An unusual dependence of viscosity on the water content in mixtures of water with oligomeric triblock copolymers of ethylene and propylene oxides

Lubomír Šimek
Faculty of Technology, Technical University, Zlín, Czech Republic

and Stanislav Petřík
Plastservis Ltd, Zlín, Czech Republic

and Miloslav Bohdanecký*
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague 6, Czech Republic

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The addition of small amounts (less than 10%) of water to liquid oligomeric triblock copolymers (PEP) of ethylene oxide (E) and propylene oxide (P) increases the viscosity, η, above that of pure liquid oligomers. Comparison with the concentration dependences of viscosity, $\eta(c)$, for oligomeric homopolymers leads to the conclusion that the unusual shape of the dependences for PEP copolymers is due to the interaction of water molecules with hydrophobic propylene oxide units.

(Keywords: viscosity; aqueous solutions; triblock copolymers)

Introduction

The original aim of this work was to investigate the effects of copolymer composition on the viscosity of aqueous solutions of oligomeric triblock (type PEP) copolymers of ethylene oxide (E) and propylene oxide (P), with emphasis on the transition from the non-free-draining flow regime at low concentrations to the free-draining flow regime at high polymer contents[1]. It was found, however, that concentrated solutions of PEP exhibit an unusual concentration dependence of viscosity, which is absent with the corresponding homopolymers in aqueous and non-aqueous solutions. It cannot be interpreted in terms of the standard theory and is probably connected with the interaction of water molecules with propylene oxide units.

Experimental

Hydroxyl-terminated triblock copolymers of ethylene oxide and propylene oxide (*Table 1*) were provided by the Institute of Petrochemical Research (Prievidza, Slovak Republic) and were identical to those used in previous research[2-5].

Solutions in distilled water were prepared by shaking overnight weighed amounts of the components at room temperature. Concentrations were expressed as polymer weight fraction, w_2.

Viscosity was measured by a Rheotest viscometer at 25°C.

Results and discussion

In *Figure 1* the viscosity, η_M, of aqueous solutions of PEP copolymers is plotted against the polymer concentration. The striking feature of these plots is that the η_M values at low water contents are higher than those for undiluted polymers, η_2. This effect is unusual with polymer–diluent systems; the only analogy we know of has been described by Hespe *et al.*[6] with aqueous solutions of a branched EPE copolymer ($M_n = 4800$, $w_E = 0.135$). The increase in viscosity associated with diluting the polymer with water was very dramatic, amounting to one order of magnitude.

For short polymer chains, where entanglement effects on viscosity may be neglected, the viscosity, η_2, of liquid polymers is written[1] as a product:

$$\eta_2 = F_2(X)\zeta_2 \tag{1}$$

where $F_2(X)$ is the structure-dependent factor and ζ_2 is the friction factor per main chain atom or atomic group taken as a friction centre. The structure factor:

$$F_2(X) = (N_A/6)(\langle S^2\rangle_o/M)(Z/v_2) \tag{2}$$

is proportional to the number of polymer chains per centimetre cubed (N_A/Mv_2), the mean square distance $\langle S^2\rangle_o$ of the friction centre from the centre of mass, and the number of friction centres ($Z = M/m_a$) of mean molecular weight m_a each. It is controlled by the large-scale structure and configuration of the chain. The friction factor, ζ_2, is assumed to reflect local intrachain and interchain forces between neighbouring centres.

In polymer–diluent systems, the number of polymer molecules per centimetre cubed is diminished to $\varphi_2 N_A/Mv_2$ and the friction factor is decreased to $\zeta_2 k(\varphi_2)$, where $k < 1$ and φ_2 is the polymer volume fraction.

Our working hypothesis is that the unusual effect of water on the viscosity of PEP copolymers is due to a supramolecular (pseudo-network) structure, which makes the response of a chain to systematic motions depend on the presence of other chains, as with entangled systems[1], and enhances the molecular friction coefficient by a factor

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* To whom correspondence should be addressed

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Table 1 Characteristics of copolymers PEP[a]

Sample code	x_E	w_E	M_n
PEP I/1	0.407	0.343	1090
PEP I/2	0.57	0.502	1040
PEP I/3	0.74	0.688	1280
PEP II/2	0.57	0.502	2000

[a] w_E, Weight fraction of ethylene oxide units; x_E, molar fraction of ethylene oxide units; M_n, number-average molecular weight[2]

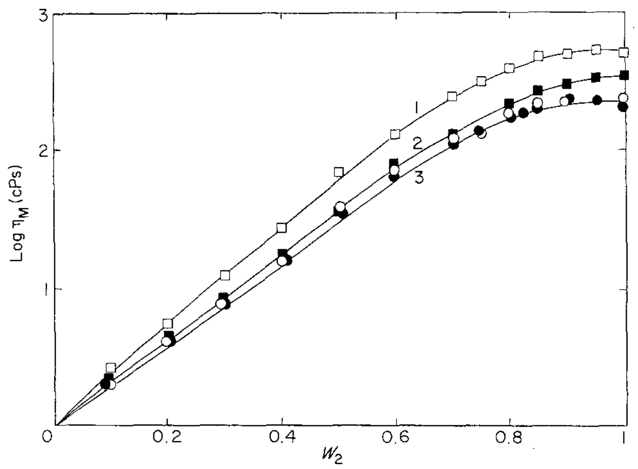

Figure 1 Dependence on polymer concentration of viscosity, η_M, of aqueous solutions of PEP copolymers at 20°C: ●, I/1; ○, I/2; ■, I/3; □, II/2. Curves: 1, II/2; 2, I/3; 3, I/1

