Eur. Polym. J. Vol. 26, No. 3, pp. 375-377, 1990
Printed in Great Britain. All rights reserved

0014-3057/90 $3.00 + 0.00

SOLUBILITY IN WATER OF TRIBLOCK (PEP) COPOLYMERS OF ETHYLENE AND PROPYLENE OXIDES

Lubomír Šimek
Faculty of Technology, Technical University, Gottwaldov, Czechoslovakia

Stanislav Petřík and František Hadobaš
Research Institute for Plastics and Rubber Technology, Gottwaldov, Czechoslovakia

Miloslav Bohdanecký
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia

(*Received* 19 *May* 1989)

Abstract—Aqueous solutions of hydroxyl-terminated triblock copolymers of ethylene and propylene oxides display turbidity, both on heating and cooling. The lower critical solution temperatures increase with increase in the content of ethylene oxide units. Phase diagrams obtained with acetyl-terminated copolymers are more involved and give evidence of an important effect of end groups.

INTRODUCTION

Aqueous solutions of homopolymers of ethylene (E) and propylene (P) oxides are known to display lower critical solution temperatures (LCST) [1-3], the limiting values of LCST for $M \to \infty$ being $Q_L \simeq 96°$ for PEO and $Q_L \simeq -56°$ for PPO [1]. Triblock copolymers of these ethers where the central block is formed by a sequence of propoxamer units (EPE copolymers) also phase separate on heating but some of them also exhibit microphase formation at temperatures between 0° and LCST [4, 5].

This paper describes the phase behaviour of aqueous solutions of copolymers (PEP) where the central block is composed of a sequence of ethoxamer units.

EXPERIMENTAL PROCEDURES

Copolymers (PEP)

These were provided by the Petrochemical Research Insititute, Prievidza, Czechoslovakia, and were identical with those used previously [6].

Acetyl-terminated copolymers (PEP-Ac)

These were prepared by acetylation under conditions prescribed for the determination of hydroxyl groups. A mixture of dried PEP, acetic anhydride and freshly distilled pyridine (in weight proportion 3:1:6) was heated in a closed vessel at 80° for 4 hr. Excess of anhydride was neutralized by 20% aqueous NaOH. The oil layer containing the diacetate of the copolymer was separated from the aqueous layer and distilled to remove water and pyridine (at 40–45° and 2 kPa, then at 110° and 0.2 kPa). The rest of sodium acetate which precipitated from the product was removed by filtration. The hydroxyl end-groups were determined by the standard method (Table 1). Before use, the PEP and PEP-Ac samples were dried in a desiccator over phosphorus pentoxide for three days at 25°.

Solutions in distilled water were prepared by shaking the weighed components overnight at room temperature. They were charged into small thin-wall glass ampoules (1 cm^3) and tightly closed.

Measurements of cloud point temperatures in the range from −65 to 150° were performed in three baths (acetone/dry ice; cryostat; silicone oil). The rates of heating and cooling were about 0.5° min^{-1}. Cloud point temperatures were obtained by visually observing the onset of disappearance of cloudiness. Phase transitions were reversible and reproducible.

RESULTS AND DISCUSSION

Hydroxyl-terminated PEP copolymers

Aqueous solutions of all PEP copolymers with hydroxyl end-groups become cloudy both on heating (at temperatues t'') and cooling (at temperatures t') (Fig. 1). The dependences of t'' vs c are very moderate at concentrations <*ca* 50% ($w_2 \leqslant 0.5$) and pronounced above this value. Highly concentrated solutions are stable even at 100–120°. In the concentration range investigated ($w_2 \geqslant 0.1$), the curves show no clear minimum so that an exact value of LCST cannot be determined. We take, rather arbitrarily, the t'' temperature at $w_2 = 0.2$ as an approximate value of LCST. These values strongly increase with the mole fraction of ethoxamer units (Fig. 2) and are remarkably close to those for EPE copolymers of the same molecular weight [4].

Following common practice, we compare them with the values computed from the LCST values for homopolymers of the same molecular weight, assuming additivity (broken line on Fig. 2). The LCST value for PEO (at $M = 10^3$) has been estimated by extrapolating to $\bar{M}_n = 10^3$ the plot of $1/t''$ vs $1/\bar{M}_n^{1/2}$ (for data, see Refs [2, 3]). There is some disagreement about LCST for PPO at $\bar{M}_n = 10^3$. A very low value has been reported [7] but more recent results are higher and fall in the range 20–30° [8–10].

