BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 1, pp. 137–141, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/95/$10.00+0.00

Toluene self-diffusion in solutions of linear and crosslinked polystyrene

Elena Ilyina*†‡ and Hans Sillescu†
† Institut für Physikalische Chemie, Universität Mainz, Welderweg 15, 55099 Mainz, Germany and ‡ Institute of Chemical Physics, Russian Academy of Science, 117977 Moscow, Russia
(Received 25 October 1993; revised 16 June 1994)

Toluene self-diffusion coefficients in solutions of linear and crosslinked polystyrene (PS) at concentrations up to 30 wt% polymer have been determined over the temperature range 143–230 K using the ^{1}H n.m.r. static gradient stimulated echo method. At similar polymer concentrations, the diffusion coefficient values of toluene were higher for mixtures with crosslinked PS than for solutions containing linear PS. On cooling and approaching the solution glass transition, the amplitude decays in diffusion and spin-relaxation measurements become non-exponential and are interpreted in terms of a two-component decomposition. The estimated fraction of the toluene motionally bound to polymer increases on temperature reduction and is less for mixtures containing crosslinked PS beads.

(Keywords: toluene; self-diffusion; polystyrene)

INTRODUCTION

The rotational and translational motion of small molecules in polymer solutions has been the subject of numerous n.m.r. investigations[1–7]. Although there has been significant progress in understanding concentration and temperature dependence of rotational correlation times and self-diffusion coefficients of solvent molecules, many questions remained unresolved. In order to perform a complete study on how solvent dynamics is affected by temperature and concentration, it is preferable to choose a system where the diffusion of small molecules is not complicated by bonding with a polymer and where the solvent and solute remain miscible over a wide range of experimental conditions. Polystyrene (PS)–toluene solutions are well suited for such a study and have been the focus of many investigations[8–12]. Consequently, many parameters needed for the analysis of experimental data are now available. This system, however, remains important for testing the theories on molecular motion in polymer solutions, and the appearance of new experimental data continues to contribute to their refinement.

PS and toluene form a mixed glass over the entire concentration range examined[11,12]. In a very detailed study[13] on the PS–toluene system from the analysis of deuteron relaxation data and spectral line shapes it was concluded that the glass transition in this system is determined by PS dynamics at polymer concentrations down to 40 wt% and by that of toluene at lower polymer concentrations, where the solvent mobility becomes rather complex. In this work we studied toluene self-diffusion at polymer concentrations below 40 wt% and at temperatures down to 143 K in order to extend the available diffusion data and to complement existing information on toluene reorientation obtained from ^{2}H relaxation measurements[13]. In addition, toluene self-diffusion coefficients were determined in mixtures of crosslinked PS beads, under similar conditions, to examine the effect of polymer crosslinking on the solvent translational mobility at low polymer concentration.

EXPERIMENTAL

Samples. Protonated toluene and fully deuterated polymers were used for the diffusion and relaxation experiments. The toluene was purchased from FA Merck, Darmstadt and was used as received, while linear PS-d_8 ($M_w = 97\,000$, $M_w/M_n = 1.07$) was provided by the Max-Plank-Institute for Polymer Research, Mainz. The procedure for preparing crosslinked PS-d_8 beads has been described in a previous publication[14]. The polymers were crosslinked with disoprophenylbenzol in such a way that 10 or 20 monomers, respectively, existed between crosslinks. The radii of the beads swollen in toluene were 16.7 and 21.2 nm, respectively, as determined by dynamic light scattering, while the radii of the dry beads were 13.1 and 13.6 nm. Consequently, the degree of swelling for the beads with the lower crosslink density was higher than that of the tightly crosslinked beads approximately by a factor of two. The gels and solutions looked uniformly dissolved.

