Melt Viscosity of Oligomeric Triblock Copolymers (Type PEP) of Ethylene and Propylene Oxides

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SYNOPSIS

Melt viscosity η at 25°C of four oligomeric triblock copolymers consisting of a central block of ethoxamer units and two end blocks of propoxamer units (PEP) ($M_n \times 10^{-3} = 1$ and 2; mole fraction of ethoxamer units $x_E = 0.41, 0.57$, and 0.74) was analyzed in terms of the theory advanced by Berry and Fox. The structure-dependent factor $F(X)$ was deduced from the intrinsic viscosity data, and the mean friction factor per friction center ζ was computed from η and $F(X)$. At a fixed molecular weight, it increases with increasing x_E. The dependence of ζ versus x_E was compared with curves computed from the data for homopolymers. The best agreement was obtained if the following values of the inherent friction factor (log ζ_0) were used: -10.25 for poly(ethylene oxide) PEO and -10.65 for PPO. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The Newtonian viscosity of liquid linear polymers can be expressed by the equation (cf. Ref. 1)

$$\eta = F(X)\zeta \tag{1}$$

where $F(X)$ is the structure-dependent factor and ζ is the friction factor per main chain atom or atomic group. The former is controlled by the large-scale structure and configuration of the chain whereas the latter is controlled by local intra- and intermolecular forces between the segments of the chain. Below the critical entanglement molecular weight, M_c, the structure factor is written as

$$F(X) = (N_A/6)(\langle s^2 \rangle_0/M)(Z/v_2) \tag{2}$$

$$Z = M/m_a \tag{3}$$

where N_A is the Avogadro constant, Z is the number of main chain atoms or atomic groups considered as friction centers, M is the polymer molecular weight,

v_2 is the polymer specific volume, m_a is the mean molecular weight per friction center, and $\langle s^2 \rangle_0$ is the unperturbed mean square radius of gyration of polymer molecules. The ratio $\langle s^2 \rangle_0/M$ is characteristic of the chain conformation and equilibrium flexibility.

The friction factor depends on the temperature by the equation[1]

$$\zeta = \zeta_0 \exp[B/(T - T_0)] \tag{4}$$

By combining Eqs. (1) and (4) we obtain the Vogel equation

$$\ln \eta (= \ln A + B/(T - T_0) \tag{5}$$

where

$$A = F(X)\zeta_0 \tag{6}$$

The intrinsic friction factor ζ_0 per friction center depends somewhat on the structure of the chain[1] and, at $Z < 30$, also on the molecular weight.[2] The B and T_0 parameters depend on M at low molecular weights and attain their asymptotic values, B_∞ and T_0^∞, at molecular weights of the order of magnitude of 10^3. The T_0 temperature is the temperature at

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which the configurational entropy and free volume of the polymer liquid become zero or where the extrapolated relaxation time becomes infinite.[3] The B parameter is related to the internal barriers to rotation of main chain bonds in the isolated polymer chain.[4]

If B, T_0, v_2, and $\langle s^2 \rangle_0/M$ are independent of the molecular weight, the melt viscosity at $M < M_c$ should be proportional to the first power of M. Higher values of the quotient $d \ln \eta/d \ln M$ at $M < M_c$ are assigned to the molecular weight dependence of either of these parameters.[5]

With copolymers, both the structure and friction factors depend on the composition. The effect of composition on the former can easily be predicted. The m_a values are obtained by simple interpolation between those for homopolymers, and the specific volume can be measured. The values of $\langle s^2 \rangle_0/M$ are deduced from dilute solution properties, e.g., intrinsic viscosity, by standard procedures (cf. Ref. 6). On the contrary, the effect of composition on the friction factor is an open problem that has so far been examined with two or three copolymers only.[7]

In this work we discuss the dependence on copolymer composition of the melt viscosity of triblock copolymers (type PEP) consisting of a central block of ethylene oxide units and two end blocks of propylene oxide units. From the intrinsic viscosity data we evaluate the structure-dependent factor $F(X)$. By combining it with the melt viscosity, we calculate the friction factor and compare it with the values computed from parameters B, T_0, and ζ_0 for homopolymers (PEO, PPO). To have a firm basis for this work we first review and analyze the data on these parameters, which are available in literature.

