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ORIGINAL CONTRIBUTION

Yasuyuki Maki
Naoki Sasaki
Mitsuo Nakata

Elongational flow studies on flexible polymer chains in a pseudo-solvent

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Y. Maki · N. Sasaki (✉) · M. Nakata
Division of Biological Sciences,
Graduate School of Science,
Hokkaido University,
060–0810 Sapporo, Japan
E-mail: nasa5131@sci.hokudai.ac.jp
Tel.: +81-011-706-3809
Fax: +81-011-706-4993

Abstract The dynamics of isolated high molecular weight (M_H) polymer chains dissolved in a nonentangled semidilute solution of a low molecular weight (M_L) polymer were investigated by monitoring the elongational flow birefringence. Because of its nonentangled nature, a low molecular weight matrix polymer solution is regarded as a pure solvent (a binary pseudo-solvent). A ternary solution consisting of a small amount of a high molecular weight probe polymer and the binary pseudo-solvent is effectively a dilute solution of the probe polymer. It was observed that the birefringence from the orientation and/or stretching of the probe polymer chains starts to increase rather abruptly at a certain critical strain rate, $\dot{\varepsilon}_c$, and the spatial birefringence pattern is localized along the elongation axis, characteristics that are reminiscent of the coil-stretch transition of flexible polymer chains in a simple dilute solution. The relaxation time for the chain extension, τ_{el}, defined as the reciprocal of the critical strain rate $\dot{\varepsilon}_c$, was determined at various temperatures, matrix polymer concentrations c_L, and test chain molecular weights M_H. It was found that τ_{el} varied with molecular weight as $\tau_{el} \sim M_H{}^a$, with a ranging from 1.3 to 1.8, which is roughly consistent with the molecular weight dependence of the non-free-draining Zimm relaxation time. A scaled relaxation time $\tau_{el}kT/\eta$, which can be used to estimate the radius of gyration R_g of the probe polymer, decreased with increasing c_L, indicating contraction of the high molecular weight polymer due to a screening of the excluded volume effect caused by the matrix polymer in the pseudo-solvent.

Keywords Flow birefringence · Coil-stretch transition · Poly(ethylene oxide) (PEO) · Aqueous solution · Ternary solution

Introduction

de Gennes [1, 2] prediction of a transition from a random coil to a fully extended state for a single polymer chain in a persistent elongational flow has led to many theoretical and experimental studies on this “coil-stretch transition” [3]. These works have established that, in an elongational flow, the onset of segment orientation and whole chain extension set in rather abruptly at an extension rate proportional to the inverse of the longest relaxation time of the Zimm model, τ_1 [1, 2, 3, 4, 5, 6]:

$$\dot{\varepsilon}_c = \frac{A}{\tau_1}, \tag{1}$$

where A is a numerical constant of the order of unity. The factor $A=0.5035$ was derived from theoretical calculations based on a bead-spring model with hydrodynamic interactions [5]. Experimentally, no general agreement about the exact value of A has been reached [7]. There are many reports stating that A is approximately unity, although much higher values, 5–14, have also been reported [8]. The longest relaxation time τ_1 is written as [9]

$$\tau_1 = \frac{\eta_s[\eta]M}{A_1 kTN_A}, \tag{2}$$

where η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, M is the molecular weight, k is the Boltzmann constant, T is the absolute temperature and N_A is the Avogadro number. The non-dimensional numeric factor A_1 is 0.822 for a free-draining chain, and 1.184 for a non-free-draining chain with preaveraged hydrodynamic interactions [7, 9].

According to Eqs. 1 and 2, $\dot{\varepsilon}_c$ should scale with polymer molecular weight as

$$\dot{\varepsilon}_c \propto M^{-3v}, \tag{3}$$

where v is Flory's exponent, equal to 0.50 for a Θ solvent and 0.59 for a good solvent. Several groups have reported exponent values consistent with Eq. 3, while the Bristol group reported that the exponent is 1.5 irrespective of solvent quality [3].