Self-diffusion. The self-diffusion coefficients, *D*, of toluene have been measured on a home-built high power n.m.r. spectrometer using ^{1}H n.m.r. three-pulse stimulated echo method in the (static) stray field gradient[15] of the cryomagnet. The advantages and disadvantages of the static gradient stimulated echo (SGSE) method *versus* the pulsed gradient spin echo (PGSE) technique and a description of the spectrometer have been presented

---

* To whom correspondence should be addressed at: UMHC, Box 609, 420 Delaware St. SE, Minneapolis, MN 55455, USA

earlier[16]. In this work we performed measurements with a 17 T m^{-1} gradient at a 40 MHz ^{1}H frequency and a 45 T m^{-1} gradient at 90 MHz. The error of the measurements did not exceed 10%.

In a SGSE experiment, characterized by the sequence $(90°)_x-\tau-(90°)_x-t-(90°)_x-\tau-$'echo', the height of the echo amplitude, $A(\tau,t)$, for $\tau \ll t$, is given by[15]:

$$A(\tau,t)=A_0 e^{-2\tau/T_2} e^{-t/T_1} e^{-\gamma^2 g^2 D\tau^2 t} \qquad (1)$$

where γ is the gyromagnetic ratio, g is the magnetic field gradient, and T_1 and T_2 are the spin-lattice and spin-spin relaxation times, respectively. T_1 decay is usually small during the diffusion measurement and can be neglected. In our case, D was obtained by varying τ at constant t. At temperatures above 160 K, $A(\tau,t)$ values were single-exponential when plotted as a function of τ^2 (*Figure 1*). This indicated that diffusion dominated the decay of the echo amplitude, and that the toluene exchange between different possible states of motion was faster than a few milliseconds. At lower temperatures in the highly viscous regime, T_2 started to dominate the decay of $A(\tau,t)$, and since the exponent in the T_2-dependent factor [equation (1)] depends only linearly on τ, a strong upward concavity is clearly seen in the curves $\log A(\tau,t)$ *versus* τ^2.

At temperatures below 170 K, T_2 was determined independently by using the Hahn echo method[17]. The echo amplitude $A(\tau)$ in this experiment [e.g. $(90°)_x-\tau-(180°)_x-\tau-$'echo'] is affected by both the relaxation and diffusion processes, although through a different relationship, namely:

$$A(\tau)=A_0 e^{-2\tau/T_2} e^{-(2/3)\gamma^2 g^2 D\tau^3} \qquad (2)$$

In the highly viscous regime, however, D was small (note that $\tau \ll t = 100$ ms), therefore T_2 can be considered to be the only factor dominating the Hahn echo amplitude attenuation. The amplitude attenuation curves corresponding to equations (1) and (2), respectively, for both kinds of echo experiment are shown in *Figure 2* as functions of τ. This figure clearly illustrates that even at 143 K the SGSE method is sensitive to the translational diffusion of toluene in 30% PS solution: the attenuation of the echo amplitude occurs faster in the three-pulse experiment. In this viscous regime, however, the accuracy of the diffusion measurement is considerably diminished due to the strong dependence of $A(\tau,t)$ on T_2 which became non-exponential at temperatures below 170 K. The analysis was complicated furthermore since the stimulated echo decays could not be fitted with single values of D and T_2 (*Figure 2*). We assigned the longer relaxing part of the curves to 'fast' liquid-like toluene and the short time behaviour to 'slow' toluene surrounding the polymer as suggested in prior investigations on solvent relaxation and diffusion within polymer solutions[10]. The diffusion coefficients of the 'slow' toluene were assumed to be negligibly small in comparison to those of the 'fast' toluene. Then without taking T_1 into account, the expression for $A(\tau,t)$ became:

$$A(\tau,t)=A_{0\mathrm{fast}} e^{-2\tau/T_{2\mathrm{fast}}} e^{-\gamma^2 g^2 \tau^2 t D_{\mathrm{fast}}} + A_{0\mathrm{slow}} e^{-2\tau/T_{2\mathrm{slow}}} \qquad (3)$$

