Macromolecules **2000,** *33,* 5308−5309

End Group Effects on Liquid−Liquid Demixing of Polystyrene/Oligomethylene Solutions. Polystyrene/Dodecyl Acetate Solubility

Attila Imre*,† **and W. Alexander Van Hook***,‡

Chemistry Department, KFKI Atomic Energy Research Institute, H-1525 Budapest, Hungary; and Chemistry Department, University of Tennessee, Knoxville, Tennessee 37996-1600

Received March 14, 2000
Revised Manuscript Received May 5, 2000

Introduction

The solubility of polystyrene (PS) has been studied in various organic solvents including alkanes, esters, ethers, etc.[1] Such solutions are well-known examples of weakly interacting polymer solvent systems. The lower alkyl acetates are convenient solvents for PS, and although in one sense acetates are typical weakly interacting solvents, they do have special characteristics. Those alkyl acetates examined to date are the poorest of the Θ-solvents (i.e. exhibiting the smallest Θ-gap, thus PS/methyl acetate and PS/*tert*-butyl acetate solutions show ($\Theta_{LCST} - \Theta_{UCST}$) to be only 50−60 K.[1,2]).[3] For $n \leq 3$, LL (liquid−liquid) UCST's (upper critical solution temperatures) are known for PS/n-$C_nH_{2n+1}O(CO)CH_3$ solutions but LL LCST's (lower critical solution temperatures) lie at unreachable high temperatures. For somewhat longer alkyl chains (C_4−C_6), UCST's are not observed (presumably having shifted below the freezing point of the solutions), but LCST's have been reported.[4,5]

Reasoning from the values of UCST for small carbon number, Prausnitz and co-workers[2,5] concluded that solvent quality in PS/n-$C_nH_{2n+1}O(CO)CH_3$ solutions is a monotonic function of chain length with $\partial LCST/\partial n > 0$ and $\partial UCST/\partial n < 0$. So far as UCST is concerned, however, this interpretation cannot be correct because long chain acetates may be properly considered as $CH_3(CO)O-$ terminated oligoethylenes. It is well-known that PS and polyethylene are incompatible[6] (even though their lower oligomers are compatible), and compatibility worsens with chain length. In support we note that UCST's for PS/n-alkanes and PS/n-alcohols (i.e. −H- and −OH-terminated oligoethylenes) show distinct minima around $n \sim 7$;[7−9] see Figure 1. These results are consistent with results on PS/chloroalkane, PS/cyclohexylalkane, and PS/phenylalkane solutions[1,10−14] which also show a monotonic increase in UCST with n (but without the minimum observed for the alkanes, alcohols, and (now) acetates). Although end groups have remarkable effects on PS solubility,[1] it is expected in every case that alkyl chain effects must dominate at large n. An initial decrease in UCST vs chain length (n) in any PS/oligomer system must eventually damp out, go through a minimum, and then increase. At high enough n, this results in incompatibility. Thus, the location of the minimum is solvent quality and carbon number dependent. Similar minima have been observed in other polymer/oligomer-solvent mixtures including OH and acetate-terminated poly(propylene glycol)/oligodimethylsiloxanes.[15]

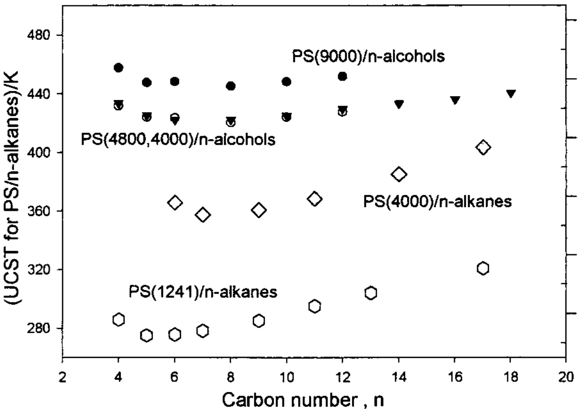

Figure 1. UCST vs n for PS/n-$C_nH_{2n+1}CH_3$ and PS/n-$C_nH_{2n+1}OH$ (n-alkanes and n-alcohols) solutions. The data are from refs 1, 9, and 19. UCST's for alcohol solutions are on the right ordinate: small solid circles = $M_w(9000)$; small open circles = $M_w(4800)$; small solid and inverted triangles = $M_w(4000)$. UCST's for alkane solutions are on the left ordinate: large open diamonds = $M_w(4000)$; large open hexagons = $M_w(1241)$

