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Elongational flow study of poly(styrene sulfonate) in dilute solution

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The elongational flow measurements were made for dilute polystyrene sulfonate solutions of three different molecular weights at low added-salt concentration. The results obtained show that the polymer chains are rigid-rod-like at low salt concentrations and that the flexibility of chains increases with salt concentration. At very low salt concentrations, an unusual dependence of retardation on strain rate has been observed; the retardation decreases with increasing strain rate after showing a maximum, and further the sign of birefringence changes. A possible interpretation has been proposed for this response of polymer chains against an elongational flow field. © 1997 Elsevier Science Ltd.

(Keywords: polyelectrolyte; poly(styrene sulfonate); elongational flow)

Introduction

It is well-known that the flexibility of a charged polymer chain increases with counterion concentration, and hence that the conformation of polymer chains changes from a highly expanded chain to a flexible random coil with added-salt concentration. An elongational flow technique is a powerful method to investigate dynamical properties of polymer chains. In this method, an elongational flow field with a stagnation point induces the chain extension and/or alignment which are registered by the light transmitted through crossed polars. It has been reported that for flexible chains a birefringent zone is localized along the stream line passing through a stagnation point, and retardation shows a sudden increase against strain rate, which corresponds to a coil-stretch transition, while the birefringence is non-localized and retardation increases continuously with strain rate for rigid rod-like molecules[1]. Thus, the flexibility of polymer chains can be studied both from a birefringence pattern and from the strain rate dependence of retardation.

A few experimental results have been reported for elongational flow studies on polystyrene sulfonate (PSS), a typical polyelectrolyte[2–5]. These results showed that the chain flexibility increased with counterion concentration, but the interpretation of the results at low counterion concentration is still under debate.

In the course of re-examining the behaviour of dilute PSS solutions at low counterion concentration under an elongational flow field, we have observed an unexpected dependence of retardation on strain rate at very low counterion concentration; the retardation decreases and further changes the sign with increasing strain rates. In this paper, the results are presented and a mechanism has been discussed for this unusual strain rate dependence of retardation.

Experimental

The material used was PSS, purchased from Scientific Polymer Products in the form of a sodium salt. The molecular weight, M_w, the polydispersity, M_w/M_n, the polymer concentration, c_p, and the range of added-salt concentration, c_s, studied are given in *Table 1*. The polymers were dialysed against pure water to remove excess salt and the salt concentration is taken as zero for the dialysed solutions. The salt used was sodium chloride. For preparing the PSS aqueous solutions with low added-salt concentration, 1% NaCl aqueous solution was added to the polyelectrolyte solution in small drops, and for large c_s solutions powder NaCl was dissolved into the solutions.

The elongational flow field was created by an opposed-jets system[1]. The opposed jets are composed of two glass capillaries with inner diameter $2r$ of 0.9 mm, and outer diameter of 7 mm placed in separation $2d$ of 0.6 mm. The uniaxial extensional flow field with a stagnation point at the centre was created by sucking the solution from the opposing glass capillaries. The strain rate $\dot{\epsilon}$ at the stagnation point is calculated from the volumetric flow rate Q and the jet dimensions by $\dot{\epsilon} = Q/(2\pi r^2 d)$. The highest strain rate achieved in the present system was about $2 \times 10^4\ \mathrm{s}^{-1}$ for dilute PSS aqueous solutions.

The orientation of polymer molecules is registered by the birefringence. The optical axis is perpendicular to the jet symmetric axis and passing through the stagnation

Table 1 List of the poly(styrene sulphonate) solutions studied

Solution	M_w	M_w/M_n	Polymer concentration c_p (wt%)	Added-salt concentration c_s (mol l^{-1})
PSS05	5.05×10^5	1.17	0.08	0–3.5×10^{-3}
PSS08	8.01×10^5	1.16	0.06	0–1.7×10^{-2}
PSS12	1.19×10^6	1.24	0.06	0–4.0×10^{-3}

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point. A polarizer and an analyser are mutually crossed at 45° to the symmetry axis of the jets. In the intensity measurements the laser beam was focused down to about 0.2 mm in diameter. Since the retardation induced by the flow in the present study was always much less than the wavelength of light (also less than the saturation limit of the detector), the retardation is proportional to the square root of the intensity of light transmitted through crossed polars. No hysteresis in retardation was observed in both increasing and decreasing strain rate measurements in the present study. A quarter-wave plate was used for compensating stray birefringence and for confirming the sign of birefringence.

