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Effect of Concentration and Polydispersity on Flow Birefringence of Polystyrene*)

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With 2 figures

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Introduction

The measurement of flow birefringence is a well-known technique for the investigation of polymers in solution (1, 2).

A stress-optical law has experimentally been established for these liquid systems (3). For simple shearing flow the stress-optical law takes the particular form:

$$\Delta n \sin 2\chi = 2\, p_{12}\, C$$
$$\Delta n \cos 2\chi = (p_{11} - p_{22})\, C \qquad [1]$$

where p_{12} is the applied shear stress; p_{11} and p_{22} are evoked normal stresses on planes perpendicular to the stream lines and to the direction of the velocity gradient; χ is the extinction angle and represents the orientation of the stress and the refractive index ellipsoids with respect to the flow lines; Δn is the birefringence in the 1,2 plane and C is a constant called the stress-optical coefficient.

C has been the subject of investigation by a number of authors, particularly *Tsvetkov* (1), since it is intimately related to the structure of the monomer units constituting the polymeric chain.

According to the theory of rubber elasticity one obtains (5):

$$C = \frac{(n^2+2)^2}{n}\,\frac{2\pi}{45}\,\frac{\alpha_1-\alpha_2}{kT} \qquad [2]$$

where n is the average refractive index of the melt or solution, $\alpha_1 - \alpha_2$ is the optical anisotropy of the random link and kT has the usual meaning. From eq. [2] it follows that C should not be dependent on concentration or any long chain properties of the polymer such as molecular weight and molecular weight distribution. In particular it is also independent of the special type of the distribution function (6) of the chain coordinates. This function appears to be quite different for the shear flow of fluid systems or the extension of rubbery materials.

Further, there exists a very close relationship between the normal stress difference $(p_{11} - p_{22})$ and the shear stress p_{12} under conditions of steady flow, and the dynamic moduli G' and G'' found from sinusoidal oscillations of small amplitude. This relationship is not only to be found in some phenomenological theories of viscoelastic behaviour (7, 8), but can also be predicted from the molecular theories of, for example, *Rouse* (9), *Zimm* (10) and *Lodge* (11), although the latter have not explicitly done this (12). The said relations read:

$$\lim_{q\to 0}\frac{p_{12}}{q} = \lim_{\omega\to 0}\frac{G''}{\omega} \qquad [3]$$

$$\lim_{q\to 0}\frac{p_{11}-p_{22}}{2\,q^2} = \lim_{\omega\to 0}\frac{G'}{\omega^2} \qquad [4]$$

where q is the shear rate (velocity gradient) in the steady flow experiment and ω is the circular frequency in the dynamic experiment. *W. Philippoff* (13) has experimentally indicated the validity of the above relations for some dilute solutions. For the bulk polymers used in this investigation the relationships [3] and [4] have been confirmed experimentally at this Institute. From eqs. [3] and [4], and the theory of viscoelasticity, the following relationship can then be drawn:

$$\lim_{q\to 0}\frac{p_{11}-p_{22}}{2\,p_{12}^2} = \lim_{\omega\to 0}\frac{G'}{(G'')^2} = J_e. \qquad [5]$$

The quantity on the right hand side is the steady state compliance J_e. It is well known from the molecular theories (14) of viscoelasticity of linear polymers in dilute solutions:

$$J_e = a\,\frac{M_{z+1}\,M_z}{M_w\,cRT}. \qquad [6]$$

In this equation, $a = 0.4$ according to the *Rouse* theory (9), c is the concentration in

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grams per cubic centimetre of the solution (for the bulk polymer it corresponds with the density), M_w is the weight average molecular weight, M_z and M_{z+1} are the usual higher averages of the molecular weight distribution which can in principle be found from sedimentation measurements. The importance of the mentioned higher moments of the molecular weight distribution upon the flow properties of polymers in solution was first pointed out more than twenty years ago (15). It will be remembered that the theory of *Rouse* has originally been developed for free draining molecules. When the intramolecular hydrodynamic interaction is taken into account (10), a corresponding equation can be derived for J_e, where factor $a = 0.205$ and somewhat lower molecular weight averages are involved.

