polymer papers

A light-scattering study of poly(2-alkyl-2-oxazoline)s: effect of temperature and solvent type

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Solutions of poly(2-ethyl-2-oxazoline), PEOX, and poly(2-methyl-2-oxazoline), PMOX, in water and PEOX solutions in several alcohols were characterized by light scattering. The second virial coefficients in water were found to decrease with increasing temperature, reflecting lower critical solution behaviour due to hydrogen bonding. This resulted in negative values of the excess enthalpy Δh^E and entropy of dilution Δs^E for PEOX and PMOX in water. The magnitudes of Δh^E and Δs^E were higher for PMOX than for PEOX. The magnitudes of Δh^E and Δs^E for PEOX increased with molecular weight. The second virial coefficients of PEOX in water were systematically lower than in ethanol, isopropanol and n-butanol.

(Keywords: poly(2-ethyl-2-oxazoline); poly(2-methyl-2-oxazoline); static light scattering)

INTRODUCTION

There is considerable interest in water-soluble polymers because of their importance in controlling the colloid stability and rheology of ceramic suspensions, emulsions and coatings. Environmental concerns in the chemical process industry have heightened this interest. Non-ionic water-soluble polymers constitute an important and still poorly understood class of polymers due to the lack of a rigorous equation of state relating polymer and solvent structure to solution properties. Polymer adsorption is typically described in terms of a polymer–solvent interaction parameter, either in the form of a Flory χ parameter[1-3] or an excluded volume term[4,5], and a polymer segment–surface interaction term χ_s (ref. 3). This paper focuses on the characterization of the polymer–solvent interactions in various solvents for poly(2-alkyl-2-oxazolines) as part of a programme to develop diblock copolymer steric stabilizers. Poly(2-ethyl-2-oxazoline), PEOX, has been used in the synthesis of two novel diblock systems – poly(dimethyl siloxane-2-ethyl-2-oxazoline)[6] and poly(methyl vinyl ether-2-ethyl-2-oxazoline)[7]. There is reason to believe that PEOX will function as an effective anchor block on surfaces with hydrogen-bonding groups such as hydroxyl groups on metal oxides. A corresponding study of the segmental adsorption free energy of PEOX on silica from water and ethanol is the subject of a related paper[8].

PEOX, and poly(2-methyl-2-oxazoline), PMOX, are amorphous, non-ionic, tertiary amide polymers with repeat units illustrated in *Figure 1.* In the most comprehensive study to date of the solution properties of PEOX, Chen *et al.* characterized a polydisperse sample of PEOX by static and dynamic light scattering as well as by osmotic pressure measurements of PEOX in water and ethanol[9]. Phase-separation measurements demonstrated that PEOX exhibits lower critical solution temperature (*LCST*) behaviour in water with the θ-temperature = 56°C. The temperature dependence of the second virial coefficient revealed that the excess enthalpy of dilution, Δh^E, was negative due to hydrogen bond formation between the carbonyl (–C=O) group on the polymer and water. Fourier transform infra-red

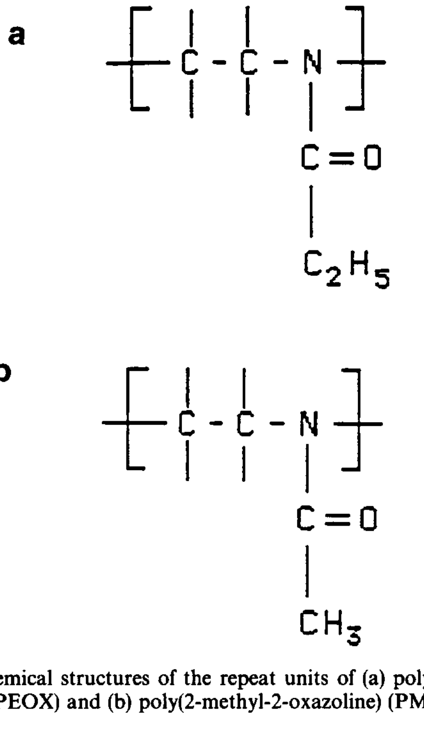

Figure 1 Chemical structures of the repeat units of (a) poly(2-ethyl-2-oxazoline) (PEOX) and (b) poly(2-methyl-2-oxazoline) (PMOX)

