

Molecular Weight Distribution and Rheological Properties of Polyisobutylene Solutions

NOBORU NISHIDA,* DAVID G. SALLADAY, and
JAMES L. WHITE, *Department of Chemical and Metallurgical
Engineering, The University of Tennessee, Knoxville, Tennessee 37916*

Synopsis

The molecular weight distribution of a series of polyisobutylenes was determined using osmotic pressure measurements, gel permeation chromatography, and intrinsic viscosity. All of the polymers except for one, a blend of the highest and lowest molecular weight constituents, had similar moderate molecular weight distributions. The "extended chain length" method of calibrating the gel permeation chromatograph for polyisobutylenes was found to be effective. Steady state and transient shear stresses and normal stresses were measured on 5% decalin solutions of these polymers. The zero shear viscosity increased with the 3.3 power of molecular weight, and the zero shear normal stress coefficient $(\sigma_{11} - \sigma_{22})/\Gamma^2$ varied with the 7.5 power. Relative elastic memory as measured by $(\sigma_{11} - \sigma_{22})/\sigma_{12}$ or stress relaxation increased with increasing molecular weight (and at constant number- or weight-average molecular weight) with breadth of distribution. Stress overshoot also correlated with this tendency.

INTRODUCTION

One of the most important and indeed interesting problems of the polymer industry is the relationship of molecular weight distributions of polymers and their processing and performance behavior. The resolution of this problem generally breaks down to first finding an appropriate method of evaluating the molecular weight distribution and secondly to relating this to rheological properties.¹ Experimental studies of the relationship of rheological properties to molecular structure not only have use for this problem but also for evaluating molecular theories of polymeric materials and for appropriate framing constitutive equations for such media.

The gel permeation chromatograph,² which allows measurement of molecular weight distributions from a simple chromatographic experiment, is certainly the major development in polymer characterization methods during the last decade. Indeed, it has been widely used in industry for characterization and control.³ Difficulties arise when polymers other than those used to calibrate the instrument are studied. Various methods of converting

* Present address: Sapporo Medical College, Sapporo, Japan.

elution volume to molecular weight have been proposed in the literature, notably the Moore-Hendrickson method, which presumes elution volume is a unique function of the extended chain length.² A second method, due to Benoit and co-workers,⁴ takes elution volume to be a unique function of the radius of gyration and utilizes the Einstein-Kuhn-Flory theory of dilute solution viscosity and the experimental intrinsic viscosity-molecular weight relationship to carry out the conversion. As polymer molecules take the form of random coils in dilute solution, one would expect the approach of the latter authors to be the better one. Indeed, our group has utilized this idea in explaining the characteristics of chromatographic columns packed with porous adsorbents.⁵ The Moore-Hendrickson approach is a cruder one, which becomes equivalent to that of Benoit et al. when the polymer-solvent interaction of the two systems are identical.

The rheological properties of polymer fluids are particularly well understood for two types of motions: (1) the region of small deformations in which the stress may be represented as a linear integral of the strain history and (2) long duration laminar shearing motions for which the stress matrix may be expressed^{6,7} as follows:

$$\begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{vmatrix} = - \begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{vmatrix} + \begin{vmatrix} \beta_1 \Gamma^2 & \mu \Gamma & 0 \\ \mu \Gamma & \beta_2 \Gamma^2 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (1)$$

where 1 represents the direction of flow, 2 represents the direction of shear, σ_{ij} are the stress components, p is the pressure, Γ is the shear rate, μ is the non-Newtonian shear viscosity, and β_1 and β_2 are normal stress coefficients. The effect of molecular weight distribution on rheological properties of concentrated polymer systems has long been investigated, and the influence in particular of molecular weight on viscosity and linear viscoelastic properties of narrow molecular weight distribution polymers has been well calibrated.^{8,9} In recent years, attention has been given to the variation of normal stresses with absolute molecular weight.^{10,11} Most of the recent research has been with extremely narrow-distribution alkyl lithium polystyrenes. The problem of the effect of molecular heterogeneity on rheological properties has also received attention,¹⁰⁻¹⁴ though admittedly most of the effort has been devoted to linear viscoelastic characteristics.¹²⁻¹⁴

This paper contains a study of (1) measurements of the molecular weight distribution of a series of polyisobutylenes using a Waters Associates gel permeation chromatograph (GPC), osmometry, and intrinsic viscosity and (2) the measurement of rheological properties of solutions of these polymers using a Weissenberg rheogoniometer. In particular, we will look at the nonlinear properties such as normal stresses, stress overshoot, and stress relaxation following rapid flows. The rheological properties of the polymer solutions are compared to the molecular weight distributions.

