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H/D Solvent Isotope Effect on Miscibility in the Polystyrene−Methyl Acetate System

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Introduction

The recent studies by Imre and Van Hook[1] revealed that the traditional division of solvents into three classes: good solvents, theta (Θ) solvents, and poor solvents is rather conventional. Some solvents designated (Θ) may undergo a Θ-to-poor transition and others nominally designated as poor show a poor-to-Θ transition. Raising or lowering pressure they were able to move the system from poor-to-Θ or Θ-to-poor thus demonstrating the continuity of the solvent quality. Recent isotope studies in polymer systems[2–6] have shown that solvent quality is also sensitive to the isotope substitution. The results obtained so far indicate that H/D substitution in a solvent makes the miscibility worse, and we feel that H/D substitution would be also capable to induce the Θ-to-poor transition. The effect would manifest itself by an increase in Θ_U and a decrease in Θ_L,i.e. the Θ-gap should shrink with increasing D content in solvent, and at high enough D content the two branches eventually touch and ultimately system collapses into the hourglass configuration. In order to demonstrate "$\Theta \rightarrow$ poor" continuity one needs a system showing a small enough Θ-gap. According to the review[7] and the more recent report,[1] polystyrene/methyl acetate seems to be an appropriate test system. The authors tried to induce the "$\Theta \rightarrow$ poor" transition applying negative pressure—unfortunately they were unable to reach a low enough negative pressure to directly observe the hypercritical junction at either M_w.

In this work, we present the results of the solubility of polystyrene in methyl acetate and deuterated acetate showing that the isotope substitution may be a very valuable variable of the same significance as pressure or molecular weight. In the present study, we have used polystyrene samples of the lowest polydispersity available.

Experimental Section

Polystyrene samples of well-defined molecular weight and molecular weight distribution were obtained from Pressure Chemical Co., Pittsburgh, except for a sample of the highest $M_w = 13.2 \times 10^6$, which was obtained from Polymer Laboratories, Amherst, MA. Methyl acetate (analytical grade) was obtained from Aldrich. It was twice distilled and dried using molecular sieves of 5 Å. Deuterated methyl acetate was synthesized from deuterated acetic acid (CD_3COOD, 99.5 atom % D from Aldrich) and deuterated methanol (CD_3OH, 99.8 atom % D from Aldrich) by using a classical method. The level of deuteration determined by NMR was at least 99%. Deuterated methyl acetate (CD_3COOCD_3) was dried over 5 Å molecular sieves as well. The polymer samples were vacuum-dried (~50 °C) and solutions made up gravimetrically. The apparatus and the details of the procedure for determining the cloud points have been described in detail elsewhere.[8,9] The accuracy of the cloud point determination is better than ±0.01 K for the lower branch and ±0.1 K for the upper branch.

Table 1. Critical Parameters from the Scaling Equation: $|\phi - \phi_c| = At^{\beta}$ for Polystyrene + Methyl Acetate System with Fixed $\beta = 0.325$

system	ϕ_c	UCST/LCST
	UCST	
PS400/MA	0.0498	294.81 ± 0.01
PS400/MA-d	0.0504	327.25 ± 0.01
PS2000/MA	0.0215	305.68 ± 0.01
PS13200/MA	0.0109	312.88 ± 0.01
	LCST	
PS400/MA	0.0501	400.8 ± 0.1
PS400/MA-d	0.0484	381.7 ± 0.1
PS2000/MA	0.0190	389.8 ± 0.1
PS13200/MA	0.0104	382.8 ± 0.1

Results and Discussion

Methyl acetate is normally classified as a Θ-solvent for polystyrene. It means that this solvent can dissolve polymer of the arbitrarily high M_w at concentrations as high and higher than the critical concentration, provided the temperature lies between the upper and lower Θ-points, Θ_U and Θ_L temperatures, respectively. The inspection of the available data[7] reveals a large number of measurements—mostly these are old and of low precision miscibility data and some of them have been even not reliable enough to be used in the fitting procedures.[7] Consequently Θ-temperatures scatter strongly: 316 K < Θ_U < 322 and 382 K < Θ_L < 387 K. Using the experimental values from the miscibility measurements for PS400, PS2000, and PS13200 with methyl acetate, the phase diagrams were constructed and are shown in Figure 1. The data show that the solubility curves represent the phase diagrams with upper (UCST) and lower solution temperatures (LCST). The statistical analysis employing nonlinear least-squares fit based on the scaling equation[10,11] with fixed critical exponent ($\beta = 0.325$) leads to the critical temperatures and critical concentrations—they are listed in Table 1. In general, the present results are compatible with the earlier data and they extend the critical temperatures far beyond the existing limit. It is also worth to note the remarkable dependence of the critical concentration expressed in volume fractions on M_w. By using the Schultz−Flory equation,[12] Θ-temperatures were determined, they are equal to 316.5 and 379.8 K for upper (Θ_U) and lower (Θ_L) branches, respectively.