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(*FT*i.r.) spectroscopy demonstrated that hydrogen bonds formed between PEOX and deuterium oxide. The excess entropy of dilution, Δs^E, was negative as well due to the specific association of the water molecules with the PEOX chain. PEOX was found to be more soluble in ethanol than in water. PEOX is soluble in a variety of solvents, particularly those capable of forming hydrogen bonds[10]. PEOX is compatible with a number of polymers for the same reason[10–12]. Nothing has been reported on the solution properties of PMOX.

In this paper, we studied well defined PEOX homopolymer samples by static light scattering in water and several alcohols. We report values of the excess enthalpy and entropy of dilution for PEOX in water for molecular weights in the range $\approx$20–60 kg mol^{-1} as part of our work to understand how the behaviour of PEOX in solution is related to its adsorption behaviour[8]. Second virial coefficients were also measured for PMOX to study the effects of polymer structure on polymer–solvent interactions.

EXPERIMENTAL

Materials and solution preparation

PEOX and PMOX were synthesized over a range of molecular weights using a cationic living polymerization process which has been described by Saegusa *et al.* previously[13,14] and Liu *et al.*[6,7,15]. The living nature of the polymerization makes it possible to prepare di-and tri-block copolymers from these monomers[14] and allows for functional termination[15,16]. Liu *et al.* established that the M_n of PEOX increased linearly with monomer conversion, suggesting that chain transfer reactions were not occurring[15]. In that same study, gel-permeation chromatography (g.p.c.) showed that PEOX homopolymer samples with $M_n \leqslant 40$ kg mol^{-1} had $M_w/M_n \approx 1.3$ (ref. 15). Those measurements were not straightforward due to the adsorption of PEOX onto components in the g.p.c. system. The typical M_w/M_n values, 1.3, were somewhat larger than expected for a living polymerization system. This might be explained by slight aggregation of the PEOX in the mobile phase (85/15 v/v THF/MeOH). In this paper, it is shown that PEOX aggregates in water and n-butanol.

Samples of PEOX were stored in a desiccator chamber prior to use since PEOX is very hygroscopic. Deionized water with a resistivity of 17×10^6 ohm cm was obtained from a Barnstead NANOPURE II$^{\mathrm{TM}}$ water purification system. Ethanol (200-proof, Aaper Alcohol and Chemical Compay) was further dried by vacuum distillation from CaH_2. Solutions for light scattering were filtered typically with 0.22 μm Acrodisk filters. The solvents were purchased from Aldrich Chemical Compay. Isopropanol (anhydrous, 99+%), n-butanol (h.p.l.c. grade) and benzene (spectrophotometric grade, 99%) were used.

Partial specific volume

The partial specific volume v_p of PEOX was determined from density measurements of PEOX in water and anhydrous ethanol using a Mettler KEM DA-300 density meter that is accurate to within ± 0.0001 g cm^{-3} at temperatures over the range 5–45$\pm$0.01°C. The values of v_p were independent of temperature with $v_p = 0.87$ cm^3 g^{-1} for water and $v_p = 0.86$ cm^3 g^{-1} for ethanol. This compares with the value of $v_p = 0.877$ cm^3 g^{-1} for an ideal solution of PEOX at 25°C derived from the density of solid PEOX of 1.14 g cm^{-3} (ref. 10). The values of v_p will be used in calculating approximate Flory χ parameters for study of PEOX adsorption on silica[8].

Light scattering

Static light-scattering experiments were performed with a Brookhaven model 2030AT instrument. The light source was an argon ion laser operated at a wavelength of 514.5 nm. Refractive index increments $\partial n/\partial c$ were measured at a wavelength of 510 nm with a Model 60/ED refractometer (Bellingham & Stanley) equipped with a differential cell.

