Polymer Bulletin 26, 117–122 (1991)

Polymer Bulletin

Chain conformation and viscometric behaviour of high molecular weight polystyrene in solvent/nonsolvent mixtures

Silvia Ioan[1], Maria Bercea[1], Bogdan C. Simionescu[2,*], and Cristofor I. Simionescu[1]

[1] "P. Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Romania
[2] Department of Macromolecules, Polytechnic Institue of Jassy, 6600 Jassy, Romania

Summary

Viscometric studies on high molecular weight polystyrene in solvent/nonsolvent binary mixtures are reported. Polymer behaviour is affected by the preferential adsorption phenomena determining the appearance of two theta temperatures, one intramolecular ($B = 0$, $\alpha = 1$) and the other intermolecular ($A_2 = 0$). For very high molecular weight polystyrene, theta intramolecular strongly approaches theta intermolecular due to a decrease in selective adsorption and in the vicinity of the theta condition the conformational transitions disappear.

Introduction

Different studies were concerned with coil dimensions of synthetic polymers in mixed solvents (1-3). Most of them involve liquid mixtures composed of a good and a poor solvent of the polymer (4).

The viscometric results obtained with samples of linear polymers show two different types of discontinuities in the dependence of $[\eta]$ on temperature, explained in terms of different mobilities of polymer side groups below and above the transition temperature. One is independent of the solvent (5-7); below the transition temperature there are strong interactions between the side groups giving rise to a rather rigid and perhaps helicoidal structure, and above it, rotation becomes easier, and the rigidity of parts of molecules disappears. The other transition is observed near the theta temperature where the macromolecular chain must exhibit the same flexibility below and above the transition point (4,8,9).

The action of mixed solvent changes the dimensions of the coil not only because of excluded volume expansion but also because the interaction between liquids modifies the unperturbed dimensions. More precisely, it has been observed that the behaviour of polymers in binary solvent systems is affected by preferential adsorption phenomena which change with the molecular weight of the polymer and which determines two different theta conditions (10). For one of these, called the intermolecular theta condition (Θ-inter), the second virial coefficient A_2 is zero, and for the other, called the intramolecular theta condition (Θ-intra), the chains obey Gaussian statistics.

Previous studies (4) on polystyrene and poly(methyl methacrylate) in binary solvent mixtures have shown that a transition phenomenon takes place in theta conditions, and the tran-

---

[*] To whom offprint requests should be sent

sition point is closely related to the intramolecular theta condition.

The present paper reports some studies on high molecular weight polystyrene (PS) in binary solvent/nonsolvent mixtures (benzene/n-hexane, benzene/methanol and benzene/isopropanol).

Experimental

Polystyrene was obtained by plasma-induced polymerization (for details on this synthesis technique, see, e.g., (11)). A PS sample with weight average molecular weight $\bar{M}_w = 3.065\mathrm{x}10^6$ was selected for this study. The solvents - benzene (B), n-hexane (nH), methanol (M) and isopropanol (iP) - were purified by standard procedures. The viscosities were measured with an Ubbelohde viscometer.

Huggins and Kraemer equations were used to analyse the data in the 20-45°C (+/- 0.02°) temperature range. Kinetic energy correction was found to be negligible.

Results and Discussion

Polystyrene/benzene/n-hexane ternary system

Previously, it has been established that PS with $\bar{M}_w < 10^6$ shows theta temperatures in a B/nH mixture at 20°C with $\emptyset_2 = 0.61$ (12) (where $\emptyset_2$ is the volume fraction of nH) and at 25°C with $\emptyset_2 = 0.653$ (13). In the present case, clear solutions could not be obtained from solvent mixtures containing higher proportions of nH. Increasing the proportion of nH in the system, the possibility of association between nH molecules themselves increases, giving rise to new conformations. The difficulties encountered in obtaining clear solutions from solvent mixtures with $\emptyset_2 > 0.54$, even at higher temperatures, may be due to this tendency of nH molecules to interact between themselves rather than with the polymer coil. A similar reasoning was put forward for poly(methyl methacrylate) in THF/H_2O (14) and CCl_4/n-alcohol (15) and for poly(styrene-co-n-butyl methacrylate) in CCl_4/n-butanol (16).