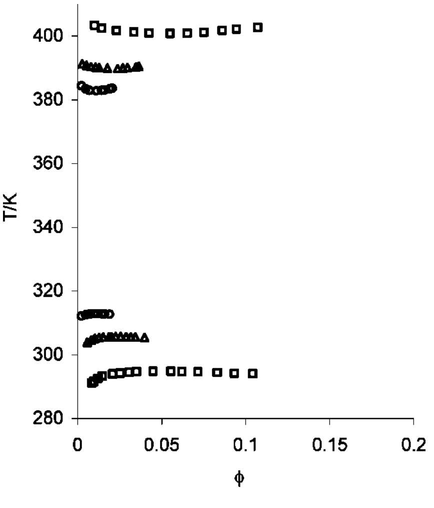

Figure 1. Phase diagrams of polystyrene + methyl acetate systems.

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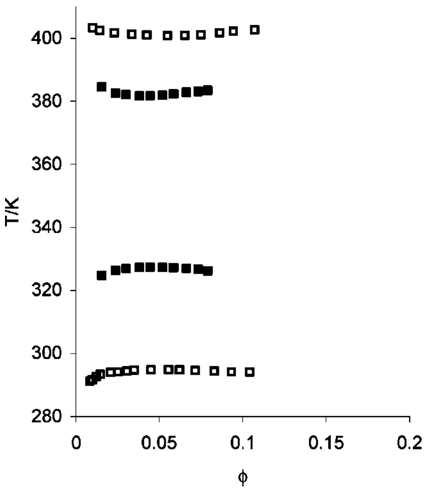

Figure 2. Effect of H/D substitution in solvent in PS400 + methyl acetate system. Open symbols refer to protiated solvent and full symbols refer to deuterated methyl acetate.

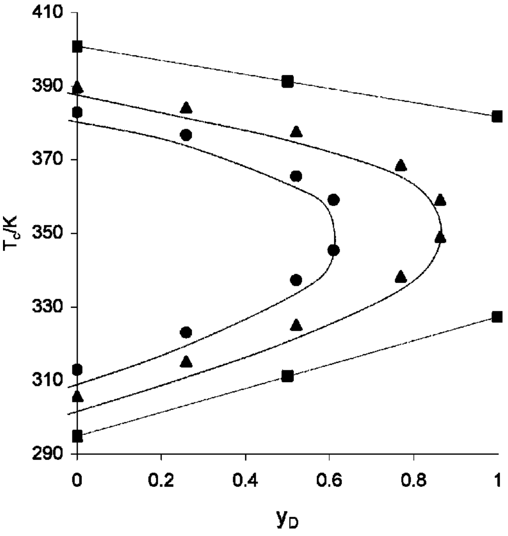

Figure 3. Solvent isotope effect on UCST and LCST transition temperatures: (■) PS400; (▲) PS2000; (●) PS13200. Lines are drawn as guides to the data.