EXPERIMENTAL

Materials

A series of polyisobutylenes (Enjay Vistanex LMMH, L100, L120) and a noncommercial high molecular weight sample made by Esso Research

and Engineering were investigated; this polymer is designated HMW. A 50:50 wt-% blend of Vistanex LMMH and the HMW polymer was prepared.

Characterization

The number-average molecular weights of the samples were determined with a Hallikainen Instruments Model 1361 automatic osmometer, and viscosity-average molecular weights were obtained from intrinsic viscosity measurements in benzene at 30°C. The molecular weight in the latter case was obtained from¹⁵

$$[\eta] = 6.1 \times 10^{-4} M_{\eta}^{0.56} \quad (2)$$

Refractive index-elution volume curves were obtained for these samples on a Model 200 Waters Associates gel permeation chromatograph. The measurements were carried out with a tetrahydrofuran solvent at 25°C. A major problem was how to interpret these curves as molecular weight distributions.

Rheological Properties

Solutions, 5%, of each of the polymers in decalin were prepared. The torque T and total thrust F were measured as a function of angular velocity Ω in a Model R16 Weissenberg rheogoniometer at 25°C. A cone with an angle ψ of 1.467° was used. The shear rate, shear stress, and principal normal stress differences were computed from the expressions^{6,7}

$$\Gamma = \frac{\Omega}{\psi}; \quad \sigma_{12} = \frac{3T}{2\pi R^3}; \quad \sigma_{11} - \sigma_{22} = \frac{2F}{\pi R^2} \quad (3a)$$

and

$$\mu = \frac{3T\psi}{2\pi R^3\Omega}; \quad \beta_1 - \beta_2 = \frac{2F\psi^2}{\pi R^2\Omega^2} \quad (3b)$$

RESULTS

Characterization

Values of the number-average and viscosity-average molecular weights of the polyisobutylene samples determined by osmometry and intrinsic viscosity are summarized in Table I. No narrow molecular weight polyisobutylene standards were available, and we were left to our devices to develop a calibration method for the gel permeation chromatograph. Three such procedures were considered. First, our column was calibrated with narrow distribution polystyrenes. The best procedure would be to take elution volume to be a unique function of radius of gyration and proceed by the method of Benoit et al.⁴ However, we have neither been able to measure the $[\eta]$ of the fractions exiting the chromatograph or obtain an $[\eta]$ - M relationship for the polyisobutylene-THF system. (Intrinsic viscosity-molecular weight relationships for polyisobutylene and polystyrene in THF at 35°C are, however, available.¹⁶) A second alternative is to follow

TABLE I
Molecular Weights of Polyisobutylene Samples

Sample	$M_n \times 10^{-3}$	$M_\eta \times 10^{-3}$	Gel permeation chromatograph ^a					
			ECL $M_n \times 10^{-3}$	ECL $M_w \times 10^{-3}$	ECL M_w/M_n	ES $M_n \times 10^{-3}$	ES $M_w \times 10^{-3}$	
LMMH	24-27	32.7	16.5	34	2.06	7.99	11.2	
L100	320	717	330	800	2.4	65.5	100	
L120	330	819	340	850	2.5	65.6	110	
HMW	1100	1602	1000	2200	2.2	144	263	
LMMH-HMW		977	31.2	1120	36	15.7	65.1	

^a ECL, Based on extended chain length; ES, based on Enjay-Staudinger molecular weights.