Equation 2 for the Zimm relaxation time can be re-expressed in terms of the radius of gyration of the polymer coil in a quiescent state, R_g, as [9]

$$\tau_1 \propto \frac{\eta_s R_g^3}{kT}. \tag{4}$$

Combining Eqs. 1 and 4, the critical strain rate can be interpreted in terms of the expansion of the coil radius. The influence of solvent quality on the scaling exponent of $\dot{\varepsilon}_c$, as in Eq. 3, has been examined by many investigators [3, 6, 7, 10]. On the other hand, there have been few studies that focus on the degree of chain expansion as estimated from $\dot{\varepsilon}_c$ (through Eqs. 1 and 4). Expansion and contraction of a polystyrene chain have been studied in cyclohexane [6] and decalin [10] for changes in temperature around the Θ point by means of an elongational flow birefringence method. The results of those studies have shown that the value of $\dot{\varepsilon}_c$ is sensitive to change in solvent quality.

Conformations of a single long chain dissolved in a mixture of chemically identical short polymers and an athermal solvent were theoretically examined by Joanny et al [11, 12]. They concluded that the short chains reduce the effective solvent power due to a screening of the excluded volume effect, and that the long test chain shrinks. There have been various experimental studies on the change in size of a long probe chain in the presence of short matrix chains [13, 14, 16, 17], but most of these works were performed using a chemically nonidentical probe-host pair [13, 14, 15, 16, 17].

In the present study, we aimed to detect the contraction of a probe polymer coil in a ternary solution by observing $\dot{\varepsilon}_c$. For this purpose, a ternary system of a small amount of high molecular weight (M_H) probe polymer dissolved in a semidilute solution of a low-molecular-weight (M_L) matrix polymer at a concentration CL was investigated using an elongational flow birefringence technique. If the matrix solution is a nonentangled system, the birefringent behavior should be similar to that of a dilute solution of high molecular weight polymer in a pure solvent. We determined $\dot{\varepsilon}_c$ of the probe polymer in a pseudo-solvent (a matrix solution of low molecular weight polymer) under various conditions (changes in temperature, c_L, and M_H), and examined the change in the radius of the probe polymer chain based on Zimm dynamics (Eq. 4).

Experimental

Materials

The test materials were solutions of poly(ethylene oxide) (PEO) in water. Each solution contained high molecular weight PEO (HMPEO) with molecular weight M_H and low molecular weight PEO (LMPEO) with molecular weight M_L. Five kinds of HMPEO samples with molecular weights of 0.790, 1.04, 1.31, 1.44 and 2.75×10^6 were purchased from Aldrich Chemical Co. The molecular weight was determined by measuring the intrinsic viscosity in benzene at 25 °C. Two LMPEO samples with $M_L=8000$ and 20000 (nominal) were purchased from Sigma Chemical Co. and Wako Chemical Co., respectively. All samples were used without further purification. The distilled water used as a solvent was prepared by a Millipore Milli-Q purification system, and 0.1%(v/v) of allyl alcohol (Wako) was added to the water to prevent oxidation of PEO. All solutions were prepared by stirring for seven days in the dark. The concentration

Table 1 Test solutions

$M_H(\times10^6)$	M_L	c_H(wt%)	c_L(wt%)
1.04	8000	0.1	30, 35, 40, 45, 50
1.31	8000	0.1	30, 35, 40, 45, 50
1.44	8000	0.1	26, 28, 30, 32, 35, 40, 45, 50
2.75	8000	0.1	25, 30, 35, 40, 45
0.790	20000	0.1	35, 45
1.04	20000	0.1	25, 30, 35, 40, 45
1.44	20000	0.1	25, 30, 35, 40, 45

