

Mixtures of Tetrabromobisphenol-A Polycarbonate and Bis(2-ethoxyethyl)ether: Examples of a Lower Critical Solution Temperature

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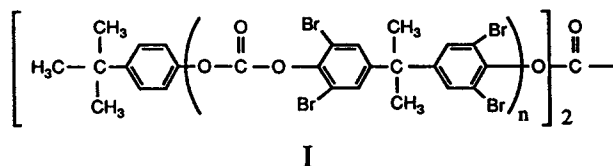
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SYNOPSIS

Tetrabromobisphenol-A polycarbonate was found unexpectedly to form mixtures with the solvent bis(2-ethoxyethyl)ether that display a lower critical solution temperature at about normal room temperature and less than about 10 wt % polymer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymer-solvent and polymer-polymer mixtures may exhibit upper critical solution temperatures (UCST) or lower critical solution temperatures (LCST).^{1,2} The former, which describe dissolution with increasing temperature, are more commonly encountered than are LCSTs, which describe phase separation with increasing temperature. The polymer tetrabromobisphenol-A polycarbonate (TBBA-PC), I (*Chemical Abstracts* registry number 28774-93-8), has been described as a potential permselective membrane material for gas separations.³



During recent solubility and phase equilibria studies with this polymer, it was unexpectedly observed that it forms solutions with bis(2-ethoxyethyl) ether, also known as diethylene glycol diethyl ether or ethyl diglyme (*Chemical Abstracts* registry number 112-

36-7), that exhibit lower critical solution temperature behavior. This note describes this behavior.

EXPERIMENTAL

The polymer was prepared by phosgenation of tetrabromobisphenol-A in the presence of pyridine in methylene chloride solvent using *p-t*-butylphenol as endblocker. It was precipitated in excess heptane. After drying, the polymer was a low-density fibrous "fluff" with relatively high surface area. The inherent viscosity was 0.412 dL/gm at 25°C in methylene chloride. The solvent ethyl diglyme, 98+%, was used as received from Aldrich Chemical Co.

Mixtures were prepared in 4 dram-capacity glass vials at room temperature. The lower viscosity mixtures were mixed on mechanical rollers for time sufficient to dissolve the polymer completely. Higher viscosity mixtures were mixed by allowing them to stand at room temperature for several days followed by repeated centrifugation that was interrupted occasionally to invert the vials. Mixtures containing up to 70 wt % polymer were thus prepared. Mixtures containing 80% polymer could not be prepared this way; such solutions could be prepared by using 80% methylene chloride as solvent for the polymer-ethyl diglyme mixtures followed by removal of the solvent at about 70–80°C.

Phase transformations were determined by using (a) a cloud-point apparatus similar to the equipment described by Bernstein et al.⁴ or (b) by hot-stage microscopy employing a Leitz Ortholux microscope equipped with a Mettler FP80/FP82 hot stage, a 32× (0.40 numerical aperture) phase-contrast objective with a free working distance of 6.45 mm, and a Heine condenser. Mixtures that had been prepared in methylene chloride contained so many irregularities, bubbles, rough surface features, etc., that it was very difficult to obtain reliable transition temperatures from them using either of these two techniques; the values reported here were obtained on samples prepared in the absence of methylene chloride.

RESULTS AND DISCUSSION

Average transition temperatures are shown in Table I for mixtures containing 5–70 wt % polymer. These temperatures are plotted vs. the concentration in Figure 1. The characteristic shape of a curve representing a lower critical solution temperature at about 25°C is best described by the equation⁵

$$\begin{aligned} \text{Transition temp (}^\circ\text{C)} \\ = 24.891 \exp[(\text{concn, wt \%} - 1.1138)^2 / 4445.9] \end{aligned}$$

Compositions below the line are homogeneous, clear, and consist of only one visible phase; those above the line are opaque, milk-white in color, and consist of one or possibly more visible phases. The transitions are completely and rapidly reversible. The temperatures are quite reproducible; those determined using the hot stage were readily reproducible to $\pm 0.1^\circ\text{C}$.