From eqs. [5] and [6] one obtains a relationship between the normal stress differences and the shear stress, which obviously holds only at sufficiently low shear rates:

$$\frac{1}{2}(p_{11} - p_{22})\frac{Mw}{cRT} = a\,\frac{M_z\,M_{z+1}}{M_w{}^2}\left(p_{12}\frac{M_w}{cRT}\right)^2 \qquad [7]$$

This expression has been derived by *Peterlin* and by *Daum* along another way (16, 17). In eq. [7] the stresses have now been put in a non-dimensional form by first expressing them as stresses per molecule and then dividing them by kT. This is convenient, as the term $p_{12}\,\frac{M_w}{cRT}$ often occurs in theories about polymer solutions and melts. At low shear rates, it is equal to the quantity β used by *Peterlin* (18) and proportional to the *Bueche-Harding* parameter (19). According to the *Rouse* theory, β is proportional to $q\,\tau$, where τ is the longest relaxation time.

For very dilute solutions of anionic polystyrenes

$$\left(\frac{M_z\,M_{z+1}}{M_w{}^2} \sim 1\right),$$

good experimental evidence tas been found for the validity of the above relationship (20), the numerical factor lying between those given by the theories of *Rouse* and *Zimm*.

The important assumption in molecular theories of dilute solutions is that the total macroscopic stress can be found by simple addition of the contributions due to each molecule. The application of this assumption to concentrated solutions and melts, however, would appear to be rather dubious. As *Ferry* (21) and later *Peticolas* (22) have suggested, this difficulty could be overcome by the use of an apparent friction coefficient which appears in relations between the stresses and the shear rate. It can be eliminated by relating normal stresses directly to the square of the shear stress.

The only condition is that the friction coefficient be equal for all molecules contained in the same polymer sample. This is clearly the case for extremely dilute solutions where, by definition, the friction coefficient is unity, and also for the bulk polymer. For intermediate concentrations it should also be true for mono-disperse polymers. For polydisperse polymers, however, it does not seem to be a good approximation, since the thermodynamic potential of the solvent is a function of the molecular weight of the solute. The low molecular weight species are expected to have more than their fair share of solvent. It will be extremely difficult to formulate this problem quantitatively. Qualitatively it can be expected that eq. [7] should involve even higher averages of the molecular weight than M_{z+1}.

This paper presents experimental evidence in support of these contentions.

Experimental

For the evaluation of eqs. [1], flow birefringence measurements are needed in combination with viscosity measurements. Flow birefringence measurements on dilute and concentrated solutions were carried out at 25 °C in an apparatus of Couette geometry (23, 24). For all solutions, bromo-benzene has been used as a matching solvent ($dn/dc = 0$). For the very dilute solutions, a correction for the contribution of the flow birefringence of the solvent has been applied according to *Sadron* (25). The flow birefringence measurements on the molten bulk polymers were carried out at temperatures close to 200 °C using a cone-and-plate apparatus (26). Viscosities of dilute solutions were determined in Ubbelohde viscometers in the Newtonian range of flow rates. Viscosities of bulk polymers were measured with a capillary type viscometer and supplemented by dynamic viscosities at very low frequencies.

The validity of the stress-optical law was confirmed by a plot of $\Delta n \sin 2\,\chi/2\,p_{12}$ vs. shear rate. In this way, the value of the stress-optical coefficient C was obtained. (First eq. [1]). In the second eq. [1], this value is used to calculate the normal stress difference $p_{11} - p_{22}$ from flow birefringence.

Materials

PS III (BASF) was investigated as a polystyrene with a broad molecular weight distribution. From viscosity measurements its weight average molecular weight was estimated: $M_w = 3.3 \times 10^5$. Its M_w/M_n is reported to be at leats 5 (27). The higher molecular weight averages are not known.