This tendency appears to be more pronounced for high molecular weight PS, where the theta condition, at 20°C, was found for $\emptyset_2 = 0.5359$ (17) (by measuring the concentration dependence of first cloud points), a value differing from literature (12). This agrees with the investigation of Berek et al. (18) that obtained a series of theta compositions of binary THF/H_2O mixtures slightly increasing with decreasing PS molecular weights ($1.2\mathrm{x}10^6$-$2.33\mathrm{x}10^5$) and ranging from 7.5 to 8.0 vol.% of H_2O.

Fig. 1 shows the plots of intrinsic viscosity against temperature for PS in pure benzene and B/nH mixtures with increasing the amount of nH. The intrinsic viscosity of PS in benzene slightly decreases with increasing temperature. The behaviour of the polymer in mixed solvents shows discontinuities in $[\eta]$ as a function of temperature for all solvent/nonsolvent ratios investigated. This type of variation has been interpreted as a conformational change of the coil in the 30-40°C temperature range; the transition point and the magnitude of the transition depend on solvent composition. Polymer side groups (phenyl rings) play an important role in bringing the change in conformations.

Literature data report a similar transition of PS (8,9) in cyclohexane (theta solvent at 34°C) at about 40°C, in a theta solvent cyclohexane (99 vol %)/ethanol (1 vol %) mixture (theta solvent at a temperature higher than 34°C) at about 46°C, in a theta solvent cyclohexane (99 vol %)/benzene (1 vol %) mixture (theta solvent at a temperature lower than 34°C) at about 37°C, and in a theta solvent CCl_4 (65 vol %)/*n*-butanol (35 vol %) at about 45°C (theta solvent mixture at 35°C) (19).

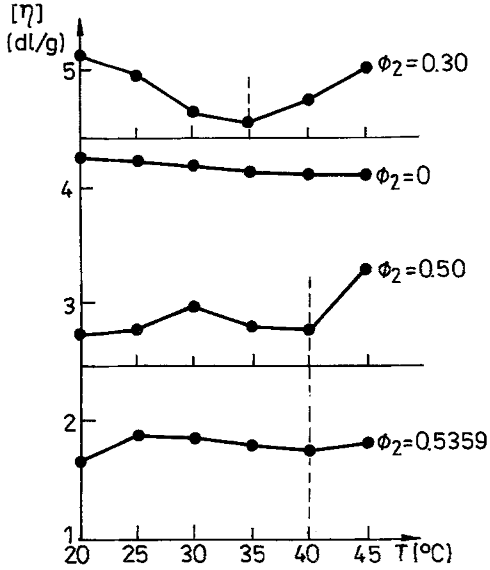

Figure 1.
Plots of intrinsic viscosity against temperature at several binary mixture compositions in benzene/n-hexane system.

The dependence of intrinsic viscosity on mixed solvent composition for different temperatures is presented in Fig. 2.

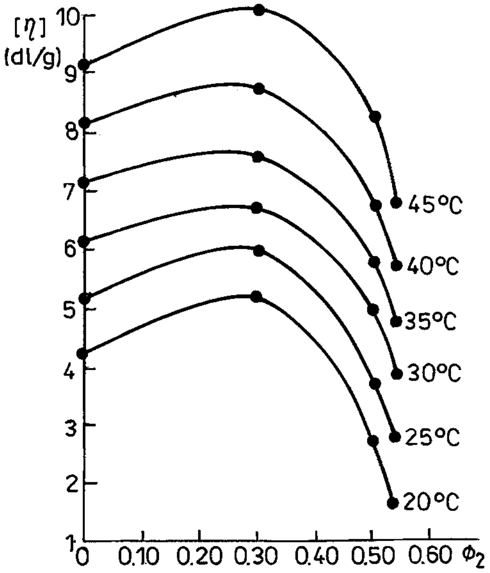

Figure 2.
Plots of intrinsic viscosity against binary mixture compositions at several temperatures in benzene/n-hexane system. The data points are shifted upward to the following amounts: 20°C - 0; 25°C - 1; 30°C - 2; 35°C - 3; 40°C - 4; 45°C - 5.

A slight increase of intrinsic viscosity with increasing the nH content up to ϕ_2=0.3, and a decrease of its value with further increase of nH content, independent of temperature, are observed in Fig. 2. Around ϕ_2=0.3 the mixed solvent acts as a good solvent for PS through nH is a poor solvent for this polymer and B is a good one. This synergistic behaviour of the mixed solvent can be compared with the cosolvent phenomenon, in which the mixture of two nonsolvents for a given polymer behaves as a good solvent for that polymer (20,21).

