

Lower Critical Solution Temperatures of Polystyrene in Alkyl Acetates

Pierre Bataille

Department of Chemical Engineering, Ecole Polytechnique de Montreal, Montreal, P.Q., Canada

Lower critical solution temperatures of polystyrene in alkyl acetates were determined, and the results were fitted into an equation predicting the critical solution temperatures.

Certain polymers in solution precipitate as the temperature is raised. The lowest temperature at which this phenomenon occurs is called the lower critical solution temperature (LCST).

The work described in this paper concerns the determination of the LCST of polystyrene in a series of alkyl acetates going from the methyl to the decyl.

Materials

The polystyrene used was obtained by fractionation of a Monsanto Lustrex H-77 sample. The fractionation was carried out essentially the same way as described by Fox and Flory (5). The fractions II, VII, and IX had molecular weights of 5.7×10^5 , 1.8×10^6 , and 9×10^4 , respectively, as determined by the viscosity method using the constants given by Bawn et al. (2).

Measuring Equipment

The measuring equipment consisted of a cell, a cell holder, and a heater. The cell (Figure 1) is made up of a Teflon ring "b" having an external diameter of 26 mm, an internal diameter of 16 mm, and a thickness of 6 mm.

The solution is held in place by a pair of pyrex disks having the same external diameter. As shown in Figure 1, the disks and Teflon ring are held together by a cell holder made of brass. This cell holder has two sections, both of which are punched out. The cell and the cell holder were isolated with asbestos and placed in a radial type oven. To follow more easily the phase separation in the solution, a lamp was placed behind the cell.

The temperature was recorded with a copper-Constantan thermocouple and a potentiometer recorder; this system was calibrated with an Anshultz thermometer standardized at the National Research Council.

Experimental

The various alkyl acetates used as solvents ranged from the methyl acetate to the decyl acetate. They were first dried over magnesium sulfate or potassium carbonate and then distilled as suggested by Weissberger (11).

Experiments were conducted at two concentrations of polystyrene: 1 and 5%. The exact concentrations are given in the tables.

The cell was half filled (about 0.5 cc) to provide for the expansion of the solution. After closing the cell hermetically, it was first heated rapidly to about 25°C below the estimated LCST and then at about 1°C/min until the critical temperature was reached. This critical temperature was first estimated by a rapid test. These experiments were repeated for each system, and the values obtained came within $\pm 0.5^\circ\text{C}$, showing a good reproducibility.

To obtain the critical temperature at infinite molecular weight, the method suggested by Flory (4) was used,

i.e., a plot was made of $1/T_c$ vs. $1/x^{1/2} + 1/2 x$, x being defined as follows:

$$x = \frac{M\bar{v}}{v_1} \quad (1)$$

where M is the molecular weight, \bar{v} the specific volume of the polymer, and v_1 the molar volume of the solvent. One notes that $1/x^{1/2} + 1/2 x$ tends toward $1/M^{1/2}$ when M is high.

The LCST values obtained are given in Table I. For illustration, some upper critical solution temperatures (UCST) are given in Table II.

Discussion

In Figure 2 the results given in Table I are plotted as critical temperature (T_c) vs. r_A . The line drawn through the points is in agreement with the following equation:

$$T_c = r_A \left(\frac{R/2 \pm \sqrt{R^2/4 - 4AB}}{2B} \right) \quad (2)$$

where r_A is the relative size of the solvent, R the gas constant, and A and B are constants.

This equation is a particular case of an equation discussed elsewhere (7) in which χ , the polymer solvent interaction parameter, is set at $1/2$, the critical condition. It suggests the hypothesis that, when a polymer is dissolved in a solvent, it creates a certain amount of order. The solvent molecules settle around the polymer molecule, thus lowering the entropy.

In the choice of r_A , a value of two was given to the acetate group and one of $1/2$ for each CH_2 or CH_3 group; thus, it is considered that one segment of polymer equals two CH_2 groups. However, one cannot deduce from these measurements independent values of A and B . One is obliged to use other methods such as viscosimetry or microcalorimetry (3).

Most probably, the pressure in the cell is not constant. Prigogine and Defay (8) have indicated that an increase in pressure of 250 atm brings a change of only 1.6°C in the critical temperature. Ham et al. (6) measured a change of 1°C for a pressure increase of 200 atm.

The work here involves pressures up to about 20 atm; therefore, the error is negligible. When experiments were

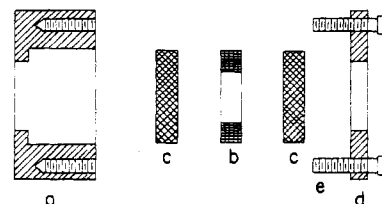


Figure 1. Cell diagram
a: Cell holder body
b: Sample container (teflon)
c: Pyrex disk
d: Cell holder cover
e: Screw

Table I. Polystyrene in Acetate (LCST)