S 111 was used as a polystyrene with a narrow molecular weight distribution:

$M_w = 2.24 \times 10^5$, $M_w/M_n = 1.04$. This material has been the subject of several previous rheological investigations (13, 28, 29, 30).

Results

The stress-optical coefficients for the bulk polymers were 4.4×10^{-10} and 4.9×10^{-10} cm²/dyne for the broad and the narrow molecular weight distribution materials, respectively. All solution measurements gave $C = 5.5 \times 10^{-10}$ cm²/dyne. Considering the temperatures at which the measurements were carried out, these results are reasonable (cf. eq. [2]).

Fig. 1 shows the results of the measurements on S 111. The method of reduction implied by eq. [7] is clearly successful. The measurements covered a temperature span of 170 °C and more than three decades of viscosity. Some of the measurements of *Janeschitz-Kriegl* (20) on a series of anionic polystyrenes of varying molecular weight are also given for comparison. One concludes that the reduction method also holds with respect to molecular weight. From fig. 1, the value of

$$\frac{1}{2}\,\frac{p_{11}-p_{22}}{p_{12}^{2}}\,\frac{cRT}{M}$$

is found to be 0.4–0.45. This is a good confirmation of the applicability of the *Rouse* theory, not only to dilute solutions but also to concentrated solutions and melts. One should remember that the solvent was a good one, so one intuitively expects the dilute solution measurements to lie closer to the result of the theory of *Rouse* than to that of the theory of *Zimm*. At values of $p_{12}M/cRT$ smaller than unity, the slope of the graph is equal to 2 within the accuracy of the measurements. This is to be expected, since in this region all viscosities were found to be independent of shear rate.

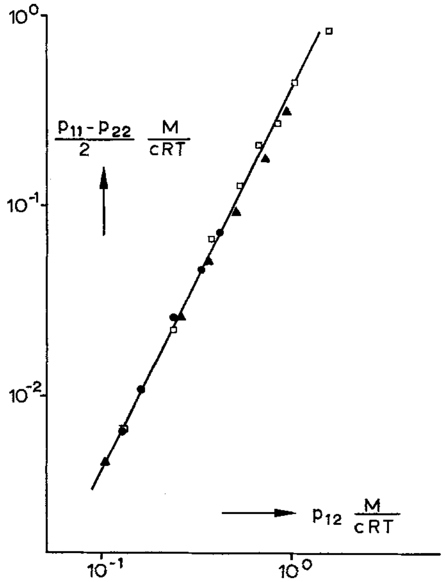

Fig. 1. Relationship between the reduced normal stress difference and the reduced shear stress for polystyrenes of narrow molecular weight distribution. ●... 25 grams/100 cc solution of S 111 in bromobenzene at 25 °C. ▲ ... S 111 in bulk at 196 °C. ☐ ... various anionic polystyrenes of molecular weights between 0.4 and 1.6×10^6 and at concentration between ½ and 1% (taken from ref. 20)

Fig. 2 shows similar measurements for the polystyrene with broad molecular weight distribution. Again measurements have covered the concentration range from very dilute solutions to the bulk polymer. The most important observation in this figure is that the results for the bulk polymer coincide with the results for the very dilute solutions. The results for the concentrated solution, however, lie completely on their own. Further measurements have also been carried out at concentrations between 1 and 25%. As anticipated, the obtained results lie between the two curves of fig. 2. (See also ref. 17.) The measurements on the bulk polymer were repeated at various temperatures between 170° and 220 °C. These results could also be reduced to the curve obtained at 200 °C.