of HMPEO, c_H, was always 0.1%(w/w) and the concentration of LMPEO, c_L, was varied from 25%(w/w) to 55%(w/w) (Table 1). Because the critical molecular weight for entanglement onset $M_c = 4400$ for PEO [18], LMPEO chains can be mutually entangled at a high LMPEO concentration c_L. The entanglement molecular weight for solutions $M_{c,sol}$ depends on the solution concentration, and is higher than M_c [19]. To estimate $M_{c,sol}$, we measured zero-shear viscosities of LMPEO solutions for various M_L ranging from 1450 to 110,000 (nominal) at $c_L = 30$ and 50%(w/w). In Fig. 1, the viscosity of LMPEO solutions is plotted against $c_L'M_L$, where c_L' is the concentration of the LMPEO in g/cm^3. It is known that a plot like Fig. 1 is independent of polymer concentration at sufficiently high polymer concentrations [19] and $M_{c,sol}$ at a concentration c can be estimated from the deflection point on the plot. From Fig. 1, it is estimated that $c_L'(M_L)_{c,sol}$ is approximately 10,000. This means that the critical molecular weight of the LMPEO solution $(M_L)_{c,sol}$ is about 20,000 at the concentration $c_L = 50\%$(w/w). It was confirmed that the c_L values used in this study corresponded to a nonentangled or marginal (very small number of entanglements) regime.

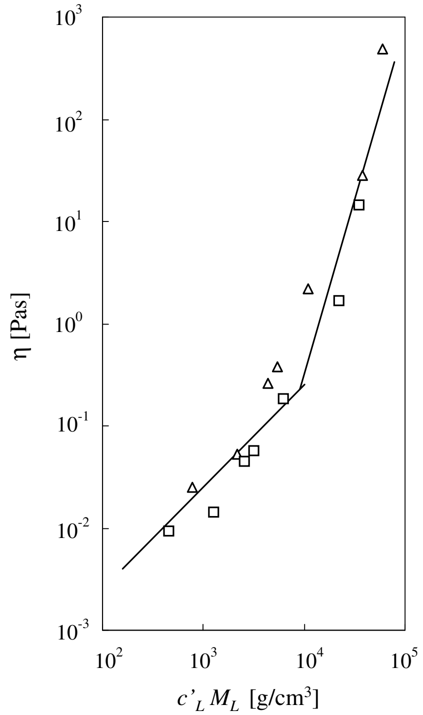

Fig. 1 Zero-shear viscosity of the LMPEO solution for various M_L values ranging from 1450 to 110000 (nominal) at $c_L = 30$ wt% (squares), 50 wt% (triangles) at 30 °C. The solid lines are straight lines with slopes of 1.0 and 3.4, respectively

Method

A steady elongational flow field was generated by a four-roller mill (FRM) system. The FRM produces a planar extensional flow with a velocity $(v_x,\ v_y,\ v_z) = (\dot{\varepsilon}x,\ -\dot{\varepsilon}y,\ 0)$. The elongational strain rate was determined geometrically according to the method of Torza [20]. The four-roller mill apparatus used in this study can generate a strain rate of up to 160 s^{-1}. The segment orientation of polymer chains was detected by observing the flow birefringence. The flow cell was placed between a crossed pair of a polarizer and an analyzer, and monochromatic light (632.8 nm) emitted from a 2 mW He-Ne laser was directed toward the center of the flow field. The polarization direction of the incident beam was set at 45° with respect to the flow direction. The intensity of the birefringent signal, I, is given by

$$I = I_0 \sin^2 2\theta \sin^2 (\delta/2),$$

where I_0 is the intensity of the incident beam, and θ is the angle between the incident polarization direction and the principal axis of the molecular refractive index (chosen to be 45°), and δ is the retardation angle, which is related to the birefringence Δn by

$$\Delta n = \frac{\lambda \delta}{2\pi d},$$

where d is the path length and λ is the wavelength of the incident light. The four-roller mill and the optical system used in the present study are described in detail elsewhere [21].