Solvent acetates	Mol wt $\times 10^{-4}$	Concn, %	LCST, K	$\frac{1}{x^{1/2}} + \frac{1}{2x}$	r_A
Methyl	9	1.14	441	3.40	2.5
	18	0.96	432	2.38	
	57	0.97	421	1.32	
	∞	...	409	...	
Ethyl	9	1.00	461	3.91	3.0
	18	0.96	452.6	2.73	
	18	4.01	452.6	2.73	
	57	1.00	448	1.52	
Propyl	9	0.98	500	4.22	3.5
	18	1.02	489.5	2.94	
	57	1.01	479.5	1.63	
	∞	...	467	...	
Butyl	9	1.09	528	4.95	4.0
	18	1.04	520.5	3.43	
	57	0.99	514	1.90	
	∞	...	506	...	
Amyl	9	4.83	552	4.95	4.5
	18	0.98	544.2	3.45	
	57	1.00	538	1.92	
	∞	...	527	...	
Hexyl	9	2.36	578	5.16	5.0
	57	0.98	560	2.00	
	∞	...	550	...	
Decyl	18	1.01	657	...	7.0
	57	1.00	650	...	
	∞	...	643	...	

Table II. Polystyrene in Methyl Acetate (UCST)

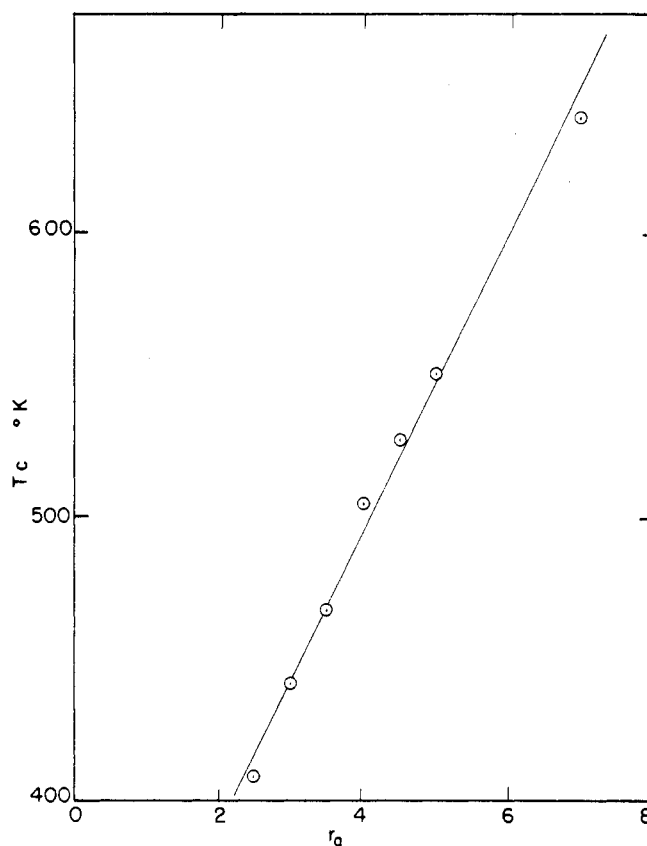
Solvent	Mol wt $\times 10^{-4}$	Concn, %	UCST, K	$\frac{1}{x^{1/2}} + \frac{1}{2x}$
Methyl acetate	9	1.14	275.0	3.11
	18	0.97	291.3	2.20
	57	0.97	301.8	1.24

rerun with the same solution, the possible degradation effect either went unnoticed or was negligible.

The concentration had little effect on the LCST. This would mean that the coexistence curve tends to be either flat or horizontal, which is in agreement with the results of other workers (7, 9, 10).

Acknowledgment

The author thanks D. Patterson for the most helpful discussions held during this work.

**Figure 2. Temperature vs. r_A in polystyrene-acetates system**

Literature Cited

- (1) Allen, G., Baker, C. H., *Polymer*, **6** (4), 181 (1965).
- (2) Bawn, C. E., Freeman, R. F., Kamalidin, A. R., *Trans. Faraday Soc.*, **46**, 1107 (1950).
- (3) Delmas, G., Patterson, D., Somcynsky, T., *J. Polym. Sci.*, **57**, 79 (1962).
- (4) Flory, P. J., "Principles of Polymer Chemistry," p 548, Cornell Univ. Press, Ithaca, N.Y., 1953.
- (5) Fox, T. G., Flory, P. J., *J. Amer. Chem. Soc.*, **73**, 1915 (1951).
- (6) Ham, J. S., Bolen, M. C., Hughes, J. K., *J. Polym. Sci.*, **57**, 25 (1962).
- (7) Patterson, D., Delmas, G., Somcynski, T., *Polymer*, **8** (10), 503 (1967).
- (8) Prigogine, I., Defay, R., "Chemical Thermodynamics," p 239, Longmans Green and Co., London, England, 1952.
- (9) Shultz, A. R., Flory, P. J., *J. Amer. Chem. Soc.*, **74**, 4760 (1952).
- (10) Tompa, H., "Polymer Solutions," Chap. 4, Butterworths, London, England, 1956.
- (11) Weissberger, A., "Techniques of Organic Chemistry," Vol VII, Interscience, New York, N.Y., 1948.

Received for review March 26, 1973. Accepted February 12, 1974.