EXPERIMENTAL

Polymers

Hydroxy-terminated triblock copolymers PEP (Table I) were provided by the Petrochemical Research Institute, Prievidza (Slovak Republic) and were identical with those used previously.[8-10] Acetyl-terminated samples were provided by Dr. F. Hadobaš (Research Institute for Plastics and Rubber Technology, Zlín, Czech Republic). They were prepared by heating dry samples of PEP with acetanhydride and pyridine (weight ratio 3 : 1 : 6) for 4 h to 80°C. The conversion was almost complete, the hydroxyl content being decreased from 3.2–3.9 wt % to 0.1–0.4 wt %.

Table I Characteristics of PEP Copolymers[a,8-10]

Sample Code	M_n	w_E	x_E	v_2 (cm³/g)
PEP				
10	990	0.14	0.18	0.987
20	865	0.21	0.26	0.957
30	1090	0.34	0.41	0.944
50	1040	0.50	0.57	0.940
70	1280	0.69	0.74	0.914
50/1	2000	0.60	0.57	

[a] M_n, number-average molecular weight (calculated from the content of hydroxyl end groups); w_E and x_E weight and mole fraction of ethylene oxide units, respectively; v specific volume of liquid copolymer at 20°C.

Solvents

Acetone and benzene were of reagent-grade purity. Before use they were dried by standard methods.

Viscometry and Densitometry

Viscosity of solutions was measured at 25 ± 0.02°C in Ubbelohde capillary viscometers adapted for subsequent dilution. The intrinsic viscosity was estimated by standard extrapolation procedures from viscosities measured at four polymer concentrations ($c \leq 0.04$ g/cm³). No viscometric corrections were necessary. Viscosity of liquid copolymers was measured at 20°C by the Rheotest viscometer. Density (at 20°C) was measured pycnometrically.

RESULTS AND DISCUSSION

Structure-dependent Factor $F(X)$ of PEP Copolymers

All quantities comprised in the structure factor, Eq. (2), depend on the copolymer composition. The mean molecular weight m_a per friction center is obtained by interpolation between the values for homopolymers ($m_a = 14.7$ and 18.3 for PEO and PPO, respectively).

Poly(ethylene oxide) of $M_n = 10^3$ is crystalline at room temperature, so the specific volume of liquid state cannot be obtained directly. For $M_n = 530$ (where the melting temperature is about 17°C)[19] the specific volume is calculated by means of the formula

$$v_2 = v_{2,0} + k_v t \qquad (7)$$

with $v_{2,0} = 0.8736$ cm³ g⁻¹ and $k_v = 0.697 \times 10^{-3}$ cm³ g⁻¹ deg⁻¹.[11] For temperatures $t = 20$ and 25°C we

obtain v_2 = 0.887 and 0.891 cm^3 g^{-1}, respectively. These values agree with the value of v_2 = 0.888 cm^3 g^{-1} obtained by Braun et al.[12] by extrapolating the density of PEO melts to room temperature. They are used to construct the reference curve in Figure 1.

The specific volume of PPO (Table I) is in good agreement with the value of v_2 = 0.995 cm^3 g^{-1} calculated by means of Eq. (7) with $v_{2,0}$ = 0.9791 cm^3 g^{-1} and k_v = 0.810 × 10^{-3} cm^3 g^{-1} deg^{-1}.[11]

Figure 1 shows that the specific volumes at 20°C of PEP copolymers are an approximately linear function of the weight fraction w_E of ethoxamer units.

Theoretical calculations (cf. Ref. 13) have shown that the ratio $\langle s^2\rangle_0/M$ for PEO is an increasing function of the number of main-chain bonds n such that it is very close to the asymptotic (random-coil) value, $(\langle s^2\rangle_0/M)_\infty$, already at n > 20 or M > 300. Thus, PEO chains with $M_n \geq 10^3$ have the conformation of random coils. In view of the similarity of the PEO and PPO chains, it is legitimate to assume that the same holds true for PPO and the PEP copolymers.

In general, the ratio $(\langle s^2\rangle_0/M)_\infty$ for copolymers need not be a linear function of composition, and positive or negative deviations from linearity are a rule rather than an exception (cf. Ref. 6). The effect of composition on $(\langle s^2\rangle_0/M)_\infty$ can be cleared up by means of the intrinsic viscosity data if the excluded-volume effect is absent or negligible.