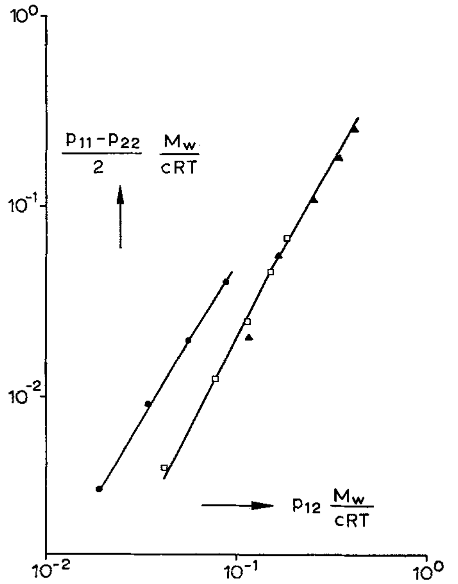

Fig. 2. Relationship between the reduced normal stress difference and the reduced shear stress for PS III (BASF., broad molecular weight distribution). ● ... 25 grams/100 cc solution in bromobenzene at 25 °C. ▲... measurements an the bulk material at 200 °C. ☐... 0.75 grams/100 cc solution in bromobenzene at 25 °C

From fig. 2, the limiting value of

$$\frac{p_{11} - p_{22}}{2\,p_{12}^2} \frac{cRT}{M_w}$$

at sufficiently low shear rates is about 2 for the very dilute solution (*s*) and the melt (compare the value of 0.4–0.45 for the monodisperse polymers as given above). It is however about 6 for the 25% solution. This is clearly a case that the concentrated solution is more elastic than the melt! It was not possible to measure very accurately at concentrations higher than 25%. However, some provisional measurements at 50% concentration were co-incident with the 25% measurements.

The slope of fig. 2 is about 2 only below

$$\frac{M_w}{cRT}\,p_{12} = 0.1\,.$$

This need not necessarily be a discrepancy with fig. 1, since the rheological behaviour is related to some average longest relaxation time. The actual longest relaxation time in a polydisperse material can be much longer.

As a final note it is pointed out that, although some authors (30) believe that the theory of *Rouse* cannot be directly applied to bulk polymers, these experimental findings give at least some support for proposals to obtain molecular weight distributions from flow measurements on the bulk polymer with the aid of the theory of *Rouse*.

Acknowledgement

The measurements on S 111 were carried out as part of a IUPAC working-party's investigation into the relationship between basic molecular structure and performance properties. The authors acknowledge their supply of this interesting material, and their permission to publish the results.

Summary

Normal stresses were estimated from viscosity and flow birefringence measurements on solutions and melts of substantially two samples of polystyrene. A large range of concentration and temperatures was covered.

The interpretation of results was tried along lines originally handled for dilute solutions only. In meeting the requirements of this method, a well-known reduction scheme with respect to concentration (and temperature) was rediscussed and applied. For the sample with a narrow molecular weight distribution this procedure was very satisfactory. For the polydisperse sample, however, the reduction with respect to concentration was only partly successful.

For this latter sample it could be shown that results on very dilute solutions corresponded with those on the bulk polymer. This is in favour of the current concept for molten bulk polymers and, in particular, of the interpretation given to polydispersity effects. Deviations at intermediate concentrations are qualitatively interpreted in terms of an inhomogeneous dispersion of solvent between high and low molecular weight species.

Zusammenfassung

Für die Abschätzung von Normalspannungen, wie sie an strömenden Lösungen und Schmelzen auftreten, wurden Daten von Viskosität und Strömungsdoppelbrechung herangezogen, die in der Hauptsache an zwei Polystyrolproben gemessen wurden. Hierfür wurde ein großer Bereich von Konzentrationen und Temperaturen bestrichen.

Für die Interpretation wurden Gedankengänge herangezogen, die ursprünglich nur für verdünnte Lösungen entwickelt wurden. Deshalb war die Verwendung eines Reduktionsschemas in bezug auf Konzentration (und Temperatur) angezeigt. Für die Probe mit einer schmalen Molekulargewichtsverteilung wurden hiermit sehr befriedigende Resultate erzielt. Für die polydisperse Probe war die Reduktion in bezug auf die Konzentration jedoch nur zum Teil erfolgreich.

