Solution behaviour of poly(methacrylic acid) in an organic theta solvent*

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(Received 9 June 1986; revised 4 September 1986; accepted 21 September 1986)

Solution-polymerized poly(methacrylic acid) was fractionated and the phase separation behaviour of the fractions was examined in *N*,*N*-dimethyl formamide/1,4-dioxane mixtures. For the 5:7 (DMF/dioxane v/v) mixture the theta temperature was found to be (27.1 ± 0.2)°C. Viscosity and light scattering measurements were made for seven fractions. The value of K_θ obtained is higher in the organic solvent than the literature reported value in aqueous solution indicating that the polymer exists in a more expanded form in the organic theta solvent.

(Keywords: poly(methacrylic acid); theta solvent; unperturbed dimensions; polyelectrolyte; conformational transition)

INTRODUCTION

Poly(methacrylic acid) (PMA) in solution undergoes a conformational transition during the course of its ionization[1,2]. PMA exists in a compact form at low degrees of ionization and in a more expanded conformation at higher degrees of ionization. The unperturbed dimensions corresponding to the two conformational forms at low and high degrees of ionization may differ. It has been reported[3,4] that some of the synthetic polyelectrolytes exhibiting ionization induced conformational transition possess larger unperturbed dimensions in organic solvents as compared with their characteristic dimensions in aqueous solutions. A large increase in intrinsic viscosity has also been observed[2] when a miscible organic solvent is added to the aqueous solutions of PMA. The reported[5] theta solvent for the unionized PMA is 0.002 N HCl at 30°C. We have examined the phase separation behaviour of unionized PMA in *N*,*N*-dimethyl formamide/1,4-dioxane mixtures in an effort to determine the theta conditions and the solution behaviour of the unionized PMA in the organic theta solvent.

EXPERIMENTAL

Methacrylic acid was polymerized in solution at 65°C using 0.1 wt.% potassium peroxydisulphate as initiator. Water/1,4-dioxane mixture is used as solvent. The details have been given elsewhere[2]. The polymer had a molecular weight (M_w) 6.5×10^5.

Methanol and diethyl ether used for fractionation were middle cuts of distilled commercial grade solvents. 1,4-Dioxane used for viscosity and light scattering measurements was purified as described earlier[2]. *N*,*N*-dimethyl formamide (DMF), LR grade, was initially dried over anhydrous $MgSO_4$ for 10–12 h and over P_2O_5 for an additional 10–12 h. It was distilled over P_2O_5 under reduced pressure. The middle cut was collected and stored over molecular sieves (4 Å) in amber coloured bottles.

The polymer was fractionated by a fractional precipitation technique from 1% (w/v) solution in methanol using diethyl ether as a non-solvent. Conventional procedures were employed except that after the addition of the non-solvent, the temperature of the mixture was lowered to obtain a homogeneous solution. In order to obtain sharp fractions, the separated fraction was redissolved in methanol and subjected to a second fractionation. The supernatant layer from the reprecipitation step was concentrated and returned to the original solution before isolating the next fraction. Seven fractions were isolated (amounting to 80% of the polymer used for fractionation) and the lower molecular weight material was discarded.

Precipitation temperatures were determined by visual observation of the appearance and disappearance of turbidity in the solution suspended in a water bath, the temperature of which was varied at the rate of 0.1°C/min. The blurring of a graduated scale viewed through the solution was taken as the onset of precipitation. The precipitation temperature determined during the heating and cooling cycles agreed to within ±0.2°C.

Light scattering measurements were carried out with a Brice-Phoenix BP-3000 series light scattering photometer using cylindrical cells. Incident unpolarized light of wavelength 436 nm was employed and scattering intensities in the angular range 35–135° were determined. Benzene was used as a secondary standard and a value of $48.4 \times 10^{-6}\ \mathrm{cm}^{-1}$ was used for Rayleigh ratio for benzene. Refractive index increment measurements were carried out with a BP-2000 series differential refractometer calibrated with aqueous KCl solutions.

The data was treated according to the Zimm method.

Viscosity measurements were carried out in an open Ubbelohde dilution viscometer with an efflux time of 132.1 ± 0.1 s for the theta solvent at 27.1°C. Kinetic energy corrections were negligible.

RESULTS AND DISCUSSION

The choice of organic solvents for PMA are severely

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* NCL Communication No. 3963

0032-3861/87/081426–03$03.00
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limited. The Mark-Houwink-Kuhn (MHK) exponent reported[6] for unneutralized PMA in methanol (0.51) indicates that methanol is a poor solvent. However, no precipitation of the dissolved PMA from its solution in methanol was observed in the temperature range of 5–45°C. Hence, mixtures of DMF, a good solvent, and **1,4**-dioxane (in which PMA could not be dissolved if the solvent is totally moisture-free) were selected for phase separation studies. The refractive indices of the solvents selected (n_D^{25}; 1.4269, 1.4203 for **1,4-dioxane** and DMF, respectively) are very close to each other’. Initially, varying ratios of the two solvents were used and precipitation temperatures were determined for a single concentration (~ 0.5 %) solution of fraction III. A solvent mixture of composition 5: 7; **DMF:1,4-dioxane** (v/v) was selected for detailed studies.