This two-state model obviously oversimplifies the real dynamics of toluene. It was found[13] that in the glass transition regime the reorientational motion of toluene in PS solutions can be characterized by a wide distribution of rotational correlation times corresponding to a variety of possible solvent environments. The question of the appropriate choice of T_2 for fitting $A(\tau,t)$ in the viscous regime became very complicated and should be the subject of further investigations. D values estimated from equation (3) by using T_2 values obtained from a biexponential fitting of the entire Hahn echo decays $A(\tau)$ were not reasonable, e.g. for the stimulated echo decay shown in *Figure 2*, D and T_2 values obtained as described above were 9.5×10^{-13} m^2 s^{-1} and 152 μs, respectively, while D for the bulk toluene at 143 K is $\sim 6 \times 10^{-13}$ m^2 s^{-1}. For evaluating D in the highly viscous regime we used as $T_{2\mathrm{fast}}$ in equation (3) the T_2 values determined from the Hahn curves within the range of τ corresponding to the longer decaying parts of $A(\tau,t)$ as shown in *Figure 2*. The fitting parameters of equation (3) for this temperature and $t = 100$ ms were: $A_{0\mathrm{slow}} = 0.85$, $A_{0\mathrm{fast}} = 0.15$, $T_{2\mathrm{slow}} = 31$ μs and the determined $T_{2\mathrm{fast}} = 122$ μs yielding $D_{\mathrm{fast}} = 3.7 \times 10^{-13}$ m^2 s^{-1}. Diffusion coefficients obtained in this way for two different gradient values were in close agreement for temperatures below 170 K.

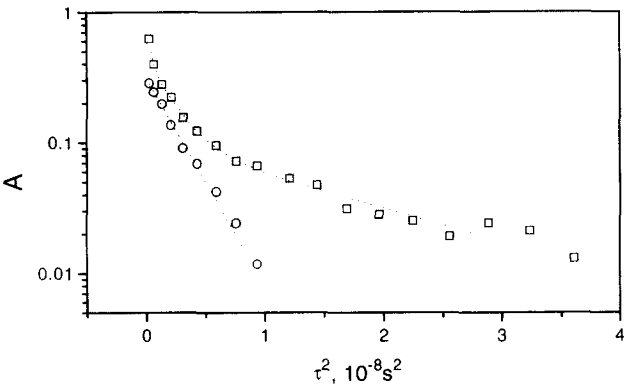

Figure 1 Stimulated echo amplitudes $A(\tau,t)$ at $t = 100$ ms for toluene in a 30 wt% linear PS–toluene solution at two different temperatures: $T = 181$ K (○) and $T = 143$ K (□). A value of 3.2×10^{-12} m^2 s^{-1} is estimated for D by linear regression for the higher temperature while the fitting parameters for the lower temperature curve are discussed in the text

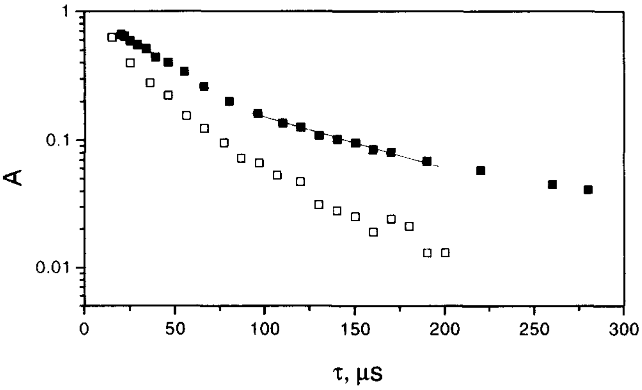

Figure 2 Stimulated echo $A(\tau,t)$ (□) at $t = 100$ ms and Hahn echo $A(\tau)$ (■) as a function of τ at 143 K in a 30 wt% linear PS–toluene solution. The solid line designates the part of the curve used for determining $T_{2\mathrm{fast}}$ as described in the text

We have to note here that at these temperatures and especially at 143 K T_2 became too short to allow the diffusion coefficients to be measured precisely by using SGSE. Thus, a temperature of ~ 150 K actually represents the lower temperature limit of the applicability of the method in the systems studied. The lowest limit on T_2 in the PGSE experiment is ~ 2 ms, e.g. in the previous

PGSE PS–toluene diffusion study[10] toluene self-diffusion could not be determined at temperatures lower than 240 K for similar polymer concentrations due to the limiting effect of T_2. Using SGSE in this study made it possible to determine toluene D at temperatures down to 160 K and to evaluate them in the proximity of the mixture glass transition, where T_2 values were $\ll 1$ ms.