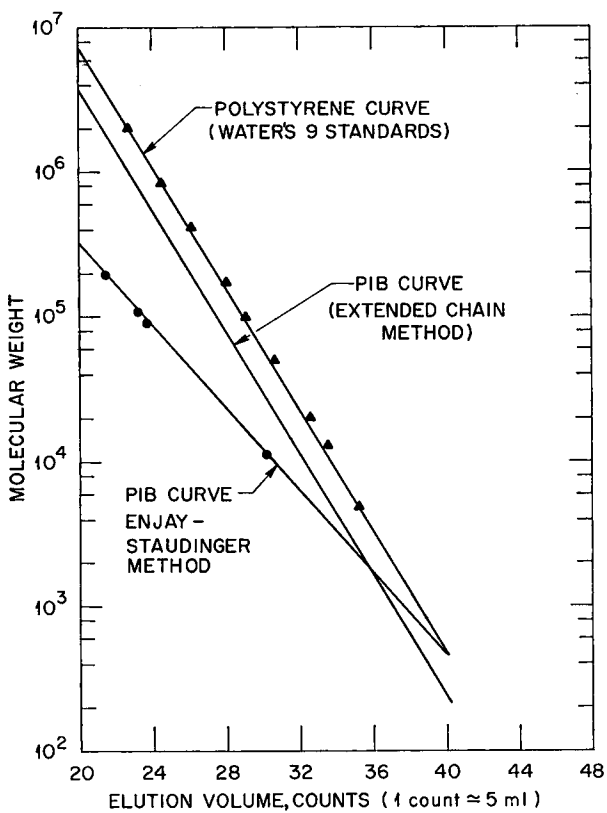


Fig. 1. Calibration curve for gel permeation chromatograph.

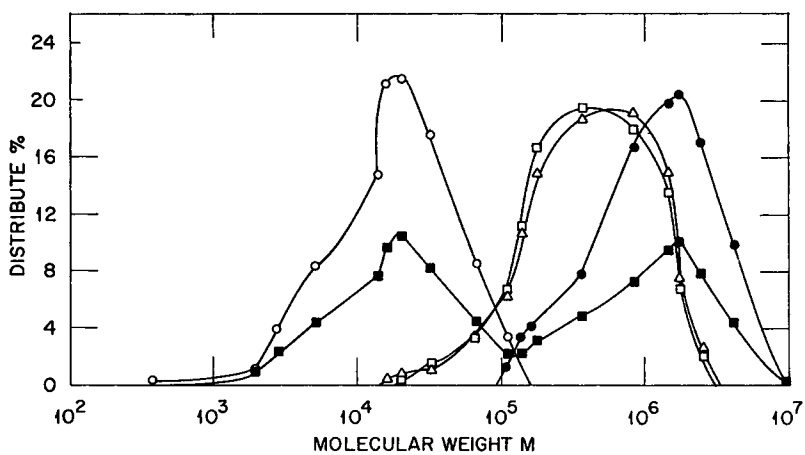


Fig. 2. Molecular weight distributions of polyisobutylenes. (O) LMMH; (□) L100; (●) HMW; (■) HMW + LMMH; (Δ) L120.

Moore and Hendrickson and presume that the molecules elute on the basis of the extended chain length²; then a polyisobutylene species at a specific elution value should have a molecular weight lower by a factor of 56/104. Finally, "Staudinger" molecular weights were made available by Enjay. These molecular weights were correlated with the peaks of the refractive index-molecular weight curves. The results are tabulated in Table I. The two suggested polyisobutylene GPC calibrations are plotted in Figure 1 together with the polystyrene calibration.

As the extended chain length calibration molecular weights are in closer agreement with the computed osmotic pressure molecular weights and the method seems to be the most reasonable of those carried out, we have utilized them in the remainder of the paper. A plot of GPC elution volume versus molecular weight for both polyisobutylene and polystyrene in a different set of columns and at a different temperature has been published by Iwama, Abe, and Homma.¹⁶ These authors find the experimental polyisobutylene molecular weight to be a slowly increasing fraction of the polystyrene molecular weight as elution volume decreases. Inspection of their data shows reasonably close agreement with the extended chain length method but not with the Enjay-Staudinger results. Figure 2 contains plots of differential molecular weight distributions of the polymers studied using the extended chain length molecular weights.

Rheological Properties

Figure 3 contains a plot of the non-Newtonian viscosity μ as a function of shear rate, and Figure 4 is a plot of $(\sigma_{11} - \sigma_{22})/\sigma_{12}$ (or $\beta_1 - \beta_2$) Γ/μ versus shear rate for these same solutions. (The reason for making a plot of such form will be apparent in the next section.) Normal stresses were not observed in the LMMH solution.