Results and discussion

Elongational flow birefringence measurements were performed for matrix polymer solutions ($c_H = 0$), and the contribution of LMPEO to the flow birefringence was

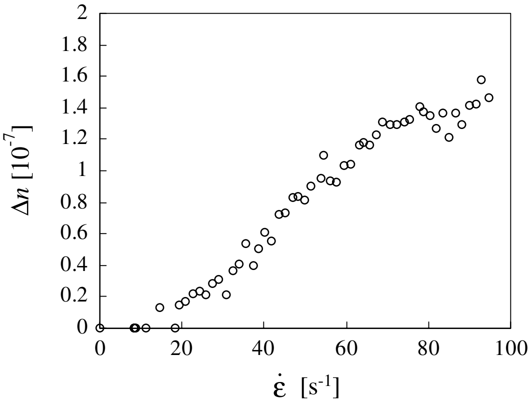

Fig. 2 Elongational flow birefringence, Δn, plotted against strain rate, $\dot{\varepsilon}$, for $M_H = 1.31\times10^6$, $M_L = 8000$, $c_L = 50$ wt% at 20 °C

found to be negligible, at least for the concentration ranges and strain rate windows used in the present study.

Figure 2 shows a typical flow birefringence, Δn, as a function of strain rate $\dot{\varepsilon}$ for the ternary system. The flow birefringence started to increase rather abruptly above a critical strain rate, $\dot{\varepsilon}_c$. The spatial birefringence pattern was localized along the outgoing axis. These characteristics of the observed birefringence are similar to those observed for a coil-stretch transition in a simple dilute solution of flexible polymers [1, 2, 3, 4, 5, 6]. It can be concluded that the observed birefringence is caused by the coil-stretch transition of a probe polymer chain.

Relaxation time of chain extension τ_{el}

Figure 3a shows the relationship between Δn and $\dot{\varepsilon}$ at various temperatures at a matrix polymer concentration c_L of 40%. As the temperature was increased, the value of Δn at a strain rate $\dot{\varepsilon}$ gradually decreased, and $\dot{\varepsilon}_c$ became larger. If we define a characteristic relaxation time associated with the extension of the probe chains, τ_{el}, as the inverse of $\dot{\varepsilon}_c\left(\tau_{el} = 1/\dot{\varepsilon}_c\right)$, τ_{el} is shown from Eq. 1 to be proportional to the longest relaxation time of the Zimm theory τ_1 ($\tau_1 = A\tau_{el}$). Figure 3b shows the same data as those in Fig. 3a replotted as a function of the normalized strain rate $r = \dot{\varepsilon}/\dot{\varepsilon}_c$. r is proportional to the Deborah number $\mathrm{De} = \dot{\varepsilon}\tau_1$. As shown in Fig. 3b, all birefringence curves were superimposed to construct a master curve.

Figure 4a shows the relationship of Δn to $\dot{\varepsilon}$ for various matrix concentrations at 30 °C. These curves also collapsed into a single curve by replotting against r (Fig. 4b). These universal curves (Figs. 2b, 4b) imply that Δn is only a function of $\dot{\varepsilon}\tau_1$. Data shown in Fig. 4b confirm that the contribution of the matrix polymer to flow birefringence is negligible.

Molecular weight dependence of τ_{el}

In order to obtain the exponent 3ν in Eq. 3, the logarithm of τ_{el} was plotted against log M_H. The plot