Figure 1 shows the plots of the precipitation temperature, T_p vs. polymer concentration, C, for the six fractions examined. Although at low polymer concentration the precipitation temperature increases with increasing concentration, the maxima in these plots cannot be located with any accuracy. The method of **Flory–Osterheld**[8] was therefore employed. Precipitation temperatures at finite concentrations for the varying molecular weight samples were determined from the curves in ***Figure 1.*** Plots of $1/T_p$ vs. $(1/x^{1/2} + 1/2x)$, (where x is the degree of polymerization) were constructed and extrapolated linearly to zero abscissa (infinite molecular weight). The intercepts obtained were further linearly extrapolated to zero concentration of the polymer. The reciprocal of the intercept obtained (300.1 ± 0.2 K) shows the theta temperature for the system PMA in DMF/1,4-dioxane (5:7, v/v) as 26.9°C.

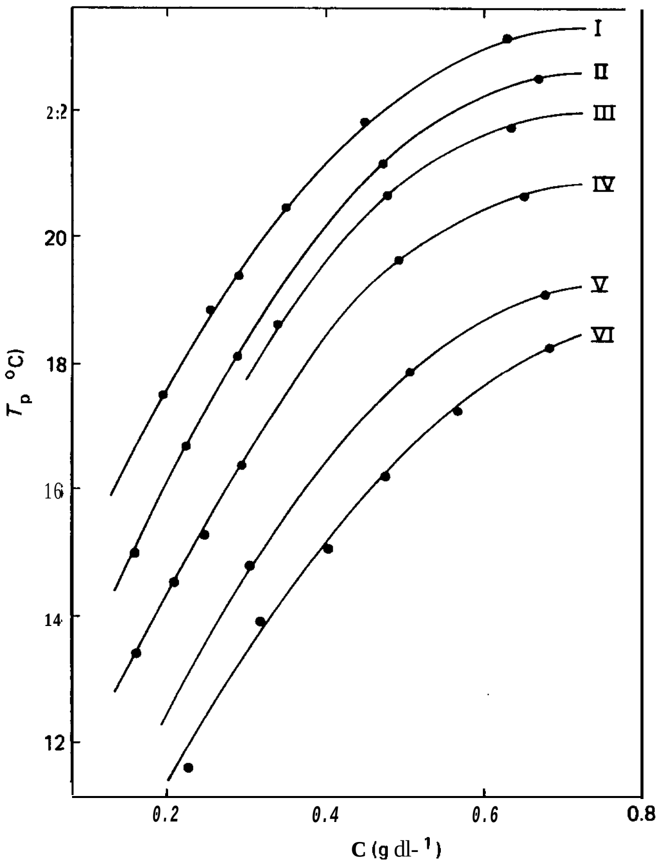

Figure 1 Variation of the precipitation temperature, T_p with concentration, C for PMA in **DMF/1,4-dioxane (5:7 v/v)** mixture. Fraction number is shown along the curve. Ordinate for fraction VII is shifted by +0.5°C

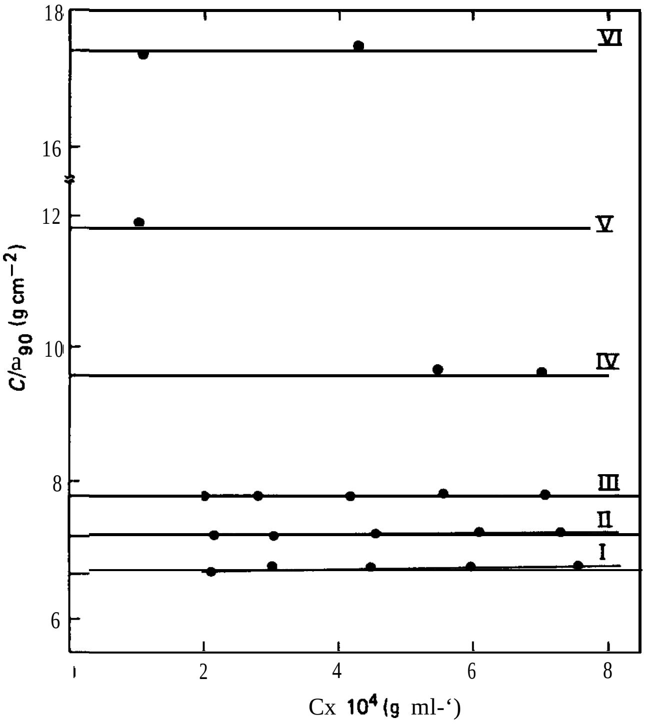

Figure 2 Excess scattering, ***C/R,,*** ***vs.*** concentration, C plots for the PMA fractions in **DMF/1,4-dioxane (5:7 v/v)** mixture at 27.1°C