Results and discussion

Figure 1a shows the strain rate dependence of retardation B, for the solutions PSS05 ($M_w = 5.05 \times 10^5$). The sign of birefringence was negative near the stagnation point; in this paper, the negative values of retardation are plotted above the abscissa in the figures of the strain rate vs retardation. For the solutions with added-salt concentration smaller than 1×10^{-3} mol l^{-1}, retardation first increases linearly with strain rate, and tends to saturate at a higher strain rate. Birefringence is not localized, and a pair of dark bands is observed approximately parallel to the symmetry axis nearly at the edges of entrance to the capillary; the sign of observed birefringence changes across the dark bands. Both the strain rate dependence of retardation and the birefringence pattern are typical of the rigid-rod molecule behaviour[6,7].

At a salt concentration larger than 2×10^{-3} mol l^{-1}, the retardation vanishes at small strain rates, and then increases gradually with strain rate. At the same time, the dark bands are almost unobservable. Birefringence is, however, still non-localized, and not so sharp as that observed for flexible molecules. This behaviour suggests the increase in chain flexibility due to the charge screening with increasing salt concentration.

The results for the solutions PSS08 ($M_w = 8.01 \times 10^5$) and PSS12 ($M_w = 1.19 \times 10^6$) are shown in *Figures 1b* and *1c*, respectively. For the solutions PSS08 at $c_s > 6 \times 10^{-4}$ mol l^{-1}, the results are similar to those of the solutions PSS05: the rigid-rod like behaviour at low salt concentrations, and the appearance of flexibility of chain with increasing salt concentration. At still lower salt concentration, $c_s < 2 \times 10^{-4}$ mol l^{-1}, however, retardation first increases, passes through a maximum and then decreases with strain rate (*Figure 1b*).

For solutions PSS12, this peculiar phenomenon is observed more conspicuously (*Figure 1c*). At $c_s < 6 \times 10^{-4}$ mol l^{-1}, retardation shows a maximum against strain rate, and further, at $c_s < 9 \times 10^{-5}$ mol l^{-1}, retardation changes its sign with increasing strain rate (negative to positive birefringence). Although in the intensity measurement the intensity of light transmitted through crossed polars shows a minimum, the change of sign in birefringence was confirmed by a quarter-wave plate. The birefringence pattern at low strain rate is similar to that for the solutions PSS05 at low c_s concentrations, and is typical of the rigid-rod molecules. At high strain rate, where the decrease of retardation is observed, the dark bands approach the symmetric axis, and the outer region beyond the dark bands becomes very bright. The unusual approach of dark bands to the symmetric axis indicates that the relaxation time is very large[6]. At strain rates higher than the one at which the sign inversion of birefringence is detected, no dark band is discernible. For $c_s > 6 \times 10^{-4}$ mol l^{-1}, the results are similar to those of the solutions PSS05. It is to be noted that the peculiar phenomenon, i.e. the decrease in retardation and unusual approach of the dark bands to the symmetric axis, was completely reproducible; after adding the salt up to the concentration of 4×10^{-3} mol l^{-1}, the solution was re-dialysed, and then the same results were obtained.

Figure 2 shows the variation with polymer concentration in the strain rate dependence of retardation for the PSS solutions ($M_w = 1.19 \times 10^6$) at $c_s = 0$ in the range of polymer concentration, c_p, from 0.05 to 0.09 wt%.

