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Effect of temperature on the solution properties in 2-ethoxyethanol of statistical copolymers of methacrylic acid and methyl methacrylate

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SUMMARY

The temperature dependence of the second virial coefficient and intrinsic viscosity of statistical copolymers of methyl methacrylate and methacrylic acid in 2-ethoxyethanol was investigated. It was found that the Θ-temperatures of copolymers are outside the temperature range given by the Θ-values for poly(methacrylic acid) and poly(methyl methacrylate). Their dependence on the copolymer composition has a discontinuity. Simple theoretical considerations have shown that this behaviour may be expected with copolymers composed of monomer units dissolving, respectively, with absorption and evolution of heat.

INTRODUCTION

In a study of the conformational properties of poly(methacrylic acid), PMAA, in organic solvents (1), we have found that phase separation takes place in solutions of PMAA in 2-ethoxyethanol on raising temperature. Basing on the intrinsic viscosity data, we estimated the Θ-temperature to be 65°C. This polymer-solvent pair is one of the few systems where the Θ-temperature corresponding to the lower critical solution temperature (LCST) is lower than the normal boiling point of the solvent.

2-ethoxyethanol is known to be also a Θ-solvent for poly(methyl methacrylate), PMMA. In this case, however, the Θ-temperature corresponds to the upper critical solution temperature (UCST) (2,3). The difference in the Θ-values reported (39 and 27°C) is not relevant for the discussion to follow.

In this paper we present results of measurements of the temperature dependence of the second virial coefficient, A_2, and intrinsic viscosity, $[\eta]$, of statistical copolymers of methacrylic acid, MAA, and methyl methacrylate, MMA, in 2-ethoxyethanol, and point out some interesting features in the behaviour of statistical copolymers built up from monomers whose homopolymers differ in the character of the critical solution temperature in a common solvent.

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EXPERIMENTAL

Statistical copolymers of methyl methacrylate and methacrylic acid were prepared by radically initiated copolymerization at 50°C in toluene with bis-azoisobutyronitrile as initiator (samples CO-1 and CO-2) or in a water-ethanol mixture (1:1 by volume) with potassium persulfate (sample CO-3). The content of MAA units was determined by NMR according to Klesper (4). The characteristics of copolymers are collected in Table 1.

Poly(methacrylic acid) samples were fractions A-1-1b and A-2-1 (molecular weight $M_w x 10^{-6}$=2.24 and 0.52); their preparation and characterization have been described elsewhere (1).

Viscosity and light scattering measurements, including the determination of the refractive index increment, were carried out as described in Ref.(1).

Table I Characteristics of MAA-MMA copolymers

Sample	x_{MAA} [a]	$M_w x 10^{-6}$	$[\eta]_{25}$ [b]
CO-1	0.08	0.40	67
CO-2	0.20	1.19	174
CO-3	0.91	0.47	95

[a] Mole fraction of MAA
[b] Intrinsic viscosity (cm^3/g) in 2-ethoxyethanol at 25°C

RESULTS AND DISCUSSION

Fig.1 presents the temperature dependences of the second virial coefficient, A_2, for three MAA-MMA copolymers (with the mole fraction of MAA, x_{MAA}=0.08, 0.20, and 0.91) and two PMAA samples. The broken curve corresponding to PMMA was constructed on the basis of reported data (2).

It is seen that the slope, dA_2/dT, of these dependences decreases with increasing content of MAA units, chaging sign at $x_A \cong 0.2$. Since the dA_2/dT value is given mainly by the heat of dilution (5), this finding means that, as x_{MAA} increases, the copolymer solutions change from endothermic through athermal to exothermic ones. The intrinsic viscosity data (Fig.2) corroborate this conclusion.

A qualitative explanation is not difficult. Since the heat of dilution in 2-ethoxyethanol is positive for PMMA and negative for PMAA, the heat of dilution of statistical copolymers is a sum of endothermic and exothermic contributions. These contributions can match at certain composition, rendering the system athermal.