The ratio of fraction amplitudes in the biexponential fits were not as sensitive to T_2 as the values of the diffusion coefficients were. This enabled us to evaluate the fast and slow toluene fractions within our solutions as will be discussed below.

RESULTS AND DISCUSSION

In *Figure 3* the self-diffusion coefficients of toluene in solutions of linear PS are presented as a function of temperature and polymer concentration. The dependence is not unusual: D increases as temperature increases and decreases with the addition of polymer. The diffusion data for pure toluene and those for the PS–toluene solutions are in good agreement with the previously reported data[10,18]. In contrast to the diffusion temperature dependence at temperatures above 230 K, D does not exhibit Arrhenius behaviour over the whole temperature range studied; this means that the apparent activation energy of the diffusion process is a function of concentration and temperature. The temperature dependence of D is similar to that of toluene T_2[11,13], where it was found from ^{2}H relaxation measurements and ^{2}H solid echo spectra, that near the PS–toluene glass transition, toluene existed in two distinct motional environments. The motion of the slow 'solid' component was linked to that of the PS chains at temperatures below a temperature, T_{SE}, where a solid echo became observable. Motionally free toluene was denoted as a 'liquid' component. On lowering the temperature, the fraction of 'solid' toluene increased at the expense of the 'liquid' fraction until the entire mixture became a solid glass. It was found that complete solidification of toluene in toluene-rich systems occurred at temperatures below the static glass transition temperature determined by dielectric relaxation and thermal methods[12]. At approximately the same temperature values, a cross-over was observed in the T_2 temperature dependence. It manifested itself in decreasing of the slope of the curves below the cross-over temperature, T_{CO}, and occurred at higher temperatures for higher concentrated samples. T_{CO} approximately coincided with T_{SE}. This variation in the T_2 temperature dependence was presumed to be caused by a qualitative change in molecular mobility of the components in the system in the vicinity of the glass transition.

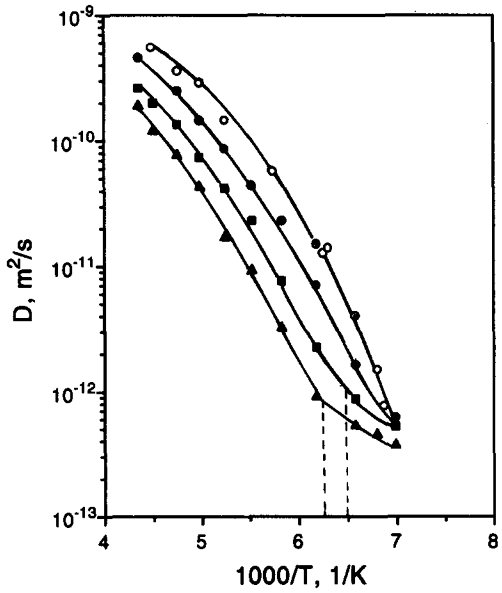

Figure 3 Temperature dependence of toluene diffusion coefficients in solutions of linear PS at different PS concentrations, c (wt%): 0 (○ and ⊙); 10 (●); 20 (■); 30 (▲). The open circles (○) are the experimental data obtained by Krueger and Weiss[18] while the dotted circles (⊙) show data obtained in this work. The broken lines signify the cross-over temperatures

A detailed description of the toluene ^{2}H relaxation data is provided here since the diffusional behaviour investigated in this work was very similar to that of the reorientational motion. The changes of slopes were also apparent in the D temperature dependence. Such behaviour of the $D(T)$ of solvent molecules in the vicinity of the glass transition has been observed for many solvent–polymer systems[19–21] and has been predicted theoretically, e.g. by the free volume theory[22]. The values of the diffusional cross-over temperatures were about 10 degrees lower than those determined from rotational motion and coincided with the temperatures where the echo attenuation became non-exponential. In our opinion, the appearance of non-exponentiality and the existence of both the solid echo and the motionally narrowed Lorentzian line in ^{2}H n.m.r. spectra[13] may be explained by the slowing down of the exchange rate between the 'slow' and 'fast' motional states of the solvent molecules at temperatures below T_{CO}. At these temperatures D and T_2 of the 'fast' liquid toluene only have been measured in our experiments. At higher temperatures, a superposition of 'fast' and 'slow' motions determines these quantities and can be described by the well known relationship for fast exchange in a two-state model[23]:

$$(T_2)^{-1} = x(T_2)^{-1}_{\mathrm{fast}} + (1-x)(T_2)^{-1}_{\mathrm{slow}}; \quad D = xD_{\mathrm{fast}} + (1-x)D_{\mathrm{slow}} \tag{4}$$

where x is the fraction of toluene molecules in the 'fast' state. Since we can expect that the mobility of 'fast' toluene has a much weaker temperature dependence than that of 'slow' toluene, the observed change of slope seen in *Figure 3* should be caused by the fact that predominantly the diffusion of 'fast' molecules is seen at $T < T_{CO}$. It should be mentioned that a Θ temperature of ~ 160 K has been estimated for PS solutions in toluene from intrinsic viscosity data determined at higher temperatures[24,25]. Whether the 'fast' and 'slow' toluene states can be related to the existence of the dilute and concentrated phases in the solutions at $T < T_\Theta$ should be investigated in a future study. Preliminary light scattering measurements indicate an increased turbidity at low temperatures.

For evaluating the 'fast' toluene fraction we used equation (3) and estimated x as:

$$x = A_{\mathrm{fast}}/(A_{\mathrm{fast}} + A_{\mathrm{slow}}) \tag{5}$$

It should be noted that x values did not depend as strongly on $T_{2\mathrm{fast}}$ as the diffusion coefficients did, e.g. at 143 K, the difference in x values did not exceed 10% after a variation in $T_{2\mathrm{fast}}$ of 25 μs. The T_2 of 'slow' toluene was hardly temperature dependent which was also in harmony with the previous $^2H-T_2$ study[11,13]. In *Figure 4* only the x values obtained from biexponential fits to equation (3) for 20 and 30% linear PS are shown since the measurements of the 10% sample were not sensitive enough to resolve the fraction of 'slow' toluene. Our results are in good agreement with those of the previous ^2H n.m.r. study.

The toluene diffusion coefficients in solutions of crosslinked PS beads were less influenced by the polymer than in solutions of linear PS. This is apparent by comparing *Figures 3* and *5* or from *Figure 6* where solutions of the same concentrations (20wt%) are compared for linear and crosslinked PS. This can be explained in the framework of the two-state model by assuming that the fraction of 'fast' toluene is larger in the crosslinked systems since a smaller number of 'sites' close to PS chains is accessible for toluene molecules in the PS network. This interpretation is in harmony with the observation that the echo amplitude decays (in D and T_2 experiments) became non-exponential at lower temperatures in the crosslinked systems and the deviations from exponential functions were less pronounced. Thus, no evident cross-over can be seen in *Figure 5* and the estimated fraction x of 'fast' toluene presented in *Figure 4* is the largest for the crosslinked system. Finally, *Figure 6* demonstrates that the highest D values were measured for the system composed of beads with the highest crosslink density. Thus, we can conclude that the space accessible to the fast component is the factor influencing toluene diffusion most in the samples under study.

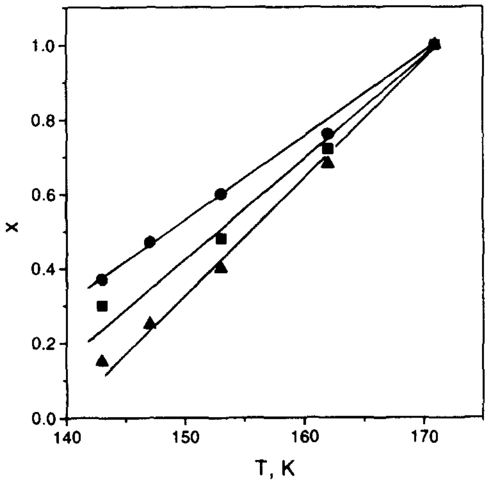

Figure 4 Calculated fractions of fast toluene in the solution of linear PS with $c=30$ wt% (▲) and $c=20$ wt% (■) and in the mixtures of PS beads crosslinked 1:10 with $c=20$ wt% (●)