The former case obtains at θ conditions where the second virial coefficient vanishes,[14] the latter can occur with short chains if the molecular weight is lower than a "critical" value for the onset of the

Figure 2   Dependence of intrinsic viscosity on composition of PEP copolymers. Temperature 25°C. Solvents: (a) benzene, (b) acetone. M_n: (O Ó) 10^3, (● ♦) 2 × 10^3. End Groups: (O ●) hydroxyl, (Ó ♦) acetyl.

coil expansion.[15] The critical region for PEO has recently been estimated[16] to be at 1 $\lesssim$ M × 10^{-3} $\lesssim$ 1.6. For PPO, it cannot be estimated but is probably similar to that for PEO. Thus, the intrinsic viscosity of PEP oligomers where 0.8 $\lesssim$ M_n × 10^{-3} $\lesssim$ 2 is not significantly affected by the excluded-volume effect and may be taken as the value corresponding to the θ state, $[\eta]_\theta$.

In the limit of nondraining random coil, $[\eta]_\theta$ is related to the ratio $(\langle s^2\rangle_0/M)_\infty$ according to

$$[\eta]_\theta = K_0 M^{1/2} \tag{8}$$

$$K_0 = 6^{3/2}\Phi_{0,\infty}(\langle s^2\rangle_0/M)_\infty^{3/2} \tag{9}$$

where $\Phi_{0,\infty}$ is the Flory viscosity constant ($\Phi_{0,\infty}$ = 2.6 × 10^{23} if $[\eta]_\theta$ is expressed in cm^3 g^{-1}).[13] Assuming $\Phi_{0,\infty}$ to be the same for homopolymers and copolymers, we can write

$$K_0 = (K_{0,A}^{2/3}w_A + K_{0,B}^{2/3}w_B)^{3/2} \tag{10}$$

for the "ideal" case where the ratio $(\langle s^2\rangle_0/M)_\infty$ of copolymers is linearly related to their composition expressed by the weight fractions (w_A, w_B) of comonomer units. For 0.4 $\lesssim$ K_0 $\lesssim$ 2.5, the dependence of K_0 versus w_A is approximately linear,[6] and so will be the intrinsic viscosity $[\eta]_\theta$ at a fixed molecular weight.

In Figure 2 the values of $[\eta]$ for PEP copolymers are plotted against the weight fraction of ethoxamer units. Straight lines connect the values for homopolymers obtained by interpolation for M = 10^3 in logarithmic plots of $[\eta]$ versus M_w constructed from

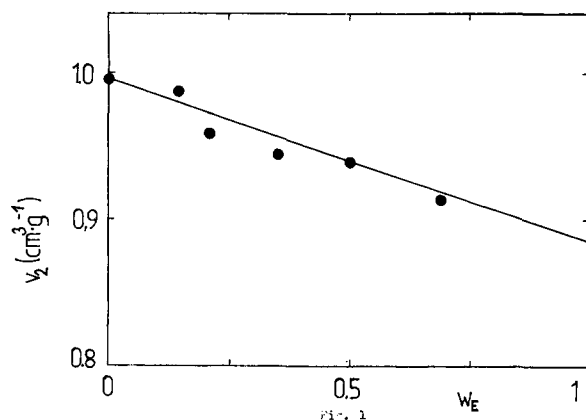Figure 1   Dependence of specific volume of liquid copolymers PEP on weight fraction of ethylene oxide units. Temperature 20°C. Data in Table I.
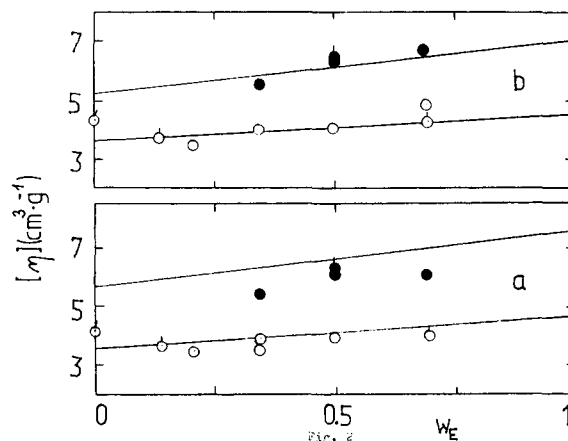
literature data. We are aware of objections that may be raised against this plot:

1. The M_n values of PEP copolymers are in the range between 860 and 1150 (Table I), but the intrinsic viscosity data are here treated as if all M_n values were equal to 10^3. Since, in this range, [η] is approximately proportional to $M^{1/2}$, the error in [η] introduced by this approximation is less than 8%.