We have also investigated the transient behavior of these solutions, in particular, the stress responses to a sudden motion or stoppage of one of the rheogoniometer platens. In Figure 5, the shear stress response to start-up from rest for the HMW solution is shown for several shear rates. A slow build-up of stress is seen at the lower shear rates and a stress overshoot at the higher shear rates. Figure 6 contrasts the transient stress for several polymer solutions at the same applied shear rate. The relatively high overshoot of the HMW and blend solutions is obvious. This was generally observed throughout the shear rates investigated. Figure 7 plots transient normal stress difference $(\sigma_{11} - \sigma_{22})$ as a function of time. However, we are not as sure of these data, inasmuch as we have found the amplifier gain to have a significant effect. Figures 8 and 9 plot shear stress relaxation following sudden stoppage of flow. Figure 8 is a normalized plot for the HMW solution at various values of shear rate. The rapid increase in rate of relaxation with increasing initial shear rate is to be noted. Figure 9 contrasts the different solutions at the same shear rate. The slow relaxation of the HMW and blend solutions relative to the other materials is seen.

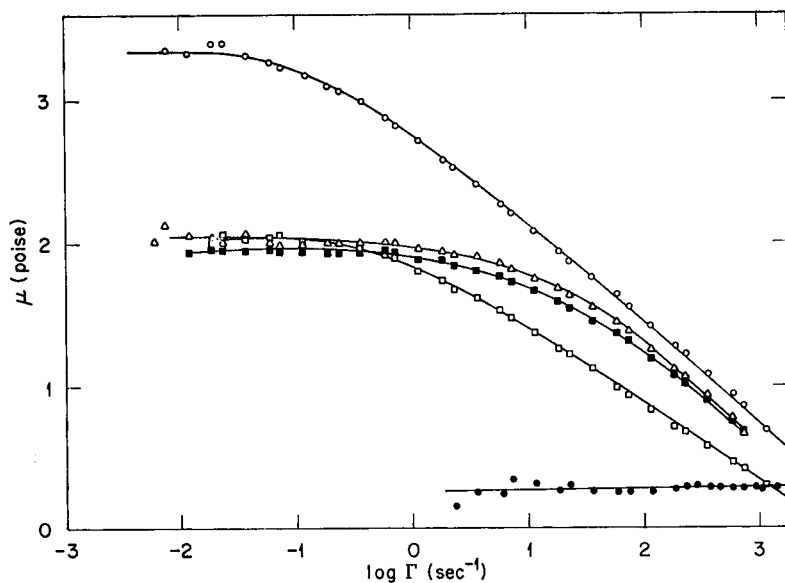


Fig. 3. Non-Newtonian viscosity of polyisobutylene solutions (25°C): (O) HMW; (Δ) L120; (\blacksquare) L100; (\bullet) LMMH; (\square) blend.

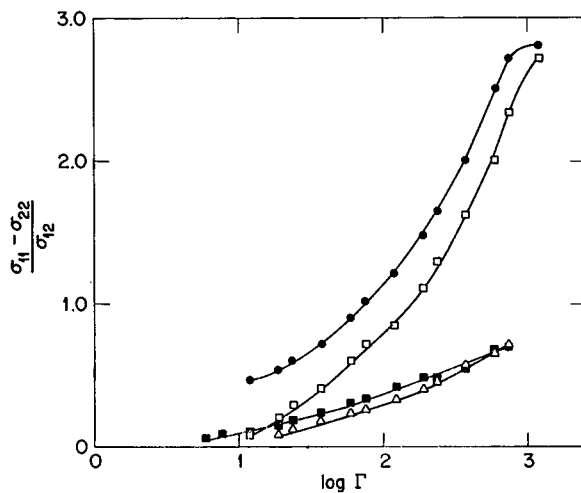


Fig. 4. Normal stress-shear stress ratio for polyisobutylene solutions: (\bullet) HMW; (Δ) L120; (\blacksquare) L100; (\square) blend.

DISCUSSION

The general observations of rheological properties reported here are in agreement with those of earlier researchers. Non-Newtonian viscosity and normal stress measurements have long been carried out on polyisobutylene-decalin solutions,^{17,18} though not with the particular ends of this

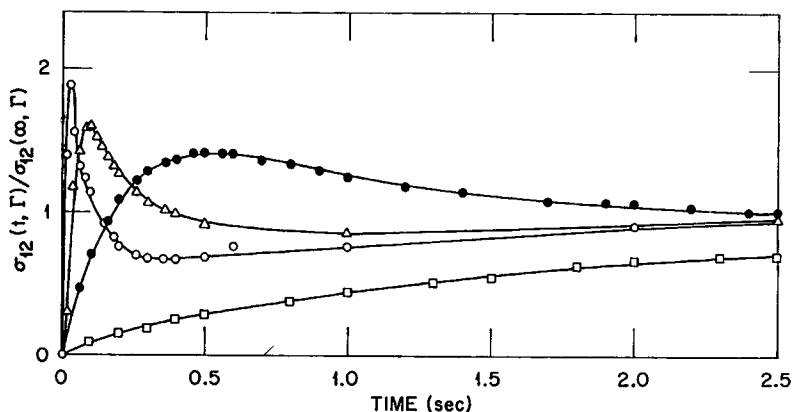


Fig. 5. Normalized shear stress growth at start-up of flow for the HMW polyisobutylene solution. Shear rates: (O) 582 sec⁻¹; (Δ) 58.2 sec⁻¹; (\bullet) 5.82 sec⁻¹; (\square) 0.185 sec⁻¹.