The angular dependent scattering intensity, $I(\theta)$, was used to calculate the Rayleigh ratio, $R(\theta)$ for polarized light according to[18]

$$R(\theta) = C_R I(\theta) \sin(\theta)(n_s/n_c)^2/I_0 \tag{1}$$

where I_0 is the incident beam intensity, C_R is an instrumental constant, and n_s and n_c are the refractive indices of the scattering solution and the calibration liquid, respectively. Benzene was used as a scattering reference to determine the constant C_R. The Rayleigh ratio for benzene measured with vertically polarized incident light at a scattering angle of 90° is $R_v(90°) = 30.4 \times 10^{-6}$ cm^{-1} (ref. 18). The effect of temperature on the Rayleigh ratio was taken into account using the method recommended by Chu[19] which corrects the ratio at a given temperature using the scattering intensity of benzene and the refractive index at that temperature[20,21]. The excess Rayleigh ratio, $\Delta R(\theta)$, $(= R(\theta)_{\mathrm{solution}} - R(\theta)_{\mathrm{solvent}})$ is related to the weight-average molecular weight M_w, the second virial coefficient A_2, and the radius of gyration R_g by[22]:

$$Kc/\Delta R(\theta) = M_w^{-1}(1 + (qR_g)^2/3) + 2A_2c \tag{2}$$

where c is the polymer concentration and q is the scattering vector defined as

$$q = 4\pi n_0 \sin(\theta/2)/\lambda_0 \tag{3}$$

where λ_0 is the incident wavelength and n_0 is the solvent refractive index. In equation (2), K is defined for vertically polarized light by

$$K = (2\pi n_0(\partial n/\partial c))^2/N_a\lambda_0^4 \tag{4}$$

where N_A is Avogadro's number. For all light-scattering experiments from 5 to 45°C, $\Delta R(\theta)$ was independent of the scattering angle within experimental error, i.e. $qR_g \ll 1$ due to the relatively low molecular weights employed and due to the relatively low degree of chain expansion of the PEOX. Thus, equation (2) can be simplified as:

$$Kc/\Delta R(\theta) = M_w^{-1} + 2A_2c \tag{5}$$

All measurements of the second virial coefficient, A_2, were made at a scattering angle of 90° with dilute solutions with polymer concentration $c \leqslant 0.01$ g cm^{-3}. A representative scattering intensity plot for the sample PEOX 30K in ethanol is shown in *Figure 2*.

RESULTS AND DISCUSSION

Molecular weight measurements

Table 1 lists values of the refractive index increment, $\partial n/\partial c$ for PEOX and PMOX at different temperatures and in different solvents. The values of M_w in *Table 2* for PEOX 20K and PEOX 30K in ethanol and isopropanol

Table 1 Refractive index increments, $\partial n/\partial c$, for poly(2-alkyl-oxazolines) at a wavelength of 510 nm

	$\partial n/\partial c$ ($cm^3 g^{-1}$)		
Polymer/solvent	5°C	25°C	45°C
PEOX/water	0.184 ± 0.002	0.176 ± 0.002	0.174 ± 0.002
PEOX/ethanol	–	0.155 ± 0.002	–
PEOX/isopropanol	–	0.155 ± 0.003	0.159 ± 0.001
PEOX/n-butanol	–	0.110 ± 0.001	–
PMOX/water	0.180 ± 0.002	0.172 ± 0.002	0.172 ± 0.002

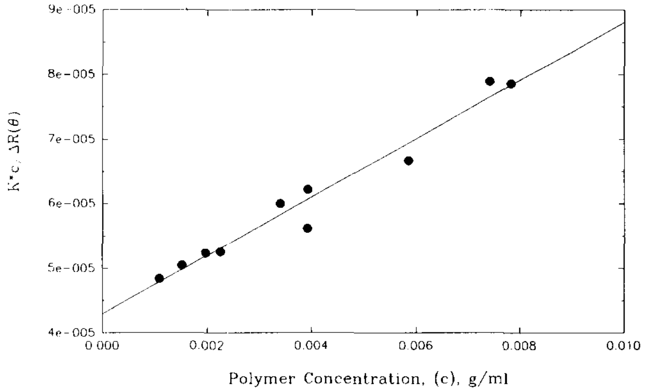

Figure 2 Light-scattering plot, $Kc/\Delta R$ (θ) *versus* c, of PEOX 30K in ethanol at 25°C and a scattering angle of 90°, equation (5)