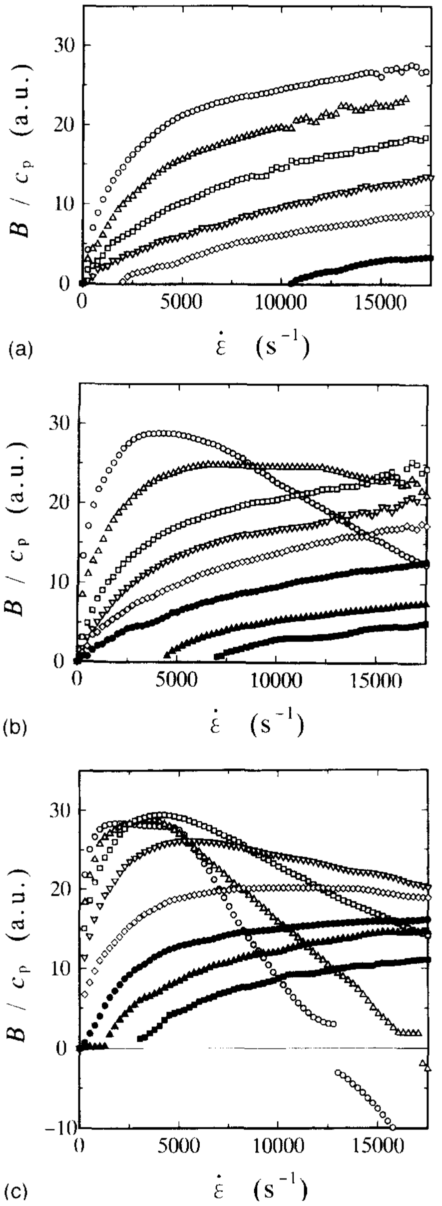

Figure 1 Variation with added-salt concentration in the strain rate dependence of retardation. (a) Solution PSS05 ($M_w = 5.05 \times 10^5$, c_p = 0.08 wt%): ○, $c_s = 0$ mol l^{-1}; △, 2×10^{-4} mol l^{-1}; □, 6×10^{-4} mol l^{-1}; ▽, 1×10^{-3} mol l^{-1}; ◇, 2×10^{-3} mol l^{-1}; ●, 3.5×10^{-3} mol l^{-1}. (b) Solution PSS08 ($M_w = 8.01 \times 10^5$, c_p = 0.06 wt%): ○, $c_s = 0$ mol l^{-1}; △, 2×10^{-4} mol l^{-1}; □, 6×10^{-4} mol l^{-1}; ▽, 1×10^{-3} mol l^{-1}; ◇, 2×10^{-3} mol l^{-1}; ●, 4×10^{-3} mol l^{-1}; ▲, 8×10^{-3} mol l^{-1}; ■, 1.7×10^{-2} mol l^{-1}. (c) Solution PSS12 ($M_w = 1.19 \times 10^6$, c_p = 0.06 wt%): ○, $c_s = 0$ mol l^{-1}; △, 9×10^{-5} mol l^{-1}; □, 2×10^{-4} mol l^{-1}; ▽, 4×10^{-4} mol l^{-1}; ◇, 6×10^{-4} mol l^{-1}; ●, 1×10^{-3} mol l^{-1}; ▲, 2×10^{-3} mol l^{-1}; ■, 4×10^{-4} mol l^{-1}

Table 2 Three regions of the response of NaPSS solutions against elongational flow field

	M_w 5.05 × 10^5	M_w 8.01 × 10^5	M_w 1.19 × 10^6
Region III	not observed	$c_s < 2 \times 10^{-4}$ mol l^{-1} (at high strain rate)	$c_s < 6 \times 10^{-4}$ mol l^{-1} (at high strain rate)
Region I	$c_s < 1 \times 10^{-3}$ mol l^{-1}	$c_s < 2 \times 10^{-4}$ mol l^{-1} (at low strain rate) $6 \times 10^{-4} < c_s < 4 \times 10^{-3}$ (whole strain rate studied)	$c_s < 6 \times 10^{-4}$ mol l^{-1} (at low strain rate) $6 \times 10^{-4} < c_s < 1 \times 10^{-3}$ (whole strain rate studied)
Region II	$c_s > 2 \times 10^{-3}$ mol l^{-1}	$c_s > 4 \times 10^{-3}$ mol l^{-1}	$c_s > 1 \times 10^{-3}$ mol l^{-1}

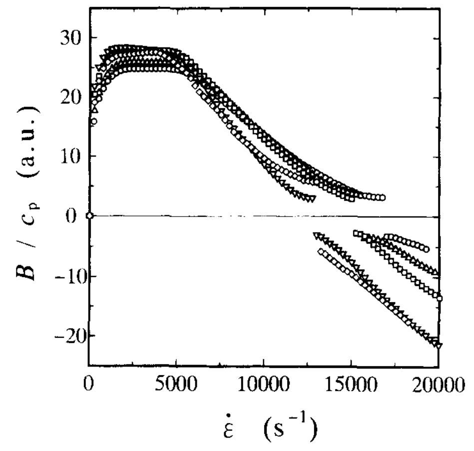

Figure 2 Variation with polymer concentration in the strain rate dependence of retardation for $M_w = 1.19 \times 10^6$ at $c_s = 0$ mol l^{-1}. ○, $c_p = 0.09$ wt%; △, 0.08 wt%; □, 0.07 wt%; ▽, 0.06 wt%; ◇, 0.05 wt%

The plots of the retardation normalized by polymer concentration vs strain rate are approximately superimposable, which indicates that the PSS solutions of polymer concentration employed here can be regarded as dilute ones.

The response of NaPSS dilute solutions against the elongational flow field is classified into three regions, as shown in *Table 2*. At relatively low salt concentration, the rigid-rod like behaviour is observed (region I). Retardation initially increases linearly with strain rate, and the birefringence pattern is non-localized with two dark bands. It is known that the neutral polystyrene molecules in good solvents are flexible random coils, and that the coils expand due to Coulomb repulsion on adding ions to the chains. In region I, both the strain rate dependence of retardation and the birefringence pattern are typical of the rigid-rod molecules. These facts indicate that the orientation of PSS molecules dominates over the chain deformation as a response of molecules to the elongational flow field.