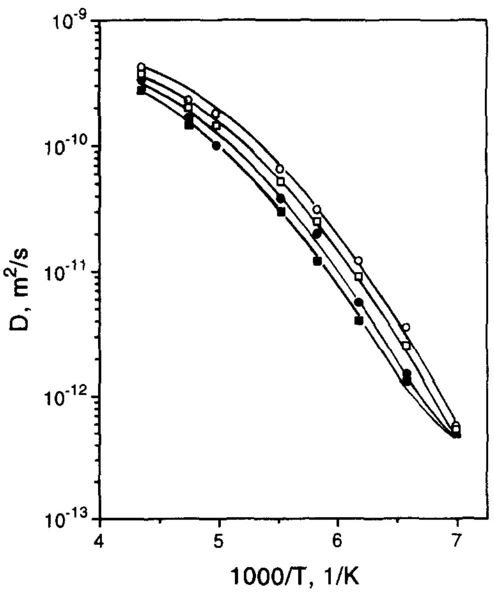

Figure 5 Temperature dependence of the toluene diffusion coefficients in mixtures of PS beads having 10 (○, ●) and 20 (□, ■) monomers between crosslinks. Open symbols refer to $c=10$ wt% while the full symbols indicate $c=20$ wt% samples

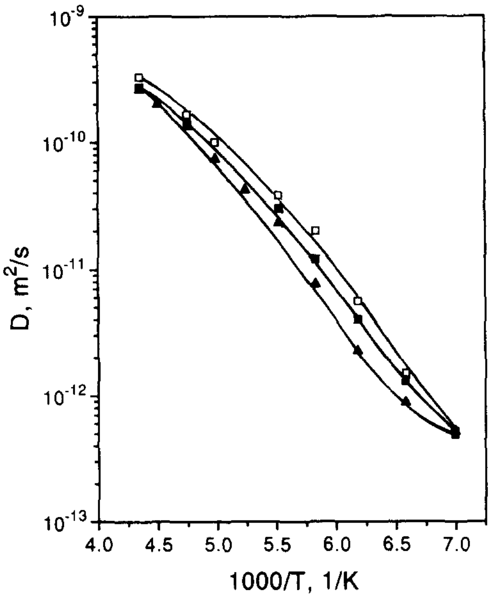

Figure 6 Toluene D values as a function of temperature in 20wt% polymer samples for linear (▲), crosslinked 1:20 (■) and crosslinked 1:10 (□) PS

The investigation of toluene self-diffusion in loosely crosslinked PS beads with large radii (compared to the molecular displacement during the diffusion time) and at high polymer concentrations[26] indicated that the diffusion rate was not significantly affected by the presence of crosslinks. It was mainly dependent on the amount of solvent in the bead and was in close agreement with the solvent diffusion rate in non-crosslinked systems at similar concentrations. In our samples with the highest crosslinking of 10 monomers between crosslinks (I), the volume fraction of the swollen beads was below the random close packing of spheres, whereas in the sample with 20 wt% beads (II) and having 20 monomers between crosslinks the swollen beads were densely packed. The volume of swollen beads of type II and the degree of their swelling were approximately twice as large as those of the beads of type I. Thus, the amount of toluene inside the swollen beads and the volume occupied for the 20 wt% sample of type I and for the 10% sample of type II were similar. The toluene D values are still larger for diffusion among the beads of type II at lower concentration (*Figure 5*) presumably due to the effect of decreased tortuosity (i.e. shorter diffusion pathway) among the smaller amount of larger beads[27].

As for the case of linear PS, the temperature dependence of toluene self-diffusion coefficients for solutions containing crosslinked PS did not exhibit Arrhenius behaviour and thus could not be characterized by a single activation energy.