2. Lines in Figure 2 correspond to the weight-average molecular weights M_w whereas the experimental data for PEP correspond to M_n. Since, however, the polydispersity of polyethers is typically low $M_w/M_w \lesssim 1.1$, using M_n instead of M_w is admissible.

3. Differences in the [η] values in the two solvents might be assigned to the excluded-volume effect. In fact, they reflect small solvent effects on the unperturbed chain dimension.[16]

Figure 2 shows that the experimental values of [η] do not deviate significantly and systematically from straight lines and do not depend on the character of end groups (hydroxyl, acetyl). It leads to the conclusion that the values of ($\langle s^2 \rangle_0/M)_\infty$ for PEP copolymers can be computed from those for homopolymers under the assumption of additivity.

The values of ($\langle s^2 \rangle_0/M)_\infty$ for homopolymers depend somewhat on the solvent in conformity with theoretical prediction.[13,16] Those used here are arithmetic means (0.13 × 10^{-16} cm^2 for PEO and 0.11 × 10^{-16} cm^2 for PPO) of values for 12 and 8 solvents, respectively.[16] The values of ($\langle s^2 \rangle_0/M)_\infty$ × 10^{16} cm^2 for different solvents were in the range between 0.10 and 0.14 for PEO and from 0.094 to 0.13 for PPO.

The structural factor $F(X)$ of PEP copolymers is calculated according to Eqs. (2) and (3) with the values of v_2, m_a, and ($\langle s^2 \rangle_0/M)_\infty$ obtained by linear interpolation between the values for homopolymers at 25°C [Table I, Fig. 3(a)]. Dashed line in Figure 3(a) shows that, within 2.5%, it is a linear function of the weight fraction of ethoxamer units.

Parameters of the Vogel Equation for PEO and PPO

In this part we review the parameters of the Vogel equation for PEO and PPO with emphasis on the region where entanglement coupling of polymer chains is absent ($M < M_e \simeq 7 \times 10^3$).[17]

The parameters for ethylene glycol and triethylene glycol are obtained from viscosity data in Ref.
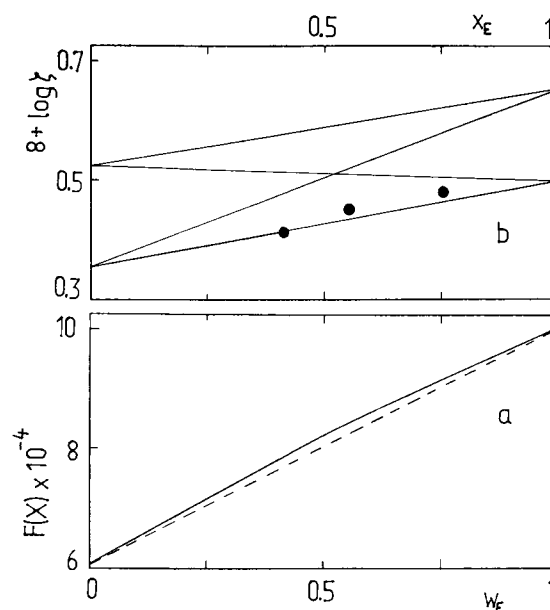

Figure 3 Dependence on copolymer composition of the structure-dependent factor $F(X)$ and the friction factor ζ. (a) $F(X)$ vs. w_E. Full curve calculated as described in text. Dashed curve calculated with assumption of additivity of $F(X)$ values. (b) log ζ vs. x_{EO} (upper scale). (●) Experimental data for PEP. Lines calculated according to Eq. (4) with parameter values given in Table II. Values at $w_E = 0$ and $w_E = 1$ correspond to two values of log ζ_0. For details see text.

18 according to the current procedure based on Eq. (11):

$$y \equiv \frac{(T_r - T)}{\log(\eta_T/\eta_r)} = \alpha b(T - T_r) + \alpha b^2 \quad (11)$$

$$B^{-1} = 2.303\alpha \quad (12)$$

where T_r is a reference temperature, η_r is the viscosity at T_r, η_T is the viscosity at temperature T, and

$$b = T_r - T_0$$

The plots of y versus ($T - T_r$) in Figure 4 are linear, and the parameters B and T_0 are evaluated from the slopes and intercepts. The result for ethylene glycol (B = 1.05 × 10^{-3} K and T_0 = 138 K) agrees very well with that found by Makhija and Stairs[19] (B = 1.01 × 10^{-3} K, T_0 = 141.6 K).