The extent to which solutions of TBBA-PC exhibit LCST behavior is not known. Over 100 organic compounds have been examined for their solvent effect on the polymer; only bis(2-ethoxyethyl) ether has been observed so far to result in a solution with an LCST. The viscosities of the mixtures vary considerably from "waterlike" consistency at low polymer concentrations to stiff and rubberlike solids at the higher concentrations. It may be noteworthy that the transition temperatures for mixtures consisting of about 15% polymer or less are at or slightly below normal room temperature; those consisting of 43.1% polymer are at normal human body temperature. The potential utility of such mixtures could encompass optical devices, solar shades and glazing applications, visible temperature-indicating panels, toys, and novelties.

CONCLUSIONS

Mixtures consisting of tetrabromobisphenol-A polycarbonate and bis(2-ethoxyethyl) ether display

Table I Transition Temperatures for Mixtures of TBBA-PC and Ethyl Diglyme

Polymer Concentration (wt %)	Average Transition Temperature ($^\circ\text{C}$)	Method
5.00	25.20	Hot-stage microscopy
10.57	25.40	Hot-stage microscopy
15.45	25.95	Hot-stage microscopy
20.58	26.75	Hot-stage microscopy
25.51	28.50	Hot-stage microscopy
30.62	30.25	Hot-stage microscopy
40.26	35.05	Cloud-point apparatus
50.70	44.40	Cloud-point apparatus
60.06	53.60	Cloud-point apparatus
70.41	73.25	Cloud-point apparatus
79.58	^a	

^a Too viscous for convenient and thorough mixing.

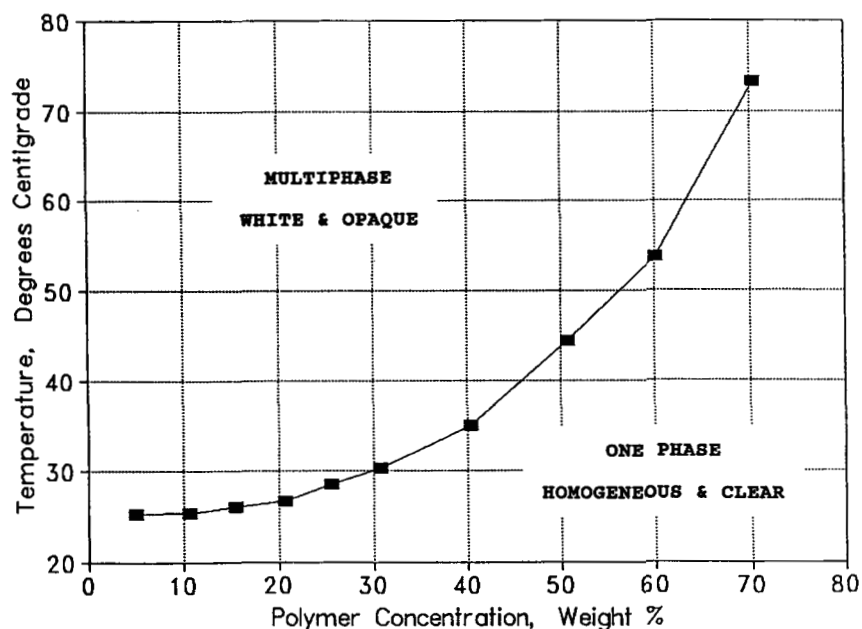


Figure 1 TBBA-PC-ethyl diglyme mixtures. Transition temperature vs. polymer concentration.

thermal properties that are characteristic of a lower critical solution temperature. The minimum temperature occurs at about 25°C for concentrations less than about 10 wt % polymer.

The polymer was supplied by James E. Magner and Thomas O. Jeanes of Central Research & Development, The Dow Chemical Co.

REFERENCES

1. O. Olibisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
2. D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, New York, 1978, Vol. 1.
3. U.S. Pats. 4,772,392 (Sept. 20, 1988); 4,955,993 (Sept. 11, 1990); 4,962,131 (Oct. 9, 1990); 4,975,228 (Dec. 4, 1990) (to The Dow Chemical Co.).
4. R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules*, **10**(3), 681-686 (1977).
5. Hewlett-Packard Program No. 00112-75-1 for HP Model 75C computer.

Received March 5, 1992

Accepted May 12, 1992