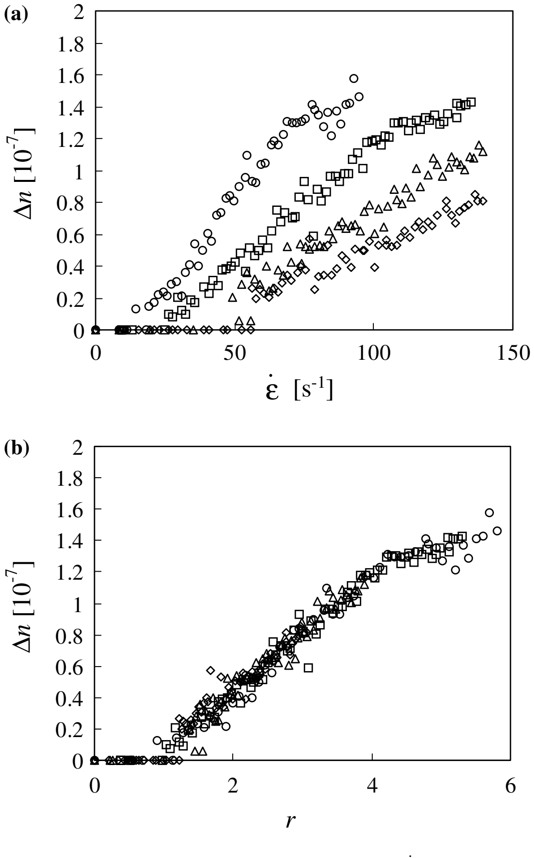

Fig. 3 Δn as a function of $\dot{\varepsilon}$ (a) and $r = \frac{\dot{\varepsilon}}{\dot{\varepsilon}_c}$ (b) for various temperatures: 20 °C (circles), 30 °C (squares), 40 °C (triangles) and 50 °C (diamonds). The test solution consisted of HMPEO with $M_H = 1.31\times10^6$ and LMPEO with $M_L = 8000$ and water. The concentration of the matrix polymer was 50 wt%

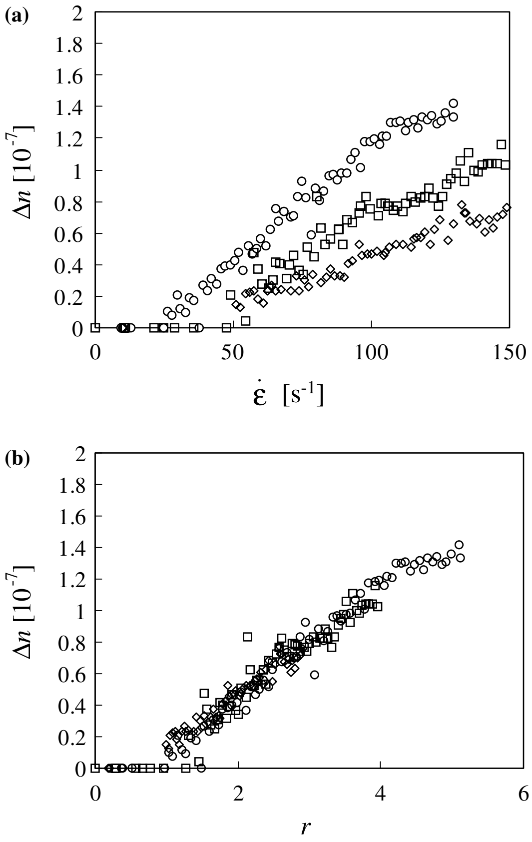

Fig. 4 Δn as a function of $\dot{\varepsilon}$ (a) and r (b) for various values of c_L: 50% (circles), 45% (squares) and 40% (diamonds). The test solution consisted of HMPEO with $M_H = 1.31\times10^6$ and LMPEO with $M_L = 8000$ and water. Measurements were performed at 30 °C

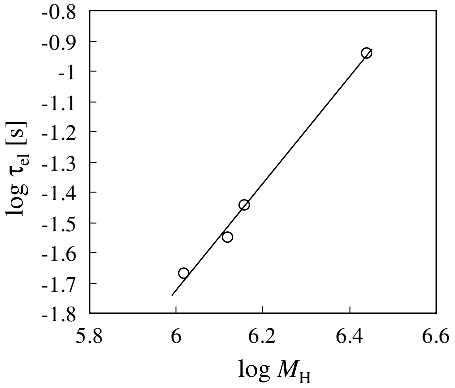

Fig. 5 Double logarithmic plot of the relaxation time of HMPEO chain extension τ_{el} and M_H. $M_L = 8000$, $c_L = 40$ wt% and the temperature was 20 °C

indicates a linear relation (Fig. 5), and slopes ranging from 1.3 to 1.8 were obtained for several values of c_L and T, as listed in Table 2. These values are roughly in accord with the Zimm theory, which predicts an exponent value of between 1.5 and 1.8, depending on the solvent quality. However, it was not clear whether there was any dependence of the exponent on the temperature or c_L from the present data. To clarify whether this means that the exponent is invariant, or whether this indicates a failure to determine the dependence of the exponents upon the solvent quality within the precision of the experiment, we need to examine a wider range of M_H values in order to determine the exponents more accurately.