Viscosity data at 10–80°C for nine PPO samples were tabulated in detail by Kuznetsov et al.[20] They are used to complete the molecular-weight dependence of the Vogel parameters. They are plotted as
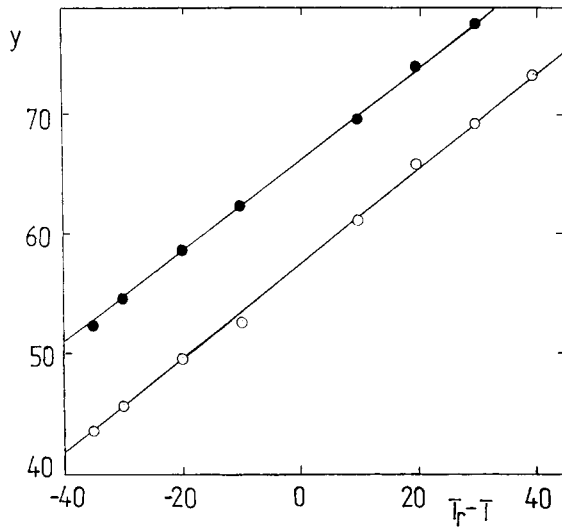
Figure 4 Estimation of T_0 and B for ethylene glycol and triethylene glycol according to Eq. (11). Data from Ref. 18: (●) ethylene glycol, (○) triethylene glycol. T_r = 313 K.

η_T/M_n (at constant temperature) against M_n in Figure 5. At $T < 323$ K they increase in the initial part and assume the asymptotic value $(\eta_T/M_r)_\infty$ at $M_n \gtrsim 3 \times 10^3$. At higher temperatures they become constant already at $M_n \gtrsim 1 \times 10^3$. From the values of $(\eta_T/M_n)_\infty$, the asymptotic value of the friction factor ζ_T^∞ at several temperatures is computed as

$$\zeta_T^\infty = (\eta_T/M_n)_\infty (v_2 m_a)/$$
$$[(N_A/6)(\langle s^2\rangle_0/M)_\infty] \quad (13)$$

The value of v_2 should be the asymptotic value for very long chains. It is estimated according to Ref. 21.

$$1/v_2 = 1.063[1 - 0.696 \times 10^{-3}(T - 180.1)] \quad (14)$$

valid for $M_n \geq 4 \times 10^3$. The asymptotic values, B_∞ and T_0^∞, are obtained according to Eq. (11) where the values of $\log(\eta_T/\eta_r)$ are replaced by $\log(\zeta_T^\infty/\zeta_r^\infty)$ (Fig. 6). The asymptotic value of the inherent friction factor ζ_0^∞ is then calculated as

$$\log \zeta_0^\infty = \log \zeta_T^\infty - \frac{B_\infty}{2.303(T - T_0^\infty)} \quad (15)$$

For temperatures from 10 to 80°C, $\log \zeta_0^\infty$ is between -10.335 and -10.567, the arithmetic mean being -10.45 ± 0.02.

The values of A, B, and T_0 have also been reported by other authors.[21-25] They are used to calculate ζ_0 according to the equation

$$\zeta_0 = \frac{(A/M)(v_2 m_a)}{(N_A/6)(\langle s^2\rangle_0/M)_\infty} \quad (16)$$

with the values of v_2 computed for the respective molecular weights from data in Ref. (11). The data are plotted against M_n in Figure 7. The plot is completed by a few values of B and T_0 obtained in studies by optical methods of the dynamics of PPO oligomers.[26,27] The correspondence of results of optical and rheological studies is remarkable.

The T_0 temperature for both homopolymers is an increasing function of the molecular weight (Fig. 7). Several empirical equations have been proposed to describe this dependence.[28] Curves in Figure 7 are computed by means of [29]

