Polymer Bulletin 43, 261–267 (1999)

Polymer Bulletin
© Springer-Verlag 1999

Static and dynamic light scattering from polystyrene/cyclohexane/toluene solutions

Amina Negadi[1,3], Michel Duval[2,*], Mustapha Benmouna[1,3]

[1] Max-Planck-Institut für Polymerforschung, Postfach 3348, D-55021 Mainz, Germany
[2] Institut Charles Sadron CRM, 6 Rue Boussingault, F-67083 Strasbourg Cedex, France
[3] Institut of Sciences, Physics Department, University of Tlemcen, Tlemcen BP119, Algeria

Received: 28 May 1999/Accepted: 8 September 1999

Summary
Static and dynamic light scattering data from polystyrene in cyclohexane and toluene mixed solvent are reported. It is found from the Zimm plot analysis of the static data that if the subtraction of solvent signal is made properly then, the results are consistent with those in toluene indicating a preferential adsorption of the good solvent. Contin analysis of the dynamic data yields two modes unlike the dynamics of polystyrene in single solvent solutions which exhibit a single mode at all polymer concentrations covered here. A possible interpretation of the fast and slow modes is given.
Keywords : Mixed Solvent; Dilute Polymer Solution; Preferential Adsorption; Static and Dynamic Light Scattering; Relaxation Modes.

Introduction

Unlike thermodynamic and structural properties (1-5), dynamic properties of polymers in mixed solvents were not given a sufficient attention and only few studies were reported using quasi-elastic light scattering (QELS). Very recently To and Choi (6) investigated the chain shrinking near the critical temperature of poly-acrylic acid in water and 2.6-Lutidine. They observed two modes and analysed their relaxation rates to see the effect of the solvent criticality condition. Combining QELS and thermal field flow fractionation Van Asten et al. (7) investigated the thermal diffusion coefficient of PS in THF/dioxane and in THF/cyclohexane and observed that THF was strongly adsorbed on the polymer. Solomon and Muller (8) investigated mixtures of PS, its oligomers and dioctyl-phtalate (DOP) with various methods including QELS with the aim of having access to the solvent-polymer interaction. Clearly a need for more efforts to elucidate the dynamic properties of polymers in mixed solvents is still strong and the present work is a contribution along these lines. Since the main purpose here is to focus on the dynamics, we give the relevent information describing the static behaviour without further details for shortness. It is beyond the scope of this note to review the extended work available in the literature on the static and quasielastic light scattering from binary PS/toluene and PS/cyclohexane systems (9-13).

Experimental

Materials and sample preparation

Polystyrene sample PS572 was prepared by anionic polymerisation under inert atmosphere according to a process described elsewhere (14). The weight-average molar mass (M_w=650000) and the polydispersity index (1.12) of the sample were determined in tetrahydrofuran (THF) by Gel

Dedicated to the memory of Claude Strazielle who left us two years ago.
* Corresponding author

Permeation Chromatography (GPC). Reagent-grade solvents were used throughout. The solutions were allowed to mix thoroughly over the course of 24 hours assisted by gentle agitation at 38°C. They were clarified by centrifugation at 18000rpm during 2 hours and then pipetted into the scattering cells.

Equipment and data analysis

The density and viscometric measurements were made at 36°C on a DMA60 densitometer (PAAR, Austria) and a Viscologic TI-1 viscometer (Sematech, France) respectively. The refractive index and refractive index increment measurements were made at 36°C and 633nm on a Abbe refractometer and on a Brice-Phoenix differential refractometer (USA) respectively.