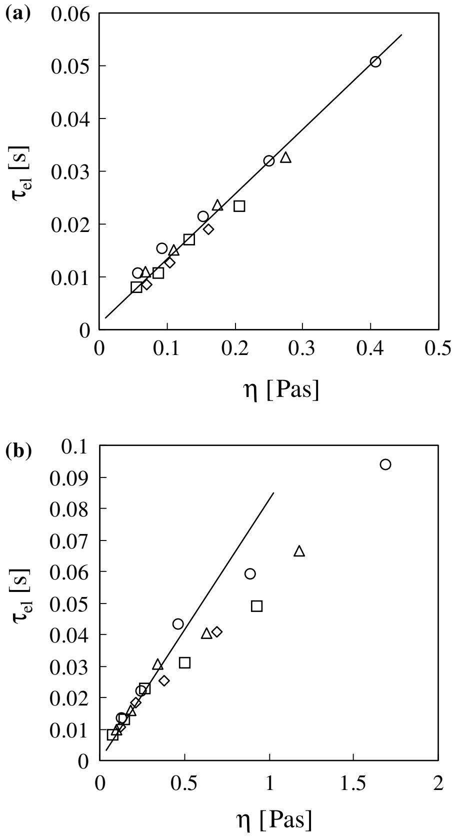

Fig. 6 τ_{el} plotted against pseudo solvent viscosity η. $M_H = 1.04{\times}10^6$ and $M_L = 8000$ (a) and $M_L = 20000$ (b). Measurements were performed at 20 °C (circles), 30 °C (triangles), 40 °C (squares) and 50 °C (diamonds)

Change in the radius of gyration R_g

Figure 6a, b shows the dependence of τ_{el} on the viscosity of the matrix polymer solution (or the pseudo solvent) η. As predicted by Martin [14] (in an expansion of the theory of Daoud and de Gennes [22]), and confirmed by an experiment on self-diffusion coefficients [17], the pure solvent viscosity η_s in Eq. 4 can be replaced by η for ternary polymer solutions when the probe polymer chain is much longer than the matrix polymer chain. Proportionality was apparently displayed in the case of $M_L = 8000$ (Fig. 6a), but a deflection at high η was observed in the case of $M_L = 20{,}000$ (Fig. 6b).

Table 2 Exponents of M_H for various conditions

M_L	c_L(wt%)	T (°C)	Exponent
8000	30	20	1.7
8000	35	20	1.5
8000	35	30	1.6
8000	35	40	1.5
8000	40	20	1.8
8000	40	30	1.7
8000	40	40	1.8
8000	45	30	1.7
20000	35	20	1.4
20000	35	30	1.3
20000	35	40	1.5
20000	35	50	1.5
20000	45	20	1.6
20000	45	30	1.7
20000	45	40	1.6

To investigate this deviation from the linear relation more closely, $\tau_{el}kT/\eta$ was plotted against c_L (Fig. 7a, b). According to Eq. 4, if the dependence of τ_{el} on c_L comes from the change in η only, $\tau_{el}kT/\eta$ should have a constant value. It was shown that $\tau_{el}kT/\eta$ decreased with increasing c_L for both $M_L = 8000$ and $M_L = 20000$. From Eq. 4, $\tau_{el}kT/\eta$ is proportional to ${R_g}^3$, where R_g is the radius of gyration of a long polymer (so a change in $\tau_{el}kT/\eta$ indicates a change in R_g with c_L). Therefore, a decreasing $\tau_{el}kT/\eta$ with increasing c_L indicates a decrease in R_g (in other words, a decrease in the effective solvent power) induced by the addition of matrix polymer chains. A change in the size of the long probe chain in the presence of a chemically identical short matrix chain