$$1/T_0 = 1/T_0^\infty + k_T/M_n \quad (17)$$

which rather well linearizes the dependence of T_0 versus M. The asymptotic values, T_0^∞, for PEO and
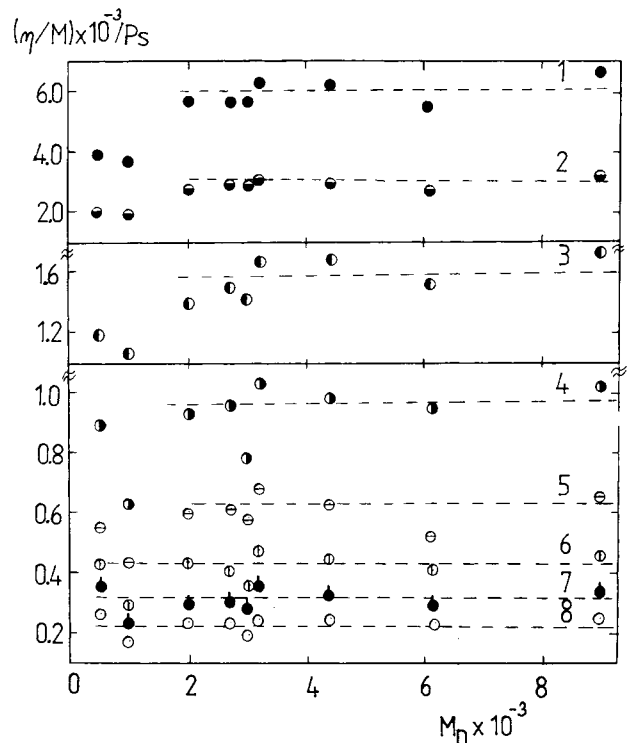

Figure 5 Plot of η_T/M_n vs. M_n for poly(propylene glycol). Data from Ref. 20 at temperatures 10, 20, 30, 40, 50, 60, 70, and 80°C (from top to bottom). Lines 1 to 8 represent asymptotic values (η_T/M_n).
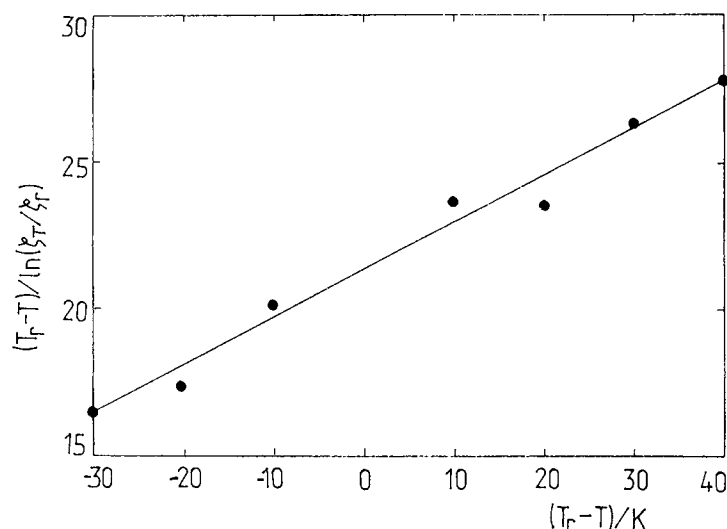
Figure 6   Estimation of parameters B and T_0 for PPO according to Eq. (11). Basic data from Ref. 20. Details of calculations in text.

PPO are, respectively, 180 and 182 K, and the k_T parameters are 0.20 and 0.18 K^{-1}. When calculating the ζ values for homopolymers in the subsequent part, we employ the T_0 values computed for M_n = 1000 and 2000 according to Eq. (17).

The B values for homopolymers slightly decrease with increasing M_n and attain the asymptotic value B_∞ = 830 K at $M_n \gtrsim 1 \times 10^3$ (Fig. 8). The B_∞ value is the same for both polymers. The trend of the dependence on the molecular weight is opposite to that found with other polymers[1,2] and can be assigned to the effect of association of terminal end groups by hydrogen bonding.[22]

In a recent study,[2] the inherent friction factor ζ_0 of epoxy resins has been found to decrease with increasing Z for $Z_n \lesssim 25$. The corresponding value of M for polyethers would be around 400. The asymptotic value for PEO reported by Privalko et al.[22] (for $M_n \geq 10^4$) is -10.25. However, the values for lower molecular weights are both lower and higher. The arithmetic mean of all the values available is -10.41 (Fig. 8).