At high salt concentrations, behaviour suggesting the appearance of flexibility is observed (region II). No retardation is detected at low strain rate and the retardation increases gradually with strain rate. The birefringence is still non-localized, but the dark bands are hardly observable. These results indicate the optical anisotropy of a chain is small at small strain rate, which results from the increase in flexibility of a chain on adding salt. The retardation observed with increasing strain rate is therefore due to the deformation of chains by the elongational flow field. Because neither the abrupt increase in retardation against strain rate nor the localization of birefringence on the symmetric axis was observed, PSS molecules are not a flexible chain like neutral polystyrene, but a semi-flexible chain. Odell and Taylor attributed similar strain rate dependence of retardation to a coil-stretch transition of a free-draining coil[8]. The results obtained in regions I and II are consistent with those by Nahr and Keller[5]. A similar behaviour was reported in collagen and DNA solutions[9,10].

At very low salt concentrations and, molecular weight larger than 8 × 10^5, the retardation decreases through a maximum, down to the opposite sign with increasing strain rate (region III). The dark bands approach the symmetric axis, and then become unobservable at high strain rate. Since the degree of the alignment and/or the deformation of chains should increase with increasing strain rate, the decrease in retardation and the sign inversion are interpreted as the results of the change in molecular conformation which reverses the major axes of the refractive index ellipsoid.

The optical anisotropy of a polystyrene chain is determined mainly by the orientation and the inclination of the phenyl side group with respect to the chain direction, with a smaller contribution from the chain backbone. A decrease in retardation with increasing strain rate was reported for an atactic polystyrene/decalin solution[1], though the strain rate at which retardation shows a maximum is larger than the present study. They attributed the decrease in retardation to the change of orientation of phenyl side group and suggested another possibility of the side group tilting[1,11]. A decrease and a minimum in the intensity of the light transmitted through crossed polars are also observed in DNA solutions[10], but the authors attributed them to the effects of turbulence, and hence the relevance to the present result is not clear.

Darinskii and Borisov have predicted that two transitions in chain conformation can occur with increasing strain rate in polyelectrolyte molecules[12]: (i) a transition from a swollen polyelectrolyte coil to a stretched chain of electrostatic blobs; (ii) a transition from a stretched chain of electrostatic blobs to a completely stretched chain of monomers. At very low salt concentrations, a chain is of completely stretched conformation of electrostatic blobs at quiescent state and a transition (i) does not exist. The stretched chains of electrostatic blobs first align parallel to the symmetric axis at a low strain rate, and this process is observed as rigid-rod like behaviour (region I). A further increase of strain rate induces a transition (ii) into a stretched chain of monomers. The change in conformation in the transition into a stretched chain of monomers may give rise to the inversion of optical anisotropy (region III). According to this scheme, transition (i) describes that from region I to region II observed at higher salt concentrations. Further quantitative investigations will be necessary to examine the above transitions.

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References

1. Keller, A. and Odell, J. A., *Coll. Polym. Sci.*, 1985, **263**, 181.
2. Miles, M. J., Tanaka, K. and Keller, A., *Polymer*, 1983, **24**, 1081.
3. Dunlap, P. N., Wang, C.-H. and Leal, L. G., *J. Polym. Sci., Part B, Polym. Phys.*, 1987, **25**, 2211.
4. Farinato, R. S., *Polymer*, 1988, **29**, 160.
5. Nahr, K. A. and Keller, A., *J. Polym. Sci., Part B, Polym. Phys.*, 1994, **32**, 1697.
6. Odell, J. A., Keller, A. and Atkins, E. D. T., *Macromolecules*, 1985, **18**, 1443.
7. Carrington, S., Odell, J. A., Fisher, L., Mitchell, J. and Hartley, L., *Polymer*, 1996, **37**, 2871.
8. Odell, J. A. and Taylor, M. A., *Biopolymers*, 1994, **32**, 1483.
9. Sasaki, N., Atkins, E. D. T. and Fulton, W. S., *J. Appl. Polym. Sci.*, 1991, **42**, 2975.
10. Atkins, E. D. T. and Taylor, M. A., *Biopolymers*, 1992, **32**, 911.
11. Odell, J. A. and Keller, A., *J. Polym. Sci., Part B, Polym. Phys.*, 1986, **24**, 1889.
12. Darinskii, A. A. and Borisov, O. V., *Europhys. Lett.*, 1995, **29**, 365.