agreed reasonably well. However, the M_w measurements in water for PEOX 20K, 30K and 60K were somewhat higher than in alcohols. We believe this is due to some aggregation of PEOX in water. Indeed, a PEOX sample with a number-average $M_n = 2\,kg\,mol^{-1}$ as determined from monomer conversion data formed aggregates in water with an apparent $M_w \approx 57\,kg\,mol^{-1}$. Aggregation of non-ionic water-soluble polymers in water was reviewed by Burchard[23] for several polymers including poly(ethylene oxide), PEO, and poly(vinyl pyrrolidone), PVP. In one study, PEO with an approximate molecular weight of $20\,kg\,mol^{-1}$ had an apparent $M_w \approx 260\,kg\,mol^{-1}$ as determined by light scattering. The aggregation of PEO in water has been attributed to hydrophobic interactions between the non-polar regions of the polymer chain[24]. PVP, whose structure is similar to PEOX, has also been found to aggregate in water and little if not at all in ethanol[23]. The higher value of M_w for PEOX in n-butanol than in ethanol and isopropanol may be due to some slight aggregation. In future work, this will be checked with experiments at other molecular weights. Thus, the values of M_w in water and n-butanol are apparent or extrapolated values while the true values of M_w were determined in ethanol and isopropanol.

The effect of aggregation on the interpretation of light-scattering results has been discussed in detail by Elias[25]. Several cases of aggregation are possible, most of them resulting in highly non-linear plots of $Kc/\Delta R(\theta)$ *versus* c (see equation (5)). In the nomenclature used by Elias, our results for PEOX correspond to the Type IVB case where the polymer is in a good solvent and the scattering plot of $Kc/\Delta R(\theta)$ *versus* c is linear but the extrapolated M_w depends upon the solvent used. In this case, the magnitude of the second virial coefficient exceeds the effect of the intermolecular association which, by itself, would lead to non-linearity. Good linearity was observed for the scattering experiment shown in *Figure 2* over the PEOX concentration range 0.001–0.008 $g\,cm^{-3}$. All of the scattering experiments were conducted in the concentration range 0.001–0.01 $g\,cm^{-3}$. We found no systematic curvature over these concentrations in any of the scattering experiments.

In water and possibly n-butanol, there is probably a distribution of unimers (single chains) and multimers (associated chains). For open association, all types of multimers can form whereas, for closed association, only two species are present – unimers and multimers with a single, fixed degree of association. It is not clear whether the association of PEOX is open or closed. Type IVB behaviour is exhibited by polymers undergoing both open and closed association[25]. In view of this, the A_2 values of PEOX in water and n-butanol represent effective averages over the associated states in solution. This is analogous to the interpretation of A_2 measurements for solutions of single chains with some polydispersity[26].

Second virial coefficients

Effect of temperature and molecular weight. The second virial coefficients of PEOX and PMOX are summarized in *Table 2*. The decrease of A_2 with increasing temperature reflects the lower critical solution behaviour of PEOX and PMOX in water. The magnitude of dA_2/dT, summarized in *Table 3* for various polymers in water, generally increased with molecular weight. The analysis of the temperature dependence of the values of A_2 for PEOX in water is simplified by the lack of systematic variation of the extrapolated M_w with temperature. The variations that do occur generally fall within the error bars for the experiments. Thus, the A_2 measurements as a function of temperature are probing the interactions of solvent with associated chains whose effective molecular weight distributions do not change very much with temperature.

To quantify further the effect of temperature on A_2, we follow the approach of Schulz and Cantow[27] who decomposed the temperature dependence of A_2 into a contribution from the excess enthalpy of dilution of the solvent, Δh^E, and a contribution from the excess entropy of dilution of the solvent, Δs^E. This analysis can be applied to aggregating systems as long as the second virial coefficient dominates the aggregation effect as shown by the linearity of the scattering plots. The excess enthalpy of dilution is given by

$$\Delta h^E = (B_2' T - B_2) c^2 V_1 \qquad (6)$$

where $B_2 = RTA_2$, $B_2' = dB_2/dT$, and V_1 is the partial molar volume of water. The excess entropy of dilution is given by

$$\Delta s^E = B_2' c^2 V_1 \qquad (7)$$

The excess chemical potential of the solvent, $\Delta\mu^E$, is then given by

$$\Delta\mu^E = \Delta h^E - T\Delta s^E \qquad (8)$$

For solutions of PEOX and PMOX in water, the excess enthalpy Δh^E and the excess entropy Δs^E were negative due to hydrogen bonding between PEOX and water. The reduced quantities $T\Delta s^E/c^2 V_1$ ($= TB_2'$) and $\Delta h^E/c^2 V_1$ for PEOX in water at 45°C, shown in *Figure 3*, became more