Static light scattering (SLS) measurements were made at 36°C using a FICA 50 (FICA, France) apparatus. The light source was a 3 mW He-Ne laser (λ=633nm). The Zimm plot method was used to determine the weight-average molar mass M_w, the radius of gyration R_G and the osmotic second virial coefficient A_2 using the classical equation :

$$\frac{KC}{\Delta R_\theta} = \frac{1}{M_W}\left\{1 + \frac{q^2 R_G^2}{3}\right\} + 2A_2C \qquad (1)$$

where ΔR_θ is the excess Rayleigh ratio and q the magnitude of the scattering wavevector. For vertically polarised incident light the optical constant K is given by :

$$K = \frac{4\pi^2 n^2 (dn/dC)^2}{\lambda_0^4 N_a} \qquad (2)$$

where n is the refractive index of the solvent, λ_0 the vacuum wavelength of incident light and N_a the Avogadro's constant.

QELS experiments were performed in the homodyne mode at 36°C using a home-built photon correlation spectrometer (15) associated with a digital correlator (ALV3000; Germany). The experimental autocorrelation functions of the scattered light $C(q,\tau)$ were analysed using the CONTIN software (16) following the classical expression :

$$C(q,\tau) = C(q,0)\int \exp(-\Gamma\tau) G(\Gamma) d\Gamma \qquad (3)$$

where τ is the time and the characteristic frequency Γ is given by :

$$\Gamma(q) = Dq^2 \qquad (4)$$

D is the translational diffusion coefficient of the particles. The concentration range covered in the present experiment is between $1X10^{-4}$ and $7X10^{-4}$ g.cm^{-3}. The highest concentration is roughly 6 times lower than de Gennes (17) overlap concentration C^*. In this dilute range, the diffusion coefficient depends linearly on the concentration as :

$$D = D_0(1 + k_d C) \qquad (5)$$

In this expression k_d is the dynamical virial coefficient or the Huggins coefficient. The hydrodynamical radius R_H of the scattering particles is related to D_0 through the Stokes-Einstein relation for a sphere (9) :

$$R_H = \frac{k_B T}{6\pi\eta_0 D_0} \qquad (6)$$

where k_B is the Boltzmann constant and η_0 the viscosity of the solvent at the absolute temperature T.

Solvent	dn/dC ($cm^3.g^{-1}$)	M_w ($g.mole^{-1}$)	A_2 X 10^4 ($cm^3.mole.g^{-2}$)	R_G (Å)	k_d ($cm^3.g^{-1}$)	R_H (Å)
T	0.1096	672000	2.68	384	75.63	241
C	0.1611	732000	0.85	319	-93.39	181
T/C	0.1353	922000	2.16	475	85.03	240

Table 1 Experimental values of the refractive index increment (dn/dC), the weight average molar mass M_w, the second virial coefficient A_2, the radius of gyration R_G, the dynamical virial coefficient k_d and the hydrodynamical radius R_H of PS572 in toluene (T), cyclohexane (C) and toluene/cyclohexane(50/50) (T/C) at 36°C.

Results and discussion

The measurements reported here are made at 36°C(±0.05) on a 50/50 (volume ratio) solvent mixture of toluene/cyclohexane. A more detailed investigation in terms of temperature and solvent composition will be the subject of a future work. Table 1 collects the results for the refractive index increments dn/dC, the molar masses M_w, the second virial coefficients A_2, the radii of gyration R_G, the hydrodynamic radii R_H, the Huggins (9) coefficients k_d.

Static light scattering and Zimm plot analysis

Static light scattering and Zimm plot analysis were performed systematically on PS solutions in toluene, cyclohexane separately and their mixture. The Rayleigh-ratio used for benzene as reference was $R_{90°}=12.55X10^{-6}$ cm^{-1}. The Zimm plot analysis yields the results given in Table 1. It shows that the molar mass of PS in the solvent mixture is overestimated by 30%. This high value is attributed to the procedure of extracting the background signal due to the solvent mixture. Indeed extrapolation to zero polymer concentration yields a much higher signal than in the case of a pure solvent mixture (ratio 1.37 and 1.26 with respect to toluene and cyclohexane). If the extrapolation to zero concentration is adopted to estimate the background signal due to the solvent, one obtains the same molar mass and second virial coefficient as in the toluene solution. Note that the molar mass and second virial coefficient are sensitive to the procedure of subtracting the solvent signal while the radius of gyration is not since it is obtained from the slope of I(q) versus q^2. Since the Zimm plots do not give further informations, they are not displayed here for shortness. The above observations are also supported by the dynamic data discussed below.