In this note we examine data on PS/alkyl acetate solutions and show the initial decrease of UCST with n leads, as expected, to a minimum which is presumably followed by regular increase to incompatibility. The interpretation is complicated by the fact that the freezing points of the n-alkyl acetate solvents also increase with n, and the minimum in UCST and the beginnings of its subsequent increase are masked by the LS (liquid−solid) phase transition.[16] However, when n is approximately 10, the temperatures of the LL (liquid−liquid) and LS transitions cross and LL is again observable. We report cloud point (CP) measurements for PS/n-dodecyl acetate at several M_W. The freezing point of this solvent is 261 K, well below UCST for PS solutions of $M_w > 5 \times 10^5$.

Experimental Section

Polystyrenes (Pressure Chemical, $M_w = 2.0 \times 10^6$, $M_w/M_n \leq 1.30$; $M_w = 9.0 \times 10^5$, $M_w/M_n \leq 1.06$; $M_w = 5.75 \times 10^5$, $M_w/M_n \leq 1.07$) and dodecyl acetate (Aldrich 97%, [112-66-3]) were used without further purification. Solutions were prepared in glass vials, then capped and mixed overnight at room temperature which is ~20−25 K above the demixing temperatures of the solutions studied. Aliquots were loaded into 2 mm ID glass capillaries and flame-sealed. CP's were determined visually in an ethylene glycol/water thermostat at six concentrations evenly spaced from 2 to 10 wt % PS-5.75×10^5, seven concentrations between 2 and 8 wt % PS-9×10^5, and 14 concentrations between 1 and 7 wt % PS-2×10^6. Cooling to the demixing temperature was carried out step by step in 0.1−0.2 K steps. In the region of the phase transition, 2−3 min were provided at each step. Waiting 5−10 min makes no difference. After waiting 2 or 3 min at the step where demixing was first observed, warming back 0.1 or 0.2 K resulted in a transparent solution. We conclude that the reported data represent the equilibrium demixing temperatures within the stated experimental error, ~±0.2 K.

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* To whom correspondence may be addressed.

† KFKI Atomic Energy Research Institute. E-mail: imre@sunserv.kfki.hu.

‡ University of Tennessee. E-mail: avanhook@utk.edu.

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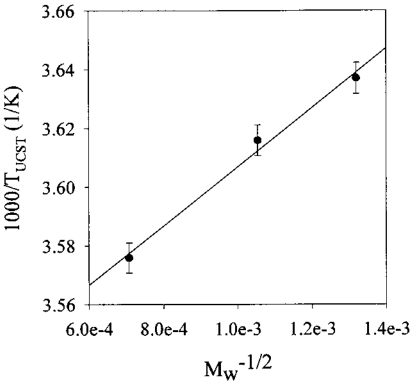

Figure 2. Modified Schultz−Flory plot for PS/*n*-dodecyl acetate. The intercept of the correlation line corresponds to $\Theta = 285.2 \pm 0.4$. The slope is 100.7×10^3 amu$^{1/2}$/K.

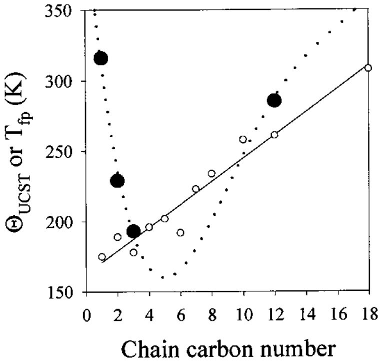

Figure 3. UCST vs *n* for PS/*n*-$C_nH_{2n+1}O(CO)CH_3$ solutions (large solid circles), and solvent freezing points, T_{FP} (small open circles).[16] The solid and dashed lines are freehand guides to the eye. UCST for $n = 12$ was determined in this paper. The other data are from the literature.[4,5,16]