Table 1 Viscosity and light scattering data for PMA fractions in **DMA/1,4-dioxane (5:7 v/v)** at 26.9°C

Fraction	$[\eta]$ (dl g^{-1})	$M_w \times 10^{-5}$	$\langle s^2\rangle_z^{1/2}$ (Å)	$\Phi \times 10^{-21}$
I	1.02	10.14	290	2.88
II	0.92	8.66	265	2.88
III	0.88	7.45	245	2.97
IV	0.78	5.62	215	2.95
V	0.67	4.06	180	3.03
VI	0.59	3.23”		
VII	0.54	2.75	150	2.93

‘Value determined in methanol

Figure 2 shows the light scattering data for the differing molecular weight PMA fractions in DMF/1,4-dioxane (5:7, v/v) at 26.9°C as plots of C/R_{90} ***vs. C.*** Straight line fits with zero slopes for the data show that the accuracy of the location of the theta temperature is satisfactory.

It is well recognized[9,10] that preferential adsorption can affect the molecular weights, osmotic second virial coefficients and the dimensions obtained from light scattering in a mixed solvent system. However, the correction for the preferential adsorption is dependent on the variation of the refractive index of the solvent mixture with the composition. When the two solvents employed have identical refractive indices, the multicomponent system may be treated by the method applicable to the (polymer/solvent) two component system”. The refractive indices of the two solvents used were close to each other and it is believed that preferential adsorption has not influenced the values obtained.

The value of dn/dc measured for the unneutralized PMA in the theta solvent was 0.099 ± 0.005 ml g^{-1}. The weight-average molecular weights, the root-mean-square radii of gyration obtained and the values of the intrinsic viscosities for the different fractions are listed in ***Table 1.***

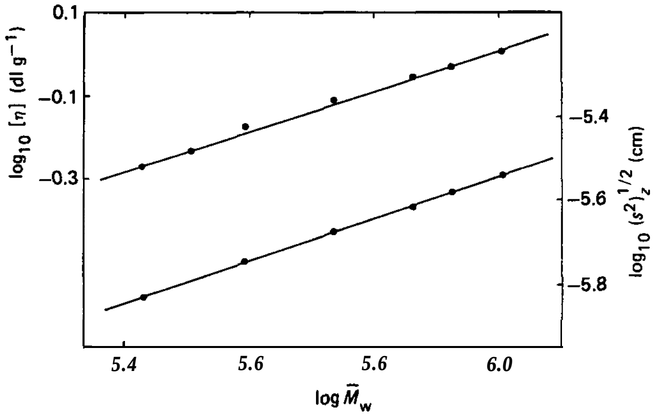

Figure 3 Intrinsic viscosity, $[\eta]$—molecular weight, M_w and dimension, $\langle s^2\rangle_z^{1/2}$-molecular weight, M_w plots for PMA in DMF/1,4-dioxane (5: 7 v/v) mixture at 27.1°C. Ordinate scale for the dimensions is shown on r.h.s.

In agreement with the data presented in Figure 2, the Zimm plots showed zero osmotic second virial coefficients.

The variation of the intrinsic viscosity and dimension with molecular weights are depicted in *Figure 3.* The relationships obtained are $[\eta]$ in dl/g and $\langle s^2\rangle_z^{1/2}$ in cm:

$$[\eta] = 1.03 \times 10^{-3} M^{0.50}$$

$$\langle s^2\rangle_z^{1/2} = 2.84 \times 10^{-9} M^{0.50}$$

The exponents obtained in the above equations confirm that unneutralized PMA exists in the unperturbed state in the solvent mixture employed.

The value of the Flory's viscosity constant Φ (listed in the last column of *Table 1*) is $2.93 \pm 0.07 \times 10^{21}$, in close agreement with the theoretically predicted limiting value of $2.82 \sim 2.87 \times 10^{21}$ for random coil polymers in theta solvents". The value for the steric factor, σ, $(\sigma^2 = \langle \gamma\rangle_0^2/\langle \gamma^2\rangle_{o,f})$ hindering free rotation around the skeletal bonds obtained is 2.13.

The reported value of the MHK constant K_θ for the unneutralized PMA in 0.002 N HCl at 30°C (theta solvent) is 6.6×10^{-4}. A low value (0.51) of the MHK exponent has been reported[6] for PMA in methanol at 26°C. However, methanol cannot be considered as a theta

observed[11,12]

10^{-4} cm^3 g^{-2} mole. A

$\pm$ 20°C in the temperature of PMA solution in methanol does not show any turbidity. The value of K_θ obtained in this investigation is 1.03×10^{-3}. Comparing

HCl and in DMF/1,4-dioxane

mixture, it is seen that PMA exists in a more expanded conformation in organic solvent, in agreement with the results reported for other hydrophobic group containing polyelectrolytes.

ACKNOWLEDGEMENT

One of us (K.S.) expresses his indebtedness to Council of Scientific and Industrial Research, New Delhi for the financial assistance.

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