Quasi-elastic light scattering

Figure 1 gives the normalised correlation function of PS572 in toluene and in the solvent mixture toluene/cyclohexane obtained under similar conditions. The insert shows the CONTIN analysis of the same experimental results. A single mode is observed in toluene while in the binary solvent mixture a fast mode appears. The correlation function of PS/cyclohexane also shows a single mode under the same conditions which is consistent with the results of Ritzl et al. (12). Solvent fluctuations become stronger and the amplitude of the fast mode increases with the solvent concentration while that of the slow mode decreases. The extrapolation to zero polymer concentration yields a high signal of the solvent mixture. This result is consistent with the observation made earlier suggesting to subtract the zero concentration limit in the Zimm plot analysis.

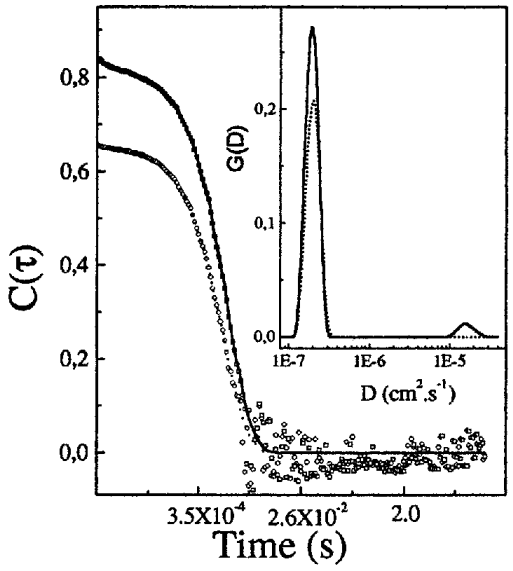

Figure 1 Correlation function of PS572 in toluene (O; C=5.34X10^{-4} g.cm^{-3}) and in toluene/cyclohexane (□; C=5.25X10^{-4} g.cm^{-3}) at T=36°C; Scattering angle θ=20°. Inset shows the CONTIN analysis of the experimental curves in toluene (-----) and in toluene/cyclohexane (——) where G(D) is the distribution function of the diffusion coefficients.

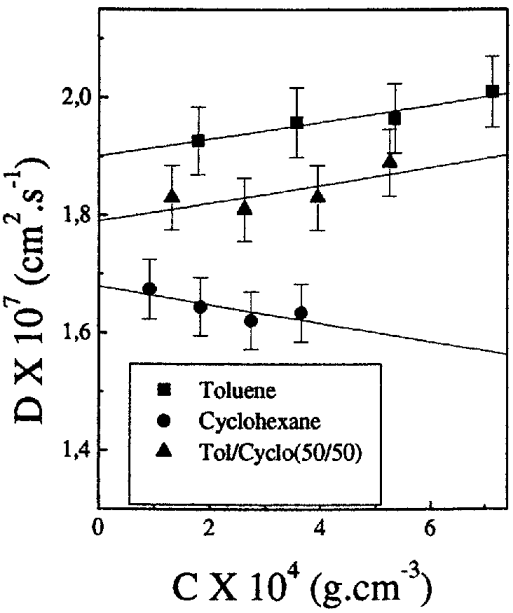

Figure 2 Variation of the diffusion coefficient of PS572 as a function of the polymer concentration at 36°C. The straight lines are the linear fits to the experimental points. The diffusion coefficient in the toluene/cyclohexane(50/50) solvent is the one which is associated with the slower mode.