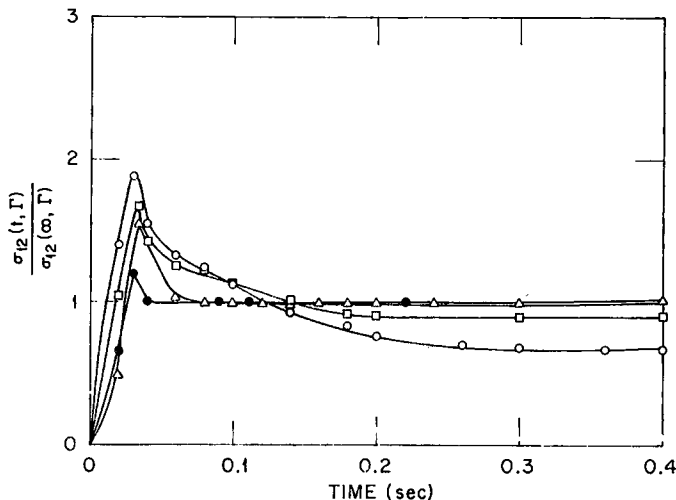


Fig. 6. Normalized shear stress growth for polyisobutylene solutions at 582 sec⁻¹: (O) HMW; (Δ) L120; (\bullet) LMMH; (\square) blend (HMW + LMMH).

paper. The transient responses shown in Figures 5 through 9 are of the same type published by Bird and his students¹⁹ on the variation of shear stress on startup and stoppage of flow. For startup experiments at low shear rates, there is a slow build-up of shear stress as predicted by linear viscoelasticity. At higher shear rates, there is overshoot, with the magnitude of the maximum increasing and the time required to achieve the magnitude decreasing as shear rate increases. Undershoot following overshoot appears at the highest shear rates. As first indicated by Bogue²⁰ (see also Bogue and White⁷ and Bird and associates¹⁹), such characteristics may be explained within the framework of the theory of nonlinear viscoelasticity.

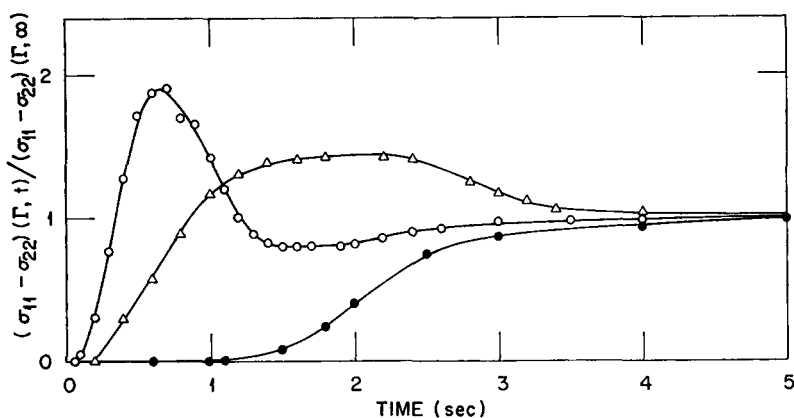


Fig. 7. Normalized normal stress growth for the HMW polyisobutylene solution. Shear rates: (O) 582 sec^{-1} ; (Δ) 58.2 sec^{-1} ; (\bullet) 5.82 sec^{-1} . Normalized normal stress difference growth $\sim t$ const. mol. wt.