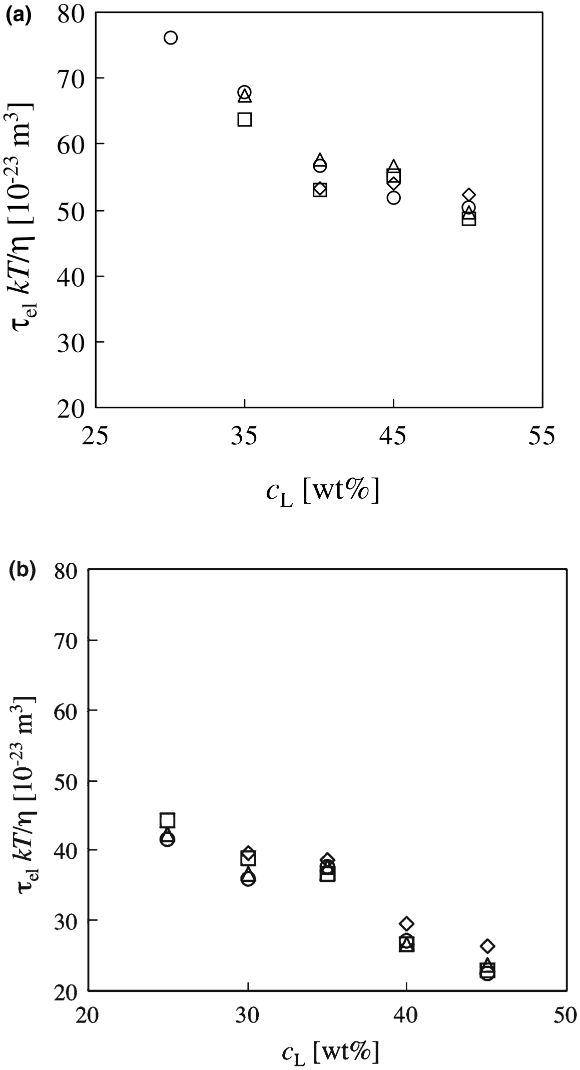

Fig. 7 $\tau_{el}kT/\eta$ plotted against c_L. $M_H = 1.04\times10^6$ and $M_L = 8000$ (a) and $M_L = 20000$ (b). Measurements were performed at 20 °C (circles), 30 °C (triangles), 40 °C (squares) and 50 °C (diamonds)

was detected for both $M_L = 8000$ and 20000. The deflection shown in Fig. 6b was found to be due to the change in R_g. Although the data in Fig. 6a show an apparently linear relation, it is actually curved slightly since both η and R_g are dependent on c_L (Fig. 7a).

Verifying the validity of Equations 1 and 4

In the present study, in order to obtain sufficient signal intensity, c_H was set at a constant value of 0.1%, which is lower than $c_H{}^*$ but not very dilute. In an elongational field, the presence of intermolecular entanglements has been reported at concentrations lower than c^* [3, 6]. Therefore, it is possible that the birefringence signal observed in this study is due to mutually entangled probe polymer chains, not isolated polymer coils. In the following discussion, we will estimate R_g from $\dot{\varepsilon}_c$ data using Eqs. 1 and 4, assuming isolated chains. The value should be comparable to the radius of gyration in Θ or a good solvent if the flow birefringence is due to isolated polymer coils. If entanglements between probe polymers exist, the apparent R_g value obtained will be much larger than expected. (As was mentioned before, the matrix polymer chains are not entangled for the c_L range used in the present study. Because the chain length of the probe polymer is much longer than that of the matrix polymer, reptation of the probe polymer will not be present. The matrix chains influence the dynamics of the probe chains via the "pseudo solvent" viscosity η and the screening of the excluded volume effect.) It should be pointed out that there are two difficulties involved with accurately estimating R_g from elongational flow birefringence. First, the actual value of the coefficient A in Eq. 1 has not been determined. The second difficulty is that the numerical constant in Eq. 4 can be dependent on solvent quality. However, the R_g values estimated from the $\dot{\varepsilon}_c$ data with the following procedure can at least provide some measure of the entanglements.