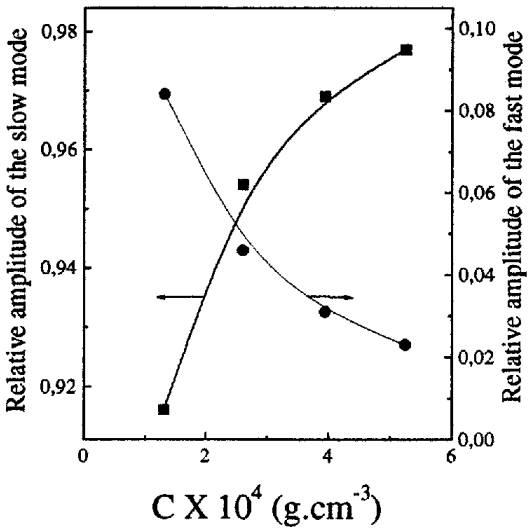

Figure 3 Variation of the relative amplitude of the fast (●) and slow (■) mode as a function of the PS572 concentration in toluene/cyclohexane(50/50) at T=36°C and θ=20°. The lines are just guide for the eyes.

a) QELS data of PS/toluene and PS/cyclohexane solutions

These QELS data show a single exponential decay under all conditions of the experiments. The relaxation frequency is proportional to q^2 in the whole q range covered here indicating a diffusive process. Figure 2 shows the variation of the diffusion coefficient as a function of the polymer concentration. In cyclohexane one observes a linear decrease according to equation(5). Kok and Rudin (18) suggested the following empirical law for PS/cyclohexane solution at 35°C :

$$D_0 = 1.3X10^{-4}\ M^{-0.497} \qquad (cm^2.s^{-1}) \qquad (7)$$

Introducing $M = 7.32X10^5$ yields $D_0 = 1.58X10^{-7}\ cm^2.s^{-1}$ which is only slightly lower than the result obtained here (i.e. $D_0 = 1.68X10^{-7}\ cm^2.s^{-1}$). According to equation (6) one obtains R_H = 181 Å and a ratio R_H/R_G=0.567 roughly 15% lower than the theoretical prediction (19) $3/(87\pi^{1/2})$ = 0.664.

The Huggins coefficient describes both static and hydrodynamic interactions according to the known result :

$$K_d = 2A_2M -= - k_f \qquad (8)$$

where k_f is the hydrodynamic contribution. In cyclohexane since A_2 is almost zero one expects a negative coefficient k_d=-k_f and D decreases when the polymer concentration increases as observed experimentally. For the toluene solution the Huggins coefficient is positive and relatively high.

Likewise the hydrodynamic radius reflects good solvent conditions. Unlike the cyclohexane case one finds a ratio R_H/R_G = 0.628 higher than the theoretical prediction (19) R_H/R_G = 0.537.

b) QELS data of PS/(toluene-cyclohexane)(50/50) solutions

The QELS data of this mixture reveal two diffusive modes with relaxation frequencies proportional to q^2. The diffusion coefficients are represented in Figure 2 as a function of the polymer concentration and the results satisfy the linear relationships :

$$D_{slow} = D_{0P}\left(1 + k_{dp}\,C\right) \qquad D_{fast} = D_{0f}\left(1 + k_{df}\,C\right) \qquad (9)$$

The slow mode is reminiscent of the polymer diffusion. The infinite dilute limit reflects the single chain diffusion coefficient :

$$D_{0P} = 1.79X10^{-7}\ (cm^2.s^{-1}) \qquad (10)$$

The variation with the polymer concentration gives a large positive Huggins coefficient k_{dp}=85.03 and indicates good solvent conditions where excluded volume interaction is overwhelmingly large as compared to hydrodynamic backflow effects. The hydrodynamic radius deduced from D_{0P} and equation (6) gives a result consistent with the toluene solvent, namely R_H = 240 Å. The fast mode is characteristic of solvent fluctuations and yields a diffusion coefficient two orders of magnitude higher than the slow mode :