Table 2 Second virial coefficients and molecular weights for poly(2-alkyl-2-oxazoline) as a function of temperature and solvent type

Sample	Solvent	T (°C)	M_w[a] (kg mol^{-1})	Second virial coefficient, A_2 (mol cm^3 g^{-2} × 10^4)
PEOX 20K	Water	5	22.9±0.9	12.2±1.4
		25	23.1±0.8	10.8±1.0
		45	23.2±0.7	9.4±1.1
	Ethanol	25	16.6±0.6	19.5±2.1
	Isopropanol	25	14.4±0.5	29.1±1.9
		45	16.5±0.4	33.8±1.2
	n-Butanol	25	20.2±0.3	20.4±1.2
PEOX 30K	Water	5	32.0	9.56
		25	34.0	7.41
		45	33.8	5.92
	Ethanol	25	23.2±1.2	22.6±1.6
	Isopropanol	25	22±0.9	30.9±1.9
		45	22.3±0.4	25.8±0.8
PEOX 60K	Water	5	67.1±0.4	8.8±0.7
		25	66.9±4.7	7.5±0.8
		45	62.1±2.3	4.2±0.5
	Isopropanol	25	47.0±0.1	9.87±0.6
		45	46.0±0.1	10.8±0.8
PMOX 20K	Water	25	21.8±1.1	17.1±1.9
PMOX 30K	Water	5	24.3	17.3
		25	23.7	13.7
		45	21.7	11.2

[a] From light scattering at scattering angle of 90°

Table 3 Effect of temperature on second virial coefficients for poly(2-alkyloxazolines)

Polymer/solvent	M_w (kg mol^{-1})	dA_2/dT (mol cm^3 g^{-2} K × 10^5)	B_2'[a] (cal cm^3 g^{-2} K^{-1} × 10^3)
PEOX 20K/water	23.1[b]	−0.7±0.01	−1.99±0.16
PEOX 30K/water	33.3[b]	−0.91±0.09	−3.85±0.35
PEOX 60K/water	65.4[b]	−1.15±0.28	−5.5±1.9
PEOX(Chen)/water	116[c]	−3.3	−19.0
PMOX 30K/water	23.2[b]	−1.52±0.1	−6.2±0.2

[a] $B_2' = \mathrm{d}(RTA_2)/\mathrm{d}T = \Delta s^E/c^2V_1$, reduced excess entropy of dilution, from equation (7)

[b] Average values from static light scattering at 5, 25 and 45°C in water with angle of 90°

[c] From static light scattering by Chen *et al.*[9]

negative with increasing molecular weight. The data from Chen *et al.* for a relatively polydisperse sample of PEOX with higher M_w ($M_w = 116$ kg mol^{-1}, $M_w/M_n = 2.4$) are also shown in *Figure 3* and are consistent with the molecular weight trend[9]. The magnitude of the enthalpic contribution to the excess chemical potential, $|\Delta h^E|$, was always greater than the entropic contribution, $T|\Delta s^E|$ in the temperature range 5–45°C. While the molecular-weight dependence of Δh^E and Δs^E cannot be explained definitively, the results suggest that the availability of the carbonyl groups in the PEOX chain to form hydrogen bonds with water increases with the molecular weight.

It has been suggested that the temperature dependence of χ be decomposed into an enthalpic term χ_H and an entropic term χ_S or equivalently, the terms κ and ψ from the original Flory–Huggins solution theory[28]. However, this approach fails to account for specific interactions such as hydrogen bonding between the polymer chain and solvent molecules.