Results and Discussion

UCST cloud point (CP) data for PS/*n*-$C_{12}H_{25}O(CO)CH_3$ solutions are reviewed in Figures 2 and 3. LL is not sharp and uncertainties in T_{CP} are $\sim\pm 0.2-0.4$ K. CP/concentration curves are remarkably flat, confirming the similar observation of Zeman and Patterson[17] for PS/$CH_3O(CO)CH_3$. This pattern may be a general characteristic of PS/acetate solutions. Because of the flatness $T_{MAX} \sim T_{UCST}$, (the true critical point lies to the high concentration side of the maximum, but the difference ($T_{MAX} - T_{UCST}$), is estimated to be smaller than the experimental error.[18]) Figure 2 is a modified Shultz-Flory plot of the CP data and yields $\Theta_{UCST} = 285.2 \pm 0.4$ K. The solvent carbon number dependence of Θ_{UCST} is shown in Figure 3, which also plots the freezing points of the normal alkyl acetates.[16] Within present experimental error these do not differ from the freezing points of the solutions, T_{FP}. For ($4 \leq n \leq$ about 10) $\Theta_{UCST} < T_{FP}$ and CP cannot be observed. Even so, because $\Theta_{UCST}(n = 12) > \Theta_{UCST}(n = 2$ and $n = 3)$, we conclude that PS/alkyl acetate solutions behave similarly to PS/*n*-alkane and PS/*n*-alcohol solutions so far as LL demixing is concerned (i.e. an initial decrease to a minimum, followed by increase to eventual incompatibility). This is noteworthy because the PS/alkyl acetate solutions are normally classified as Θ-solutions, while alkanes and alcohols are considered to be poor solvents for PS. In good solvents (e.g., PS/phenyl-alkanes, PS/chloroalkanes),[1,10,11] no minimum is found; instead, a monotonic decrease in solvent quality (increase in UCST) with *n* is observed. Comparing (UCST, $n)_{MIN}$ loci for different PS/oligomer series yields information about end group effects. Thus, CH_3COO- as end group improves PS/(oligomeric ethylene) transforming the initial poor-solvent H-terminated *n*-alkanes into Θ solvents. On the other hand, when the alkyl chain is short and end group effects dominate, CH_3COO- (the same group which improved solvent quality at intermediate and high *n*) now makes the solvent worse. Comparing end group effects on compatibility of PS/$CH_3(CH_2)_nX$ mixtures for $n > n_{min}$ one finds $X = C_6H_5 > X = Cl > X = C_6H_{11} \sim X = CH_3COO > X = OH > X = CH_3$ as judged by the ordering of UCST temperatures and/or Θ gaps.

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Materials Sciences, and the Ziegler Research Fund, University of Tennessee.

References and Notes

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(3) Some explanation of notation is appropriate. According to the Flory−Huggins model of phase equilibria in polymer solutions reciprocal upper critical solution temperatures (1/UCST) depend linearly on $M_w^{-1/2}$ (the so-called Shultz-Flory plot) yielding an $M_w^{-1/2} = 0$ intercept, $1/\Theta_{UCST}$ Although the model makes no predictions about reciprocal lower critical solution temperatures (1/LCST), it is widely accepted that a similar treatment yielding an $M_w^{-1/2} = 0$ intercept, $1/\Theta_{LCST}$, is appropriate. In the ordinary case, $\Theta_{LCST} - \Theta_{UCST} > 0$. As solvent quality deteriorates the linear Shultz-Flory approximation begins to fail and curvature develops in the ($T_{CRITICAL}^{-1}$, $M_w^{-1/2}$) plane. See the following references and/or ref 1 (above) for further discussion: Fujita, H. *Polymer Solutions*; Elsevier, Amsterdam, 1990; Chapter 9. Des-Cloizeaux, J.; Jannink, G. *Polymers in Solution*; Clarendon Press: Oxford, England, 1990; Chapter 16.
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MA000472Y