The asymptotic value of ζ_0 for PPO estimated from Kuznetsov's data (for $M_n \gtrsim 3 \times 10^3$) is -10.41. The other values are lower than this (Fig. 8). The arithmetic mean is -10.65. The ζ_0 values for PPO
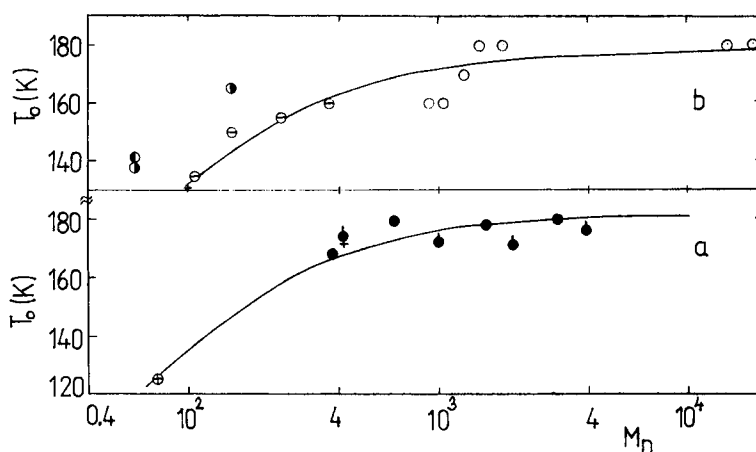

Figure 7   Dependence on molecular weight of parameter T_0 for PEO and PPO. Data for PPO (a): ($\bullet$),[21,23] ($\spadesuit$),[24] (ϕ),[25] ($+$),[26] ($\oplus$).[27] Data for PEO (b): ($\circledcirc$) ethylene glycol and triethylene glycol,[18] ($\ominus$) oligomers of ethylene oxide,[22] ($\bigcirc$) PEO samples.[22] Curves calculated by means of Eq. (7) with the parameter values given in text.
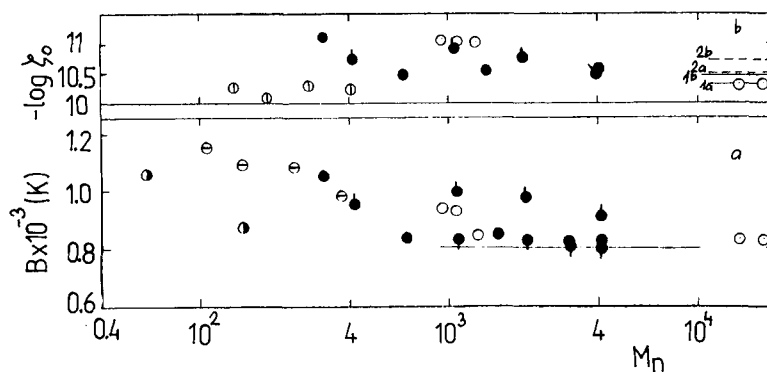
Figure 8 Dependence on molecular weight of parameters B and for PEO and PPO. Notation of points as in Figure 7. Horizontal line in (a) denotes the asymptotic value B_∞ for both homopolymers. Horizontal lines in (b) denote the ζ_0^∞ values for PEO (1a, 1b) and PPO (2a, 2b). For details see text.

are lower than those for PEO. A similar effect of substitution by bulky substituent has been described with polymethacrylates and vinyl polymers.[1]

In view of the latitude in log ζ_0, two sets of values will be used in the subsequent calculations: -10.25 and -10.41 for PEO and -10.40 and -10.65 for PPO.

Friction Factor of PEP Copolymers

The values of the friction factor ζ per friction center of PEP copolymers are computed by means of Eqs. (1)–(5) from the values listed in Table II. In Figure 3(b) they are compared with four reference curves computed with Eq. (4) under the following assumptions: (i) The B parameter is independent of the copolymer composition. (ii) The T_0 temperature of copolymers is between those for homopolymers. (iii) The factor ζ_0 is a linear function of the mole fraction of ethoxamer units.

These assumptions need a comment. The B parameter reflects the barriers to free rotation of the main-chain bonds (kinetic flexibility).[4] Since the same value has been found for homopolymers, it appears that their kinetic flexibility is the same. However, new barriers to free rotation may arise at the points connecting the blocks. We assume that they do not affect noticeably an overall quantity such as

parameter B. However, this assumption need not be legitimate with random or alternating copolymers where connections between chemically different monomer units would be more numerous. Note that Miller[7] has shown that the B parameter of random ethylene–propylene copolymers strongly deviates from additivity.

The third assumption is most questionable and should be taken as a tentative one. Anyway, in view of poor precision of the log ζ_0 data, a linear interpolation is the simplest way to account for the effect of copolymer composition.

Out of four combinations of ζ_0^∞ values for PPO and PEO [Fig. 3(b)], only the combination 1a (-10.65 for PPO and -10.25 for PEO) fits the experimental data.

This finding is supported by the results obtained with sample PEP II/2. Because of a difference in M_n, we employ slightly different values of T_0 for homopolymers. The following values of (log ζ + 8) are obtained: 0.477 (combination 1a), 0.565 (1b and 2a), and 0.650 (2b). The experimental value (log ζ + 8 = 0.509) is very close to the result of combination 1a.