For the case of an unperturbed chain with hydrodynamic interactions, the constant in Eq. 4 has been calculated [7, 9] and

$$\tau_1 = 5.85\frac{\eta_s R_g^3}{kT}. \qquad (5)$$

The coefficient in Eq. 5 applicable to arbitrary solvent quality has not been obtained as far as we know. τ_1 data from dynamic light scattering (DLS) experiments [23, 24, 25, 26] can be used to determine the constant. Re-analyzing the DLS data in the literature [23, 24, 25, 26], we obtain the constant 4.5 ± 1.3, which is smaller than in Eq. 5, and an influence of the solvent quality on

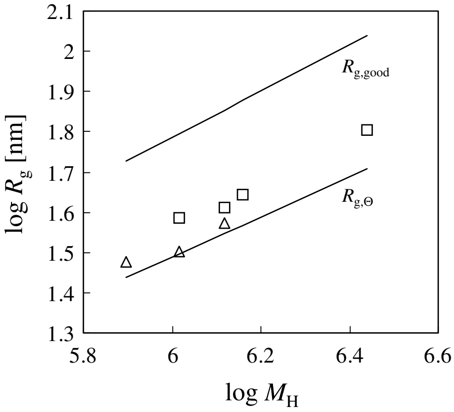

Fig. 8 R_g, as estimated from the critical strain rate, plotted against M_H. $T = 30$ °C, $c_H = 35$ wt%, $M_L = 8000$ (squares) and 20,000 (triangles)

Table 3 Radius of gyration for HMPEO estimated from flow birefringence $R_g$and calculated value for an ideal chain ($R_{g,\Theta}$) and in a good solvent (water, 25 °C) ($R_{g,good}$)

$M_H(10^6)$	M_L	c_L(wt%)	T (°C)	R_g(nm)	$R_{g,\Theta}$ (nm)	$R_{g,good}$(nm)
1.04	8000	35	30	39	31	62
1.31	8000	35	30	41	35	71
1.44	8000	35	30	44	37	75
2.75	8000	35	30	64	51	110
0.790	20000	35	30	30	27	53
1.04	20000	35	30	32	31	62
1.31	20000	35	30	37	35	71

the constant is not clearly indicated. In this study, we used $A = 0.5$ from theoretical calculations and Eq. 5 for the Zimm model in an ideal state. Values of R_g estimated from elongational flow birefringence are plotted against M_H in Fig. 8 (see Table 3). The solid lines represent R_g in the Θ state and in a good solvent (water, 25 °C) [18, 27]. R_g in a Θ solvent is calculated by [18]

$$R_{g,\Theta} = \frac{b\sqrt{N}}{\sqrt{6}},$$

where b, chosen to be 5 nm for PEO, is Ferry's structure length, and N is the degree of polymerization. R_g in a good solvent is calculated from static light scattering data by the following equation [27]:

$$R_{g,good} = 4.08 \times 10^{-18} M^{1.16}\ (\text{cm}^2).$$

Figure 8 shows that the values of R_g estimated from birefringence occur between the values of R_g in a good and those in a Θ solvent. Therefore, it is concluded that the flow birefringence observed in the present study arises from the deformation of an isolated polymer coil, not from entangled probe polymers. From the discussion above, it is obvious that a decrease in the size of the probe polymer chain in the presence of chemically identical short chains was observed by elongational flow birefringence, and this is the principal assertion of the present work.

Conclusions

The elongational flow birefringence of isolated high molecular weight poly(ethylene oxide) (HMPEO) chains dissolved in a nonentangled semidilute solution of low-molecular-weight PEO (LMPEO) was investigated. The flow birefringence curve was identified as the coil-stretch transition of the probe polymer in a pseudo solvent, and the critical strain rate $\dot{\varepsilon}_c$ was determined. The relaxation time of chain extension τ_{el}, defined as the reciprocal of the critical strain rate $\dot{\varepsilon}_c$, was derived for various temperatures, matrix polymer concentrations and test chain molecular weights. It was found that τ_{el} is proportional to $M_H{}^{1.3-1.8}$, which is roughly in accord with Zimm theory. The decrease in $\tau_{el}kT/\eta$ with increasing c_L indicates a contraction of the high molecular weight polymer due to a screening of the excluded volume effect caused by the matrix polymer.

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