The LCST values for copolymers (both EPE and PEP) are located below the line, the differences being 30–40°. Obviously, the copolymers phase-separate at lower temperatures than expected.

Table 1. Characteristics of copolymers PEP[a]

Hydroxyl terminated			Acetyl terminated	
Sample	w_c	$\bar{M}_n$	Sample	c_{OH} (%)
PEP I/1	0.343	1090	PEP-Ac I/1	0.1
PEP I/2	0.502	1040	PEP-Ac I/2	0.4
PEP I/3	0.688	1280	PEP-Ac I/3	0.2
PEP II/3	0.502	2000	PEP-Ac II/2	—

[a] w_c, Weight fraction of ethoxamer units; $\bar{M}_n$, number-average molecular weight (calculated from the content of hydroxyl end-groups); c_{OH}, weight percent of hydroxyl groups.

The cloud-point curves at low temperatures (t' vs w_2) usually have three regions (Fig. 1). At low copolymer concentrations ($w_2 < 0.4$), solutions become cloudy on cooling to temperatures between 10 and 0° (region III). At intermediate concentrations ($0.4 < w_2 < 0.7$–0.9), solutions are stable even at $-50°$ (region II). With some copolymers, phase separation (region I) is observed also at high concentrations.

The t' (w_2) curves resemble the phase diagrams of crystalline polymers in poor solvents (e.g. polyethylene in diphenyl ether [11]) which exhibit liquid–liquid separation at low polymer concentrations in addition to the liquid–solid boundary at high w_2 and where the upper critical solution temperature (UCST) is comparable to, or even higher than, the polymer melting temperature.

Region I can be interpreted as a depression by diluent of the melting temperature T_m of the crystalline polymer (for T_m values of PEP, cf. Ref. [6]), i.e. as a crystalline solid–liquid equilibrium. The absence of this region with PEP I/1 is due to its very low melting temperature.

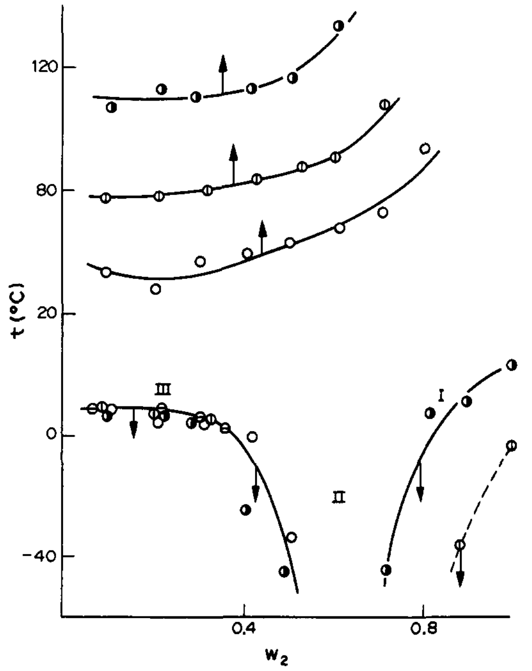

Fig. 1. Cloud point curves of the system PEP–water. Data points: ○, PEP I/1; ⦶, PEP I/2; ◑, PEP I/3. Arrows indicate onset of turbidity on heating (↑) and cooling (↓). For details see text.

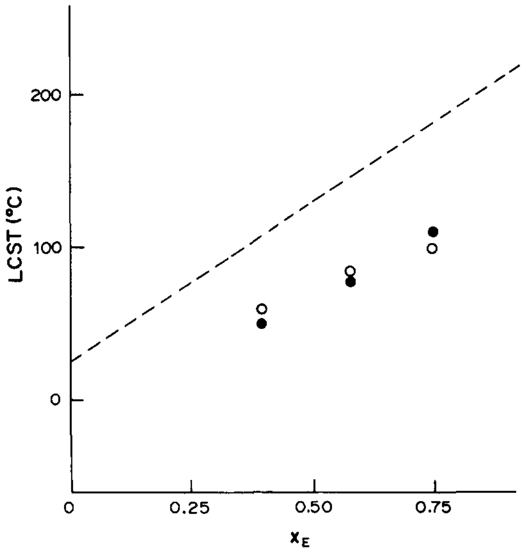

Fig. 2. Dependence of LCST on the copolymer composition. Data points: ○, PEP (this paper); ●, EPE [4]. Broken line connects LCST values for PEO and PPO at $\bar{M}_n = 10^3$.