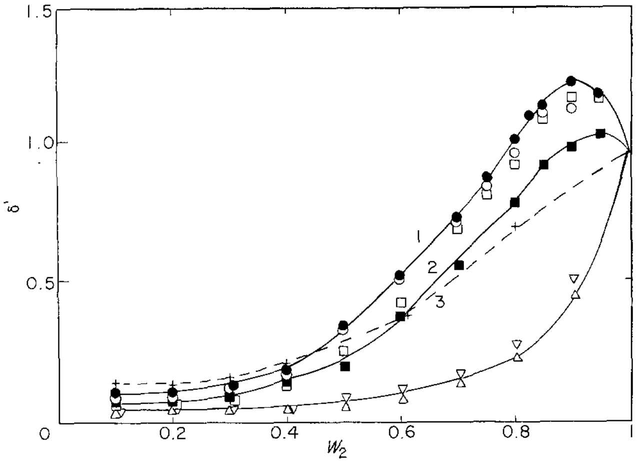

Figure 2 Dependence on polymer concentration of the parameter δ'. Symbols for PEP as in *Figure 1*. Data points for poly(propylene oxide) (PPO, $M_n = 2 \times 10^3$) in benzene (△) and methyl cyclohexane (▽) at 25°C from ref. 8. Data points for poly(ethylene oxide) (PEO, $M_n = 10^3$) in water (+) at 50°C from ref. 7. Curves: 1, PEP I/1; 2, PEP I/3; 3, PEO–water; 4, PPO–benzene

$\Gamma(\varphi_2)$. Then viscosity can be written as:

$$\eta_M = [(N_A/6)(\langle S^2 \rangle_o/M)(\varphi_2 Z/v_2)][\zeta_2 k(\varphi_2)]\Gamma(\varphi_2) \quad (3)$$

From equations (1) to (3) we obtain a criterion:

$$\delta = \eta_M/\eta_2\varphi_2 = k(\varphi_2)\Gamma(\varphi_2) \quad (4)$$

which takes account of the effect of diluent on $F(X)$ and separates it from the effects of dilution, $k(\varphi_2)$, and pseudo-network, $\Gamma(\varphi_2)$, on the friction factor. However, it does not distinguish between them. Strictly speaking, the δ parameter can be a reasonable criterion only in the region of very high concentrations. Since partial specific volumes of both components are not known, the w_2 values cannot be converted into φ_2. Therefore, the δ parameter is replaced by an accessible quantity, $\delta' = \eta_M/\eta_2 w_2$.

As shown by *Figure 2*, curves of δ' *versus* w_2 for samples PEP I/2 and II/2, which differ only in the molecular weight, overlap, whereas those for samples I/1 to I/3, with negligible differences in M but differing in composition, do not. However, all of them have a maximum at $w_2 > 0.9$. The height of the maximum decreases with increasing content of ethylene oxide units in the chain.

Note that curves for oligomers of ethylene oxide[7] display no maxima and the δ values are lower than unity over the entire concentration range. The same holds true for poly(propylene oxide) in organic solvents[8].

These facts lead us to the opinion that the unusual shape of the curves in *Figure 1* is due to the interaction of hydrophobic propylene oxide units and water. We assume that maxima on these curves result from a superposition of at least two processes with opposite dependences on concentration: a general process accompanying dilution of any polymer with a low-molecular-weight diluent, and a specific process which involves formation of supramolecular structure, diminishing the mobility of polymer segments and increasing the friction coefficient.

The general process can be discussed in terms of the free-volume theory of viscosity of polymeric liquids[1]. The friction factor, ζ_2, is assumed to be connected with the free volume of the liquid polymer by the equation:

$$\ln \zeta_2 = \ln \zeta_o + B_2/f_2 \quad (5)$$

where ζ_o is the intrinsic friction factor, f_2 is the fractional free volume and B is a constant. Diluents usually loosen the structure of polymeric liquids, thereby increasing the free volume and decreasing the friction factor and viscosity.

The 'specific' process accompanying dilution of PEP copolymers with water may involve: (i) formation of a sort of crosslinking at low water concentrations if one water molecule bridges two ethylene oxide units belonging to different chains; (ii) clustering of water molecules in contact with hydrophobic groups; (iii) association of hydrophobic units in contact with water.

Clustering of water molecules in hydrophobic media is well known and is assumed to account, for example, for positive deviations of viscosity from the values interpolated between those of the components in mixtures of benzene or toluene and water[9].

A study of sorption of water vapour by PEP copolymers[3] has shown that water molecules tend to cluster together at low concentrations of water. The Zimm–Lundberg clustering function[10] and the mean cluster size were higher the higher the content of propylene oxide units. In contrast, clustering was very low, or absent, with oligomers of ethylene oxide.

The Flory–Huggins polymer–solvent interaction parameter at $\varphi_2 \rightarrow 1$ estimated from the sorption data[10] ($\chi_o = 2.9$ and 0.8 for poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO), respectively) and the lower critical solution temperature ($LCST = 20$–30°C for PPO and 96°C for PEO[11]) show that, at normal temperatures, water is a poor solvent for PPO and a good solvent for PEO. With copolymers of ethylene oxide and propylene oxide, phase separation on heating aqueous solutions was also observed[2,6]. Some of them exhibited phenomena that were absent with PEO, such as microphase separation, formation of micelles and organized structures at temperatures between 0°C and the respective $LCST^{2,6,12-14}$. These facts give evidence of a tendency to association of propylene oxide units in contact with water.

We are not in a position to estimate the weight of these factors. However, the information presented on the interaction of water with ethylene oxide and propylene oxide units may support the proposed interpretation of the unusual dependence of viscosity on the content of diluent.

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