Figure 2 shows the effect of the isotope substitution in the solvent for PS400 sample. Deuteration of the solvent noticeably influences the solubility of polystyrene, shifting the UCST to higher and LCST to lower values thus representing lower solubility. The isotope shift in UCST and LCST is very large, much larger than that observed for typical Θ-solvent cyclohexane, but comparable with those observed for poor solvents for polystyrene, like acetone and propionitrile.[2–4] The use of the deuterated methyl acetate for polystyrene samples of higher M_w (PS2000 and PS13200) drastically changes the property of the solutions. While protiated MA is classified as the Θ-solvent and two branches are far apart (see the values of UCST and LCST listed in Table 1), for deuterated MA, already for PS2000, the system collapses into the hourglass configuration. By decreasing the deuterium content y_D (y_D, atom fraction of deuterium in the solvent) one can bring the system again into Θ-configuration. Figure 3 visualizes the "Θ → poor" transformation of the system induced by deuterium substitution—a large enough Θ-gap at $y_D = 0$ (protiated solvent) narrows as deuterium content rises and ultimately hyperdemixing appears at $y_D = 0.88$ (PS2000) or $y_D = 0.63$ (PS13200). Estimated hypercritical temperature is equal to 350.8 ± 0.8 K. For comparison purposes Figure 3 reports also the solvent isotope effect for PS400/MA solution. In this case $T_{c,U}$ increases and $T_{c,L}$ decreases linearly with solvent deuteration. Although the system is well removed from the hypercritical region for all values of y_D, the solvent isotope effect is large. The well behaved linearity establishes the methyl acetate-*h*/methyl acetate-*d* solvent mixture as ideal (within experimental precision) according to Singh and Van Hook.[13] Thus it is a striking difference in comparison with PS2000 and PS13200 where strong curvature is observed as the hypercritical point is approached. It means that dT_c/dy_D gets very large in the vicinity of T_{hcp} and isotope effect ΔT_c may be said to be hypercritically enhanced. Well removed from T_{hcp}, i.e. for small y_D, dT_c/dy_D is almost the same for PS2000 and PS13200 as for PS400—this is illustrated in Figure 4. It is also worth to mention that isotope shift of the UCST is bigger than that for LCST, also dT_c/dy_D is getting larger in the first case. In the first approximation it may be accounted for by the higher temperature used for LCST type diagram—typically the isotope effect decreases with temperature.

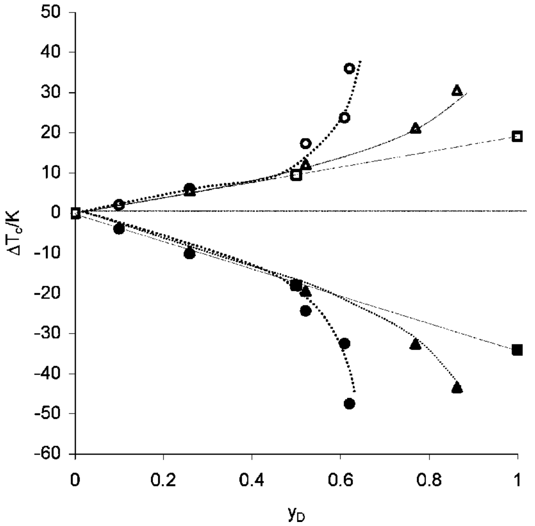

Figure 4. Isotope shifts of UCST and LCST as a function of deuterium content. Open symbols refer to UCST branch and full symbols refer to LCST branch: (□, ■) PS400; (△, ▲) PS2000; (○, ●) PS13200.

From the theoretical point of view, the influence of the isotope substitution on the phase behavior can be discussed in the frame of the theory of the condensed phase isotope effects formulated by Bigeleisen[14] and developed further by Van Hook and others.[15] When coupled with an appropriate thermodynamic model of the solutions it can in principle be employed to interpret the effect of the isotope substitution on the miscibility of liquids. Although this approach has been successfully applied in the recent studies[6,16,17] to rationalize the sign and magnitude of the miscibility isotope effect, in the present case it is not able to explain unusually large isotope shifts of the critical temperatures and their behavior close to the hypercritical point. Hence, it becomes clear that the vibrational frequency shifts themselves cannot be responsible for the observed effects, and a more rigorous thermodynamic model taking into account the peculiarities of the hypercritical state should be considered. In particular, it refers to the interaction parameter χ.

Conclusions

In this paper, we have presented the results of the solubility studies of polystyrene in methyl acetate and deuterated methyl acetate. Deuterium substitution in solvent significantly affects the solubility of the polymer. While for PS400, even for fully deuterated methyl acetate, only large shifts of the UCST and LCST are observed, for two other systems upper and lower branches merge at lower deuterium fractions, i.e. at $y_D = 0.88$ and $y_D = 0.63$ for PS 2000 and PS13200, respectively—ultimately the solutions hyperdemix and the systems collapse into the hourglass configurations. Thus for the first time we have shown that the "Θ-to poor" transition can be induced by the deuterium substitution. The effect is in a close analogy to that of pressure and it emphasizes the sensitivity of solvent quality to the isotope substitution and demonstrates "Θ → poor" continuity.

Supporting Information Available: Tables giving the characteristics of polystyrenes, cloud point temperatures for polystyrene + methyl acetate and polystyrene + deuterated methyl acetate for M_w of polystyrene equal to 4×10^5, 2×10^6 and 13.2×10^6, and critical temperatures and concentrations and a figure showing UCSTs and LCSTs. This information is available free of charge via the Internet at http://pubs.acs.org.

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