gel-like systems (1.5–2.0×10^{-8} T^2)[9]. This means a relatively high anisotropy along the tube axis, and from equation (16) this leads to $T_d \geqslant 3 \times 10^{-4}$ s, in good agreement with expectation. From the self-diffusion data, T_d can be evaluated to be $\approx 1.3 \times 10^{-5}$ s at 473 K in a solution of PS 110000 with $\phi_2 = 0.7$. At the $T_{2_{eff,min}}$ temperature of about 313 K, T_d is then of the order of 10^{-1} s, from the temperature dependence of *Figure 2*.

However, one has to keep in mind that, in our case, the tube consists of about three subchains only, but owing to the slow molecular motions at this temperature (which is only about 60 K above the glass transition temperature[27]) it is well into the anisotropic regime[28]; T_d is much greater than the inverse of the static contribution of the second moment.

It should be a subject of further investigation whether the double minimum in T_1 also reported[17] is caused by polymer–polymer contacts, as discussed in ref. 17, or is connected with tube dynamics.

CONCLUSIONS

From n.m.r. relaxation investigations information about rotational motions of macromolecules or their subunits may be obtained, and with the n.m.r. pulsed-field-gradient technique the translational motions of the macromolecules may be studied. Distinct kinds of motion are expected in the different concentration regions. In the concentrated region investigated by us the self-diffusion coefficient is determined by two concentration-dependent quantities, the monomeric friction coefficient and the tube diameter. The monomeric friction coefficient strongly decreases with increasing polymer concentration in a fractional-free-volume-like curve and closely parallels the concentration dependence of the correlation frequencies of segmental motions determined by n.m.r. relaxation investigations. The proportionality $D \propto 1/M^2\phi_2\zeta_0$ could be confirmed. The observed concentration- and temperature-dependence of the self-diffusion coefficients, as well as n.m.r. relaxation data, indicate a cooperative segmental motional process which equally causes monomeric friction and n.m.r. relaxation. Entanglements are not explicitly seen in the self-diffusion experiments. The onset of tube formation when exceeding M_{c_η} manifests itself in n.m.r. relaxation where, owing to the anisotropic motion of subchains in the tube, static contributions of the second moment arise that are not averaged out by fast thermal motions of the segments.

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REFERENCES

1 Yamakawa, H. 'Modern theory of polymer solutions', Harper and Row, New York, 1971, ch. 6

2 de Gennes, P. G. in 'Scaling concepts in polymer physics', Cornell University Press, Ithaca, 1979

3 Heatley, F. and Wood, B. *Polymer* 1978, **19**, 1405; 1979, **20**, 1512

4 Fleischer, G. and Straube, E. *Polymer* 1985, **26**, 241

5 Wesson, J. A., Noh, I., Kitano, T. and Yu. H. *Macromolecules* 1984, **17**, 782

6 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701

7 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. 2* 1978, **74**, 1789, 1802, 1818

8 Edwards, S. F. and Evans, K. E. *J. Chem. Soc. Faraday Trans. 2* 1981, **77**, 1913

9 Geschke, D. and Pöschel, K. *Colloid Polym. Sci.* in press

10 Sundukov, V. I., Skirda, V. D. and Maklakov, A. I. *Polym. Bull.* 1985, **14**, 153

11 Michel, D. 'Grundlagen und Methoden der kernmagnetischen Resonanz', Akademie-Verlag, Berlin, 1981

12 Tanner, J. E. *J. Chem. Phys.* 1970, **52**, 2523

13 Fleischer, G., Geschke, D., Kärger, J. and Heink, W. *J. Magn. Res.* 1985, **65**, 429

14 Fujita, H. *Adv. Polym. Sci.* 1961, **3**, 1

15 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581

16 Vrentas, J. S., Duda, J. L. and Ni, L.-W. *Macromolecules* 1983, **16**, 261

17 Gotlib, Yu. Ya, Lifshitz, M. I. and Shevelev, V. A. *Vysokomol. Soed.* 1975, **A17**, 1360

18 Geschke, D., Kurze, W. and Brückner, H. *Faserforsch. Textiltech. Z. Polym.* 1978, **29**, 148

19 Graessley, W. W. *Polymer* 1980, **21**, 258

20 Samulski, E. T. *Polymer* 1985, **26**, 177

21 Gotlib, Yu. Ya., Lifshitz, M. I., Shevelev, V. A., Lishanskij, I. S. and Belanina, I. V. *Vysokomol. Soed.* 1976, **A18**, 2299

22 Geschke, D., Pöschel, K. and Ludwigs, K. *Polym. Bull.* 1981, **5**, 341

23 Doskočilova, D. and Schneider, B. *Pure Appl. Chem.* 1982, **54**, 575

24 Geschke, D., Pöschel, K., Doskočilova, D. and Schneider, B. *Acta Polym.* 1985, **36**, 645

25 Cohen-Addad, J. P., Domard, M. and Herz, J. *J. Chem. Phys.* 1978, **68**, 1194

26 Müller, R. and Zachmann, H. *Colloid Polym. Sci.* 1980, **258**, 753

27 Adachi, K., Fujihara, I. and Ishida, Y. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 2155

28 Cohen-Addad, J. P. *Polymer* 1985, **26**, 197