Unlike many polymer–solvent systems investigated so far, the dependences in region I are concave downward and, in this respect, are similar to those found PEO [2]. Hager and Macrury [12] tried to fit this dependence by a curve computed according to the theory of solid-diluent equilibria in polymeric systems, assuming that the χ parameter is independent of temperature and concentration. However, the calculated curve was concave upward. Agreement between theory and experiment would probably be obtained by taking account of the concentration and temperature dependences of χ.

As for region III, there are at least three reasons which make us hesitate to interpret it as a simple liquid–liquid equilibrium.

(i) It has not been found with PEO.

(ii) The upper critical solution temperature of PEO in water is very high (*ca* 220° for $\bar{M}_n = 2 \times 10^3$ [3]) and it is unlikely that it would be decreased to 10° by copolymerization with propylene oxide.

(iii) Data points for all PEP samples (including those which have acetyl end-groups) lie on the same curve and are independent of molecular weight and composition (c.f. also Figs 3 and 4).

Figure 3a presents cloud point curves for PEP II/2 ($\bar{M}_n = 2000$). The $t''(w_2)$ dependence is similar to that for PEP I/2 and, as can be expected, the t'' temperatures are lower. However, a few degrees below the $t''(w_2)$ curve, there is a closed solubility gap which has not been observed with any copolymer of lower molecular weight.

I-PEP-Ac

For PEP-Ac I/3 the t'' temperatures are lower than for PEP I/3 but the shape of the curve $t''(w_2)$ is the same (Fig. 4). The solubility diagrams for PEP-Ac A/1 and I/2 are quite unlike those for their hydroxyl-terminated counterparts. They have a decreasing branch at low concentrations, a sharp minimum at $0.4 \leqslant w_{2,m} \leqslant 0.5$ whereupon they strongly increase

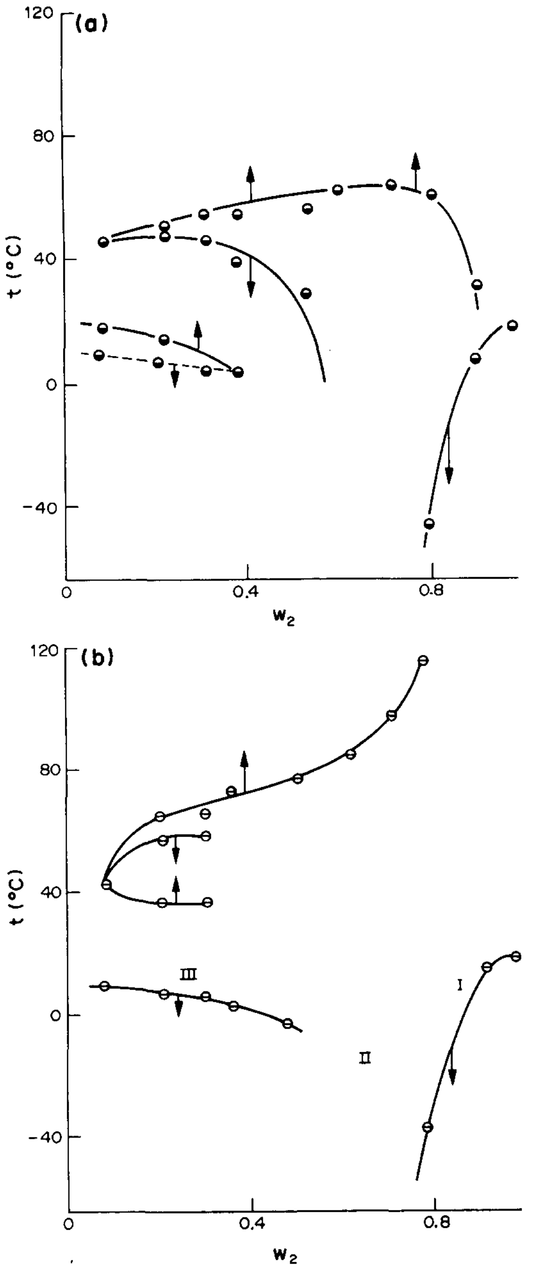

Fig. 3. Cloud point curves for copolymer PEP II/2. (a) Hydroxyl-terminated sample, (b) acetyl terminated sample. Arrows as in Fig. 1.

over a narrow range. The temperatures of the minima are 0° and 15° for PEP-Ac I/1 and 1/2, respectively.