CONCLUSION

We may conclude that the melt viscosity of oligomeric triblock PEP copolymers can be computed with fair accuracy (ca. ±15%) from those of homopolymers. The main source of uncertainty is the value of the intrinsic friction factor ζ_0 whereas the structural factor $F(X)$ and parameters B and T_0 can be obtained by linear interpolation between those for homopolymers.

Table II Asymptotic Values of Characteristic Parameters

Polymer	B_{00} (K)	T_0^{00} (K)	$-\log_0^{00}$
PEO	833	180	-10.25
PPO	833	183	-10.65

REFERENCES

1. G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261 (1967).
2. A. Kaštánek, M. Balcr, M. Bohdanecký, F. Lešek, and J. Kitzler, *J. Appl. Polym. Sci.*, **31**, 1567 (1986).
3. A. A. Miller, *Macromolecules*, **11**, 859 (1978).
4. A. A. Miller, *Macromolecules*, **2**, 355 (1969).
5. M. Bohdanecký, A. Kaštánek, and F. Lešek, *Collect. Czech. Chem. Commun.*, **50**, 2570 (1985).
6. M. Bohdanecký and J. Kovář, in *Viscosity of Polymer Solutions*. A. D. Jenkins, Ed., Polymer Science Library, Vol. 2, Elsevier, Amsterdam, 1982.
7. A. A. Miller, *Polymer*, **21**, 360 (1980).
8. S. Petřik, F. Hadobaš, L. Šimek, and M. Bohdanecký, *Eur. Polym. J.*, **28**, 15 (1990).
9. L. Šimek, S. Petřik, F. Hadobaš, and M. Bohdanecký, *Eur. Polym. J.*, **26**, 371 (1990).
10. S. Petřik, M. Bohdanecký, F. Hadobaš, and L. Šimek, *J. Appl. Polym. Sci.*, **42**, 1759 (1991).
11. L. S. Sandell and D. A. I. Goring, *J. Polym. Sci., Part A-2*, **9**, 115 (1971).
12. W. Braun, K. H. Hellwege, and W. Knappe, *Koll. Z. Z. f. Polym.*, **215**, 10 (1969).
13. P. J. Flory, *Statistical Mechanics of Chain Molecules*, Interscience, New York, 1969.
14. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
15. T. Norisuye and H. Fujita, *Polym. J.*, **14**, 143 (1982).
16. V. Kašpárková, unpublished results.
17. B. A. Smith, E. T. Samulski, L. P. Yu, and M. A. Winnik, *Macromolecules*, **18**, 1901 (1985).
18. A. Teramoto, S. Kusamizu, H. Tanaka, Y. Murakami, and H. Fujita, *Makromol. Chem.*, **90**, 87 (1966).
19. R. C. Makhija and R. A. Stairs, *Can. J. Chem.*, **48**, 1214 (1970).
20. V. N. Kuznetsov, L. V. Lesnevskaya, V. A. Petrova, V. B. Kagan, and M. S. Vilemova, *Vysokomol. Soed. A*, **11**, 213 (1969).
21. A. J. Barlow and A. Erginsav, *Polymer*, **16**, 110 (1975).
22. V. P. Privalko, Yu. S. Lipatov, and A. L. Lobodina, *Vysokomol. Soed. A*, **16**, 2771 (1974).
23. J. Cochrane, G. Harrison, J. Lamb, and D. W. Phillips, *Polymer*, **21**, 837 (1980).
24. D. H. Wang, G. Fytas, D. Lilge, and Th. Dorfmüller, *Macromolecules*, **14**, 1363 (1981).
25. M. E. Baur and W. H. Stockmayer, *J. Chem. Phys.*, **43**, 4319 (1965).
26. M. Fofana, V. Veissier, J. L. Viovy, L. Monnerie, and G. P. Johari, *Polymer*, **29**, 245 (1985).
27. L. Bokobza, Pham-Van-Gang, G. Giordano, L. Monnerie, J. Vandendriessche, and F. C. Shryver, *Polymer*, **29**, 251 (1988).
28. J. A. Brydson, in *Polymer Science*, A. D. Jenkins, Ed., Vol. 1, North Holland, Amsterdam 1972, p. 251.
29. K. Überreiter and G. Kanig, *J. Colloid Sci.*, **7**, 569 (1952).