A somewhat surprising result is found if we try to assess the dependence of the Θ-temperature on the copolymer composition. Rough Θ-values can be obtained by extrapolating the $A_2(t)$ dependences to $A_2=0$ in Fig.1. Those for x_{MAA}=0.08 and 0.20 are definitely lower than that for PMMA (all of them

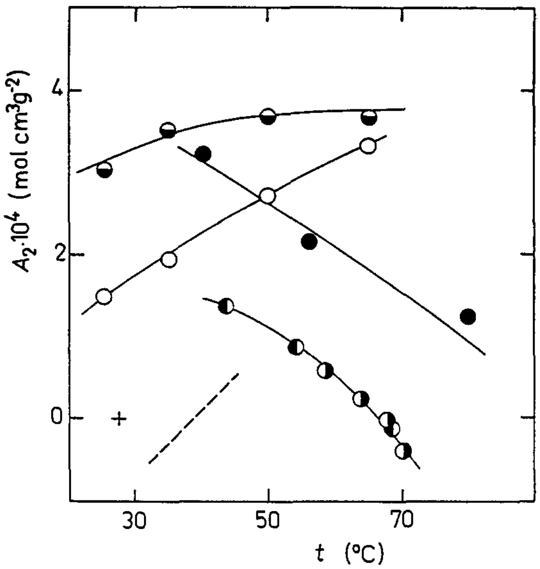

Figure 1. The temperature dependence of the second virial coefficient A_2 of MAA-MMA copolymers in 2-ethoxyethanol. Copolymers: CO-1 ○ , CO-2 ◒ , CO-3 ● . Homopolymers: PMAA A-1-1b ◑ , A-2-1 ◐ ; PMMA broken curve (calculated according to Ref.(2). Cross denotes Θ-temperature for PMMA according to Ref.(3).

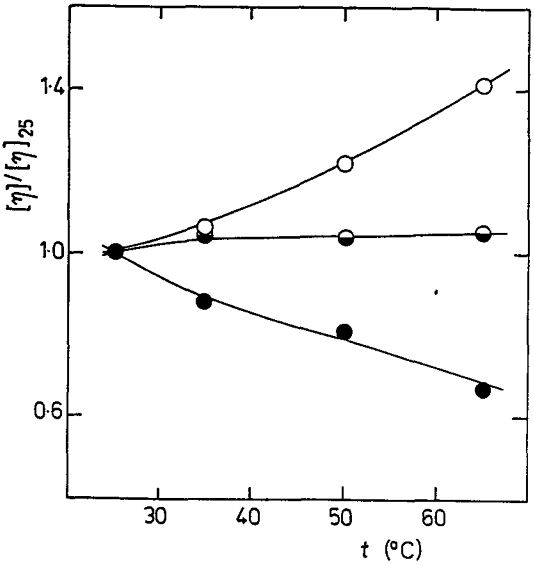

Figure 2. The temperature dependence of the intrinsic viscosity of MAA-MMA copolymers in 2-ethoxyethanol. Notation as in Fig.1. $[\eta]_{25}$ intrinsic viscosity at 25°C.

being UCST), while the Θ-temperature for $x_{MAA}=0.91$ is clearly higher than that for PMAA (both being LCST). This finding indicates that the dependence of the Θ-temperature on composition is not continuous. This is opposite to the dependences reported so far (2,6), where the Θ-values for copolymers were within, or below, the temperature range given by the Θ-temperatures for the respective homopolymers.

This difference can be accounted for qualitatively in the following way. In the vicinity of the Θ-point, the binary cluster integral β describing the excluded volume effect is expressed (2) as

$$\beta = \beta_0(1 - \Theta/T) \tag{1}$$

At T = Θ, the binary cluster integral vanishes, and the Θ-temperature is an UCST for $\beta_0>0$ and a LCST for $\beta_0<0$.

For statistical copolymers, the mean binary cluster integral, $\bar{\beta}$, is approximately expressed as (7):

$$\bar{\beta} = \beta_1x_1 + \beta_2x_2 + \Delta\beta x_1x_2 \tag{2}$$

$$\Delta\beta = 2\beta_{12} - \beta_1 - \beta_2 \quad , \tag{3}$$

where x_1 and x_2 are mole fractions of the copolymer components, and β_1, β_2, and β_{12} are binary cluster integrals for the 1-1, 2-2, and 1-2 interactions.