The temperature range between t' and t'' (where the systems are homogeneous) is narrower for acetyl terminated copolymers, and the more so the higher is the content of propoxamer units. Narrowing is particularly marked at $w_2 < w_{2,m}$ but, even at high concentrations ($w_2 > w_{2,m}$) the t'' values are reduced by acetylation. At $w_2 = 0.7$, the PEP copolymers are soluble above 100° but the corresponding diacetates phase separate on heating at temperatures between 20 and 70°.

The diagram for PEP-Ac II/2 ($\bar{M}_n \simeq 2000$) is even more complicated, particularly at lower concentrations (Fig. 3b). At $w_2 = 0.2$ there are two narrow temperature ranges where solutions are clear, and three broad temperature regions where they are cloudy.

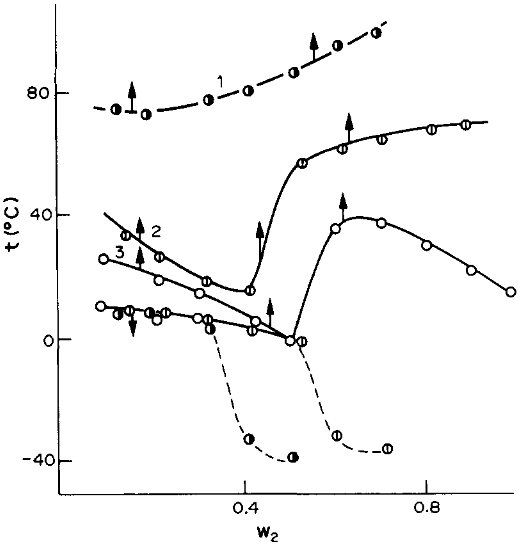

Fig. 4. Cloud point curves for PEP-Ac. Data points: ◑, PEP-Ac I-3 (1, 1a); ⦶, PEP-Ac I/2 (2, 2a); ○, PEP-Ac I-1 (3, 3a). Arrows as in Fig. 1.

Figures 3 and 4 are similar to complicated phase diagrams of non-ionic amphiphilic surfactants based on polymers and copolymers of ethylene oxide [3, 13, 14]. By analogy, micelles and organized phases may be supposed to form also with our systems.

REFERENCES

1. P. Molyneux. *Water Soluble Synthetic Polymers. Properties and Behaviour*, Vol. I, p. 58. CRC Press, Boca Raton (1982).
2. S. Saeki, N. Kuwahara, M. Nakata and M. Kaneko. *Polymer* **17,** 685 (1976).
3. G. N. Malcolm and J. J. Rowlinson. *Trans. Faraday Soc.* **53,** 921 (1957).
4. N. V. Prasad, T. T. Luong, A. T. Florence, J. Paris, C. Vautron, M. Seiller and F. Puisieux. *J. Colloid Int. Sci.* **69,** 225 (1979).
5. H. Hespe, J. Crone, E. H. Müller and E. F. Schäfer. *Angew. Makromelek. Chem.* **123/124,** 189 (1984).
6. L. Šimek, S. Petřík, F. Hadobaš and M. Bohdanecký. *Eur. Polym. J.* **26,** 371 (1990).
7. N. G. Gaylord (Ed.). *Polyethers.* Interscience, New York (1963).
8. V. N. Kuznetsov, V. B. Kogan and M. S. Vilesova. *Vӯsokomolek. Soedin A* **11,** 1330 (1969).
9. K. S. Sandell and D. A. I. Goring. *J. Polym. Sci.; Part A-2* **9,** 115 (1971).
10. Ye. S. Billimova, G. A. Gladkovskyi, V. M. Golubov and Z. N. Medved. *Vӯsokomolek. Soedin A* **22,** 2240 (1980).
11. R. B. Richards. *Trans. Faraday Soc.* **42,** 10 (1946).
12. L. S. Hager and T. B. Macrury. *J. appl. Polym. Sci.* **25,** 1559 (1980).
13. B. Lindman and H. Wennerström. In *Solution Chemistry of Surfactants. Theoretical and Applied Aspects* (Edited by E. J. Fendler and K. L. Mittah), p. 3. Plenum Press, New York (1982).
14. B. Lühmann and H. Finkelmann. *Colloid Polym. Sci.* **264,** 189 (1986).