$$D_{0f} = 2.42X10^{-5}\ (cm^2.s^{-1}) \qquad (11)$$

If one wants to attach a hydrodynamic size to this mode, one would obtain the size of a statistical segment consistent with the diffusion of solvent molecules. This mode is hardly sensitive to the polymer concentration with an extremely low Huggins coefficient $k_{df} = 208X10^{-4}$. The variations of the diffusion coefficients and the relative amplitudes of the fast and slow modes are given in Figures 2 and 3 respectively. At a relatively high polymer concentration the solvent mode decays very fast

and the scattering is almost entirely due to concentration fluctuations. If the polymer concentration decreases from $5X10^{-4}$ g.cm^{-3} to $1X10^{-4}$ g.cm^{-3} the amplitude of the fast mode increases by a factor 8. Both diffusion coefficient and relative amplitude of the slow mode increase with the polymer concentration.

Conclusion

This paper deals with the properties of PS in cyclohexane and toluene mixed solvent obtained by elastic and quasielastic light scattering. For completeness, data taken under similar conditions on PS in each of the two solvents are also presented. Zimm plots reveal that by subtracting the signal from the bulk solvent mixture, the molar mass of PS in mixed solvent is overestimated by 30%. A correction is made by subtracting the signal from the ternary mixture extrapolated to zero polymer concentration. The solvent fluctuations are enhanced by the presence of the polymer. This behaviour is confirmed by the dynamic data and the Contin analysis of the autocorrelation function of the scattered light. This treatment reveals two modes whose amplitudes and relaxation frequencies are investigated in terms of the scattering angle and the polymer concentration. The fast solvent mode speeds up with decreasing polymer concentration while the amplitude increases. Solvent fluctuations are enhanced by the presence of the polymer. Both the amplitude and the frequency of the slow polymer mode increase with the concentration. The slow mode data are similar to those obtained with toluene alone confirming the preferential adsorption. Therefore both the fast and slow modes are sensitive to the preferential adsorption of the good solvent on the polymer.

Acknowledgements

These experiments were performed during a stay of A. Negadi and M. Benmouna at the ICS at Strasbourg. They express their gratitude to the director of the ICS Dr. J.C. Wittman and to Professor H. Benoît for their invitation and warm hospitality. This paper was completed while A. N. and M. B. were at the Max-Planck-Institut fur Polymerforschung (Mainz). They acknowledge enlightening discussions with Professor T. A. Vilgis and thank Professor K. Kremer for kind invitation.

References

1 Katime I, Strazielle C (1977) Makromol Chem 178:2295
2 Nakata M, Nakano Y, Kawate K (1988) Macromolecules 21:2509
3 Scott R-L (1949) J Chem Phys 17:268
4 Shultz A-R, Flory P-J (1955) J Polym Sci 15:231
5 Strazielle C, Benoit H (1961) J Chim Phys 58:675
6 To K, Choi H-J (1998) Phys Rev Lett 80:536
7 Van Asten A-C, Kok W-Th, Tijssen R, Poppe H (1996) J Polym Sci Polym Phys Ed 34:283
8 Solomon M-J, Muller S-J (1996) J Polym Sci Polym Phys Ed 34:181
9 Yamakawa H (1971) Modern Theory of Polymer Solutions. Harper and Raw, New York
10 Scholte Th-G (1971) J Polym Sci AZ 9:1553
11 Engels Th, Belkoura L, Waermann D (1988) Bunsenges Ber Phys Chem 92:1544
12 Ritzl A, Belkoura L, Waermann D (1999) Phys Chem Chem Phys 1:1947
13 Philipps Th, Borchard W (1989) Integration of Fundamental Polymer Science and Technology, Rolduc Meeting IV, Elsevier, London
14 Lapp A, Beinert G, Picot C (1984) Makromol Chem 185:453

15 Duval M, Coles H-J (1980) Rev Phys Appl 15:1399
16 Provencher S-W (1982) Comp Phys Comm 27:213
17 De Gennes P-G (1979) Scaling Concepts in Polymer Physics. Cornell University Press, New York
18 Kok C-M, Rudin A (1981) Makromol Chem Rap Commun 2:655
19 Akcasu A-Z, Han C-C (1979) Macromolecules 12:276