Polystyrene/benzene/methanol ternary system

As already reported (10), in this system the polymer exhibits two different theta points at 25°C due to the preferential adsorption which changes the analytical composition in the interior of the coil. One of them is θ-inter (A_2 = 0) and appears at ϕ_2=0.22 (volume fraction of methanol), and the other is θ-intra (B= 0, α = 1) and appears at ϕ_2=0.255. Elias and Etter (13) reported, for PS with $(\bar{M}_w)_{app}$ = 678000, the values A_2= 0 and A_3= 2.75x10^{-3} for ϕ_2=0.222 at 25°C for this ternary system. Tsitsilianis and Dondos (4) published some viscometric results showing that a transition phenomenon takes place for PS and poly(methyl methacrylate) with solvent mixture composition in which the polymer is just above the theta condition. When two theta conditions occur, the transition point ϕ_2^* is closely related to the intramolecular theta condition. Moreover, the θ-intra varies with the molecular weight when the preferential adsorption also varies. This variation induces a modification of the transition point with the molecular weight (or the intrinsic viscosity) and obeys a relation (eqs. (1) or (2)) analogous to that giving the variation of the preferential adsorption λ with the molecular weight (eq. (3)):

$$\phi_2^* = \phi_{2\infty}^* + AM^{-1/2} \qquad (1)$$

$$\phi_2^* = \phi_{2\infty}^* + A'\,[\eta]^{-1} \qquad (2)$$

$$\lambda = \lambda_\infty + A''M^{-1/2} \qquad (3)$$

where $\phi_{2\infty}^*$ and λ_∞ represent the asymptotic limit for high molecular weight and A, A' (= $AK_\theta\alpha^3$) and A'' are constants.

We studied the high molecular weight PS at 25°C in different B/M solvent mixtures for ϕ_2 in the 0 - 0.24 domain, the data being presented in Fig. 3.

Fig. 4 compares our data with the literature ones which enclose a large molecular weight domain (lit. data (4): 0.69x10^4 - 12.3x10^4; present data: $\bar{M}_w$= 3.065x10^6). With increasing the molecular weight, the transition point shifts towards lower values of ϕ_2, so that for high molecular weight PS the transition phenomenon disappears.

Evidently, the intramolecular theta point (which is in close connection with the transition point) varies with the molecular weight in the region where the preferential adsorption also varies. For high molecular weight PS, the intramolecular theta point strongly approaches the intermolecular theta point, due to the decrease of selective adsorption, so that the observation on the disappearance of the transition phenomenon is proper.

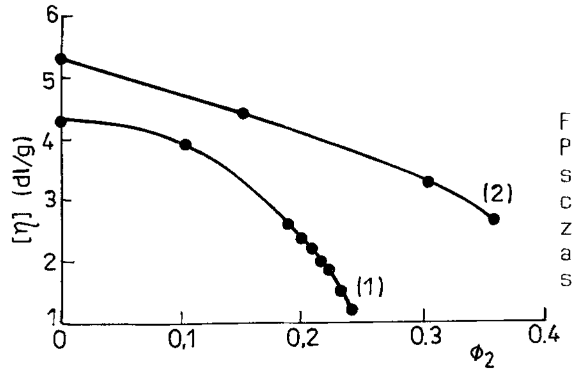

Figure 3.
Plots of intrinsic viscosity against binary mixture composition at 25°C in benzene/methanol system (1) and benzene/isopropanol system (2).