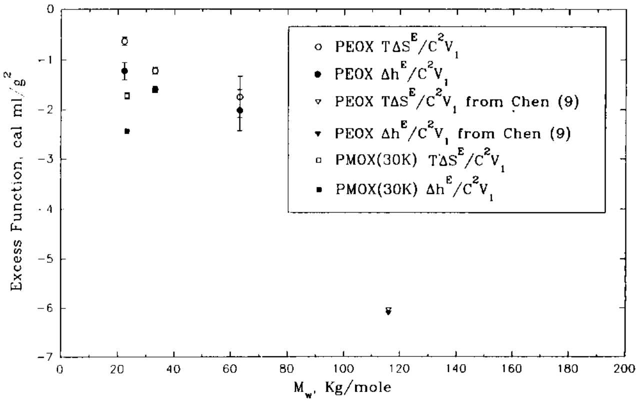

Figure 3 Reduced excess thermodynamic dilution functions enthalpy of mixing, $\Delta h^E/c^2V_1$ (equation (6)), and entropy of mixing $T\Delta s^E/c^2V_1$ (equation (7)) for PEOX and PMOX in water for 45°C plotted as a function of weight-average molecular weight. Also plotted are data from Chen *et al.*[9]

Effect of polymer structure. Both *Table 3* and *Figure 3* show that the magnitude of the reduced excess entropy of mixing, B'_2, was about 40% higher for PMOX 30K than for PEOX 20K which had a comparable value of M_w in water. This suggests that water molecules form more highly ordered structures around PMOX. The ethyl group has a greater electron-releasing capability than the methyl group. Thus, the carbonyl group in PEOX is less polar than the carbonyl group in PMOX and should form a weaker hydrogen bond with water. In addition, the more bulky and hydrophobic ethyl group probably interferes more with the formation of structures of water molecules around the PEOX backbone than does the methyl group in PMOX.

Effect of solvent type. At a given temperature, the values of A_2 for PEOX 20K, 30K and 60K in different alcohols were higher than the values of A_2 in water as seen in *Table 2*. The trends are also qualitatively consistent with estimated solubility parameters for PEOX and the solvents. The Hansen solubility parameters for water, ethanol, isopropanol and butanol are 48.0, 26.3, 23.6 and 23.2 $J^{1/2}\,cm^{-3/2}$, respectively. The solubility parameter of PEOX was estimated as $\approx 26\,J^{1/2}\,cm^{-3/2}$ by the group contribution method using values of functional groups by Fedors[29]. Better solubility and hence higher second virial coefficients are expected for polymer–solvent combinations where their solubility parameters match more closely.

CONCLUSIONS

A series of samples of poly(2-ethyl 2-oxazoline), PEOX, and poly(2-methyl 2-oxazoline), PMOX, were characterized by static light scattering. Both PEOX and PMOX displayed *LCST* behaviour in water. Measurements of the excess enthalpy and entropy of dilution of the water, Δh^E and Δs^E, respectively, provide valuable insight into solvent structuring effects around polymer segments. The excess enthalpy of dilution of the water was negative due to hydrogen bond formation between the carbonyl group (–C=O) on the polymer chain and water. The excess entropy of dilution was also negative due to the ordering of water molecules around the polymer chains. The magnitudes of Δh^E and Δs^E increased with molecular weight, suggesting that the availability of the carbonyl groups to form hydrogen bonds with water increased. The magnitude of Δs^E and Δh^E for PMOX were higher than those for PEOX, in keeping with the view that PMOX was generally more hydrophilic than PEOX. The values of A_2, Δh^E and Δs^E will be used in a companion study of the adsorption of PEOX on metal oxides[8]. Some aggregation of PEOX in water was observed which may be related to aggregation reported for other water-soluble polymers. The possibility of aggregation of PMOX in various solvents will be studied in future work. PEOX was more soluble in ethanol, isopropanol and n-butanol than in water. In future work, Δh^E and Δs^E for PEOX and PMOX will be measured in various alcohols to relate solvent structuring effects to polymer structure. Similar experiments are also planned with poly(ethylene oxide) and poly(vinyl pyrrolidone) to allow further comparisons with polymer structure.

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