Dieser Erfolg besteht darin, daß die an sehr verdünnten Lösungen erhaltenen Ergebnisse zu den an der reinen Schmelze erhaltenen passen. Dies liefert eine Stütze für die herrschenden Auffassungen über Polymerschmelzen und insbesondere über die Interpretation von Polydispersitätseffekten. Bei mittleren Konzentrationen gefundene Abweichungen wurden als Folge einer inhomogenen Verteilung des Lösungsmittels zwischen hoch- und niedermolekularen Anteilen betrachtet.

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Vorgänge vor und bis zum Bruch bei statischer und dynamischer Beanspruchung von Polykarbonat*)

Von G. Jacoby und Ch. Cramer

Mit 44 Abbildungen in 64 Einzeldarstellungen und 1 Tabelle

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1. Einleitung

Die Vorgänge beim Bruch eines Werkstoffes im Makro- und Mikrobereich spiegeln sich bis zu einem gewissen Grade auf der Bruchfläche wider. Die mikroskopische Untersuchung von Bruchflächen (Mikrofraktographie genannt) führte bei Metallen in den letzten Jahren zu einer detaillierten Beschreibung verschiedener Brucharten, wodurch theoretische Annahmen unterstützt bzw. neue Erkenntnisse gewonnen werden konnten.

Besonderes Interesse kommt bei der mikroskopischen Untersuchung der Bruchflächen dem Zerrüttungsbruch zu (1). Dieser zeigt bei vielen metallischen Werkstoffen die sog. Bruchlinien. Die Bildung von Bruchlinien ist ein wesentlicher Teil des Mechanismus des Rißfortschrittes bei vielfach wiederholter Beanspruchung, der seinerseits Rückschlüsse auf den gesamten Zerrüttungsprozeß zuläßt. Trotz ihrer Bedeutung ist über den Mechanismus ihrer Bildung noch sehr wenig Verallgemeinerungsfähiges bekannt.

Vor einigen Jahren wurde von *McEvily* u. Mitarb. erstmals nachgewiesen, daß Bruchlinien auch auf den Zerrüttungsbruchflächen von Thermoplasten auftreten (2). Die Erscheinungsform der Bruchlinien ist danach besonders bei einem Polykarbonat sehr ähnlich der, die auf den Bruchflächen von Metallen beobachtet wird. In einer anderen Arbeit konnte gezeigt werden, daß darüber hinaus die Bruchlinien bei Polykarbonat durch verschiedene Einflußgrößen in nahezu der gleichen Art wie bei Metallen verändert werden (1).

Die beobachteten Ähnlichkeiten im Verhalten der Bruchlinien bei Metallen und Thermoplasten weisen auf einen gemeinsamen Mechanismus des Rißfortschritts bei vielfach wiederholter Beanspruchung hin. Gegenstand der vorliegenden Arbeit ist es, diesen Mechanismus näher zu untersuchen, im wesentlichen durch die Anwendung mikrofraktographischer Verfahren. Obgleich das Hauptinteresse dabei auf die Zerrüttungsbruchfläche konzentriert ist, mußten andere Brucharten in die Untersuchung mit einbezogen werden, um die notwendige Ausgangsbasis zur Erklärung aller mit der Zerrüttungsbruchfläche verbundenen Phänomene zu erhalten. Außerdem ergibt sich dadurch die Möglichkeit, einen Vergleich der Bruchvorgänge von Metallen und Kunststoffen auf breiterer Basis vorzunehmen.

2. Allgemeine Eigenschaften von Polykarbonat

Für die Untersuchung wurde Bisphenol A Polykarbonat[1] ausgewählt, weil die bereits erwähnten Ähnlichkeiten im Aussehen der Bruchlinien bei Metallen und Thermoplasten bei Polykarbonat besonders deutlich hervortreten. Die allgemeinen physikalischen und mechanischen Eigenschaften von Polykarbonat sind in verschiedenen Arbeiten beschrieben (3, 4). Bisphenol A Polykarbonat hat die

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*) Vorgetragen auf der Jahrestagung der Deutschen Rheologen in Bad Ems vom 18.—19. Mai 1967.

[1] Makrolon® der Farbenfabriken Bayer A. G., Leverkusen.