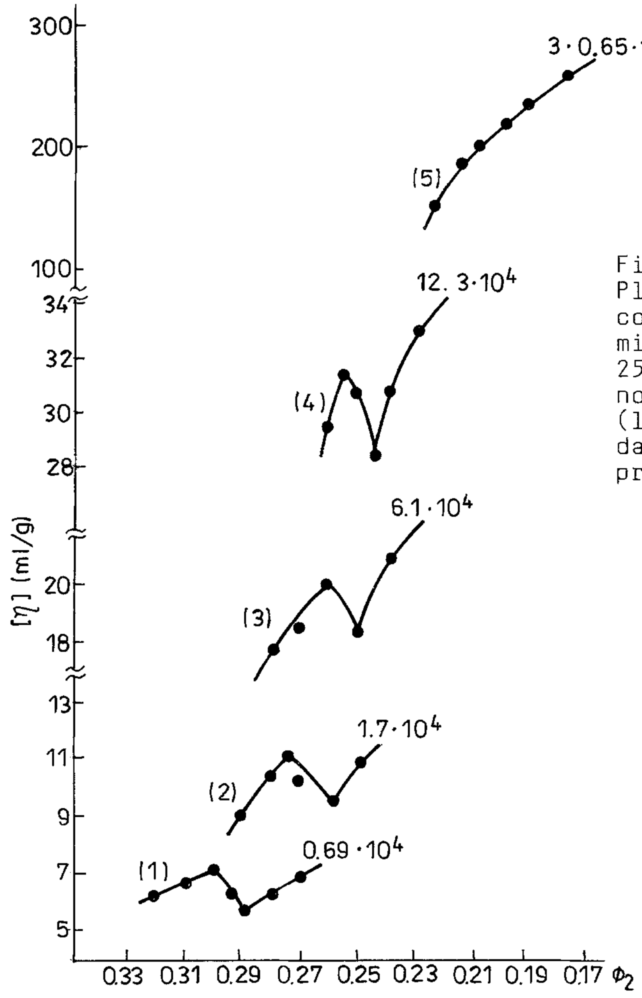

Figure 4.
Plots of intrinsic viscosity against binary mixture composition at 25°C in benzene/methanol system. Curves (1) - (4), literature data (4); curve (5), present data.

Polystyrene/benzene/isopropanol ternary system

For this system, literature data (13) present the theta conditions in a mixture containing 35.8 vol % isopropanol ($\emptyset_2$=0.358) at 25°C, when A_2 = 0 and A_3 = 0. At this solvent/ /nonsolvent ratio PS does not show preferential adsorption and inter- and intramolecular theta conditions coincide.

Fig. 3, curve 2, presents the variation of the intrinsic viscosity with mixed solvent composition $\emptyset_2$ at 25°C for high molecular weight PS. A continuous decrease of $[\eta]$ with increasing $\emptyset_2$ is observed. In the vicinity of the theta condition, no conformational transition is registered.

References

1. Nakato M, Nokano Y, Kawate K (1988) Macromolecules 21:2509
2. Nakato M, Kaji A (1988) Macromolecules 21:2514
3. Horta A, Fernández-Piérola I (1981) Polymer 22:783
4. Tsitsilianis C, Dondos A (1985) Polymer 26:1838
5. Dondos A, Rempp P, Benoit H (1973) Makromol. Chem. 171:135
6. Katime I, Roig A, Gutierrez Cabanas P (1974) Eur. Polym. J. 10:897
7. Katime I, Gutierrez Cabanas P, Vera R (1981) Polym. Bull. 5:25
8. Tsitsilianis C, Pierri E, Dondos A (1983) J. Polym. Sci. Polym. Lett. Ed. 21:685
9. Tsitsilianis C, Dondos A (1984) Makromol. Chem. Rapid Commun. 5:625
10. Dondos A, Benoit H (1961) J. Polym. Sci. B 7:335
11. Simionescu B C, Popa M, Ioan S, Simionescu C I (1982) Polym. Bull. 6:415
12. Gruber U (1964) Thesis E. T. H. Zurich
13. Elias H G, Etter O (1963) Makromol. Chem. 66:56
14. Katime I, Cesteros L C, Ochoa J R (1982) Polym. Bull. 6:447
15. Katime I, Ochoa J R, Teijon J M (1965) J. Chem. Soc. Faraday Trans. 81:783
16. Rashid H U, Usman U (1990) J. Polym. Sci. Polym. Lett. 28:65
17. Ioan S, Bercea M, Simionescu B C (in press) Mem. Secţiilor St. Acad. Rom.
18. Spychaj T, Lath D, Berek D (1979) Polymer 20:437
19. Rashid H U, Asubakar S D (1989) J. Polym. Sci. Polym. Lett. 27:5
20. Masegosu R M, Prolongo M G, Hernández-Fuentes I, Horte A (1984) Macromolecules 17:1181
21. Wolf B A, Molinari R J (1973) Makromol. Chem. 173:241

Accepted January 31, 1991 C