CONCLUSIONS

The toluene self-diffusion coefficients in solutions of linear and crosslinked PS at concentrations up to 30 wt% polymer were determined over the temperature range 143–230 K. The temperature dependence of D did not follow Arrhenius behaviour and was similar to that of toluene ^{2}H spin-spin relaxation times[13]. In the solvent-rich regime, toluene self-diffusion in solutions of linear and crosslinked PS appeared to be dictated by the space accessible for the free diffusion of the solvent. Consequently, the lowest D values were measured for the system containing uncrosslinked PS. Upon cooling and approaching the solution glass temperature, the amplitude decays in T_2 and D measurements became non-exponential and were interpreted in terms of a two-component decomposition. The estimated fraction of 'slow' toluene motionally bound to polymer increased upon temperature reduction and was less for the mixtures comprised of crosslinked PS beads.

ACKNOWLEDGEMENTS

A. Doerk and V. Frenz are gratefully acknowledged for the preparation and characterization of crosslinked PS beads. We thank F. Fujara for his assistance with the diffusion experiments and J. Zielinsky for helpful discussions. One of the authors (E.I.) also wishes to thank the Alexander-von-Humboldt Foundation for making it possible for her to visit Germany and to participate in this research.

REFERENCES

1 Meerwall, E. D. *Adv. Polym. Sci.* 1983, **54**, 1

2 Maklakov, A. I., Skirda, V. D. and Fatkulin, N. F. 'Self-diffusion in Polymer Solutions and Melts', Kazan State University, Kazan, 1987

3 *R. Soc. Chem. Spec. Period Rep.* 1976, **5**, 316

4 *R. Soc. Chem. Spec. Period Rep.* 1981, **11**, 228

5 Sillescu, H. and Brussau, R. G. *Chem. Phys. Lett.* 1970, **5**, 535

6 Moseley, M. E. and Stilbs, P. *Polymer* 1978, **19**, 1133

7 Ilyina, E., Daragan, V. and Prisment, A. E. *Macromolecules* 1993, **26**, 3319

8 Maklakov, A. I. *Vysokomol. Soedin. Z.* 1983, **A25**, 1631

9 Pickup, S. and Blum, F. D. *Macromolecules* 1989, **22**, 3961

10 Nagara, B., O'Connor, R. D. and Blum, F. D. *J. Phys. Chem.* 1992, **96**, 6417

11 Roessler, E., Sillescu, H. and Spiess, H. W. *Polymer* 1985, **26**, 203

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

13 Roessler, E. *Ph.D Dissertation* University of Mainz, 1984

14 Antonietti, M., Bremser, W. and Schmidt, M. *Macromolecules* 1990, **23**, 3796

15 Kimmich, R., Unrath, W., Schnurr, G. and Rommel, E. *J. Magn. Res.* 1991, **91**, 136

16 Fujara, F., Geil, B., Sillescu, H. and Fleischer, G. *Z. Phys. B.* 1992, **88**, 195

17 Farrar, T. C. and Becker, E. D. 'Pulse and Fourier Transform NMR', Academic Press, London, 1971

18 Krueger, G. J. and Weiss, R. Z. *Naturforsch.* 1970, **25a**, 777

19 Stannett, V. T. and Williams, J. L. *J. Polym. Sci. C* 1965, **10**, 45

20 Brown, W. and Chitumbo, K. J. *Faraday Trans.* 1975, **71**, 12

21 Hadj Romdhane, I. and Danner, R. P. *AIChE J.* 1993, **39**, 625

22 Vrentas, J. S. and Duda, J. L. *J. Appl. Polym. Sci.* 1978, **22**, 2325

23 Zimmermann, J. R. and Brittin, W. E. *J. Phys. Chem.* 1957, **61**, 2325

24 Fox, T. G. and Flory, P. J. *J. Am. Chem. Soc.* 1951, **73**, 1915

25 Tau, H.-M., Moet, A., Hiltner, A. and Baer, E. *Macromolecules* 1983, **28**, 16

26 Pickup, S., Blum, F. D. Ford, W. T. and Periyasamy, M. *J. Am. Chem. Soc.* 1986, **108**, 3987

27 Haus, J. W. and Kehr, K. W. *Phys. Rep.* 1987, **150**, 265