Assuming for simplicity Δβ to be zero, we obtain from eqns (1) and (2):

$$\Theta = (\beta_{o,1}\Theta_1x_1 + \beta_{o,2}\Theta_2x_2)/(\beta_{o,1}x_1 + \beta_{o,2}x_2) \tag{4}$$

We define the quantity $(\Theta - \Theta_2)/(\Theta - \Theta_1)$ which, according to eqn (4), is

$$(\Theta - \Theta_2)/(\Theta - \Theta_1) = -(\beta_{o,1}/\beta_{o,2})(x_1/x_2) \tag{5}$$

If $\beta_{o,1}/\beta_{o,2}>0$, i.e., if the critical solution temperatures for homopolymers are of the same type, the quantity $(\Theta - \Theta_2)/(\Theta - \Theta_1)$ is negative, hence the Θ-temperatures of copolymers lie between those of homopolymers. The data reported so far (2,6) refer to the case where both homopolymers have the upper critical solution temperature. Downward deviations from the prediction observed with some of them can be assigned to the effect of the mixed term $\Delta\beta\ x_1x_2$ in eqn (2). The quantity Δβ was positive in all cases, so that, for β to be zero, the sum of the first terms in eqn (2) had to be negative and the Θ-temperature lower than that calculated according to eqn (4), i.e. with Δβ = 0.

To explain the results for the MMA-MAA copolymers in 2-ethoxyethanol, we need not invoke the effect of the Δβ term because the ratio $\beta_{o,2}/\beta_{o,1}$ is negative. Then the quantity $(\Theta - \Theta_2)/(\Theta - \Theta_1)$ is positive, so the Θ-temperatures of copolymers should be outside the temperature range given by the Θ-values of PMMA and PMAA. Since, moreover, the denominator in eqn (4) is zero at $x_1/x_2 = -\beta_{o,2}/\beta_{o,1}$, the depen-

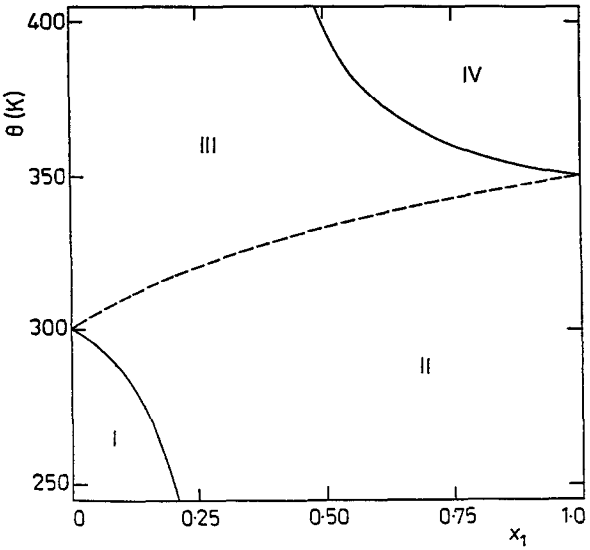

Figure 3. Dependence of the Θ-temperature on composition of statistical copolymers calculated according to Eqn (4) for Θ_1 = 350 K and Θ_2 = 300 K. Broken curve for $\beta_{o,1}/\beta_{o,2} = 2$. Solubility range (for $M \to \infty$) in III and IV for $\beta_{o,1} > 0$ and in I and II for $\beta_{o,1} < 0$. Full curves for $\beta_{o,1}/\beta_{o,2} = -2$. Solubility range (for $M \to \infty$) in I and IV for $\beta_{o,1} > 0$, and in II and III for $\beta_{o,1} < 0$.

dence of the Θ-temperature on composition is discontinuous. This is illustrated by Fig.3 presenting a dependence of Θ vs x_1 calculated according to eqn (4) with Θ_1 = 350 K, Θ_2 = 300 K, and $\beta_{o,1}/\beta_{o,2}$ = 2 and -2. The curve for the latter case has the same shape as the estimated dependence for the MMA-MAA copolymers.

It may be concluded that such a behaviour can be expected with statistical copolymers, if one of the corresponding homopolymers has an UCST and the other a LCST, i.e., if the copolymers are composed of monomer units dissolving, respectively, with absorption and evolution of heat.

Since the Θ-temperature is the limiting value of the CST for $M \to \infty$, the conclusions of the present study should be taken into account when fractionating copolymers of the above type or studying their solubility (cf. Fig.3) or phase equilibria, particularly if the samples are heterogeneous in composition.

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