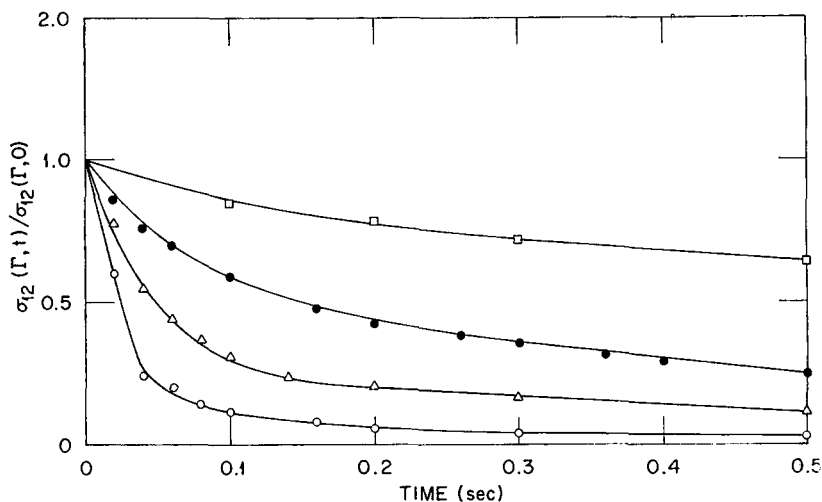


Fig. 8. Normalized shear stress relaxation in the HMW polyisobutylene solution following a steady flow. Shear rates: (O) 582 sec^{-1} ; (Δ) 58.2 sec^{-1} ; (\bullet) 5.80 sec^{-1} ; (\square) 0.185 sec^{-1} .

The curves of Figure 8 showing the more rapid decay of shear stresses at higher shear rates indicate the probable deformation rate dependence of the maximum relaxation time (and indeed the entire spectrum), which was impressed on the authors in recent discussions with Profs. M. Yamamoto, D. C. Bogue, and T. Kotaka.

The main purpose of this paper is to look at the effect of molecular weight and molecular weight distribution on rheological properties. In Figure 4, $(\sigma_{11} - \sigma_{22})/\sigma_{12}$ is plotted versus shear rate for several polymer solutions. This dimensionless stress ratio is more or less equivalent to the Weissenberg

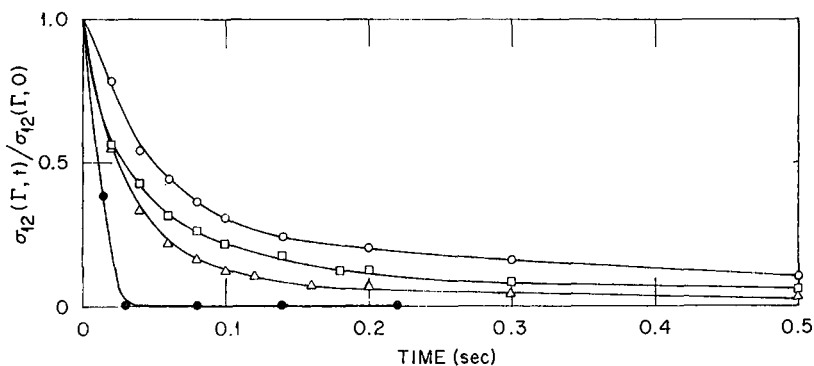


Fig. 9. Normalized shear stress relaxation in polyisobutylene solutions following a steady flow, with $\Gamma = 58.2 \text{ sec}^{-1}$: (O) HMW; (Δ) L120; (\bullet) LMMH; (\square) blend.

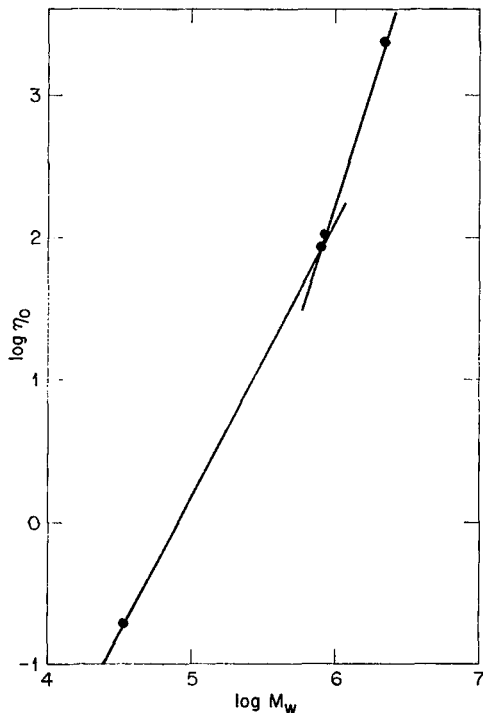


Fig. 10. Molecular weight dependence of the zero shear viscosity for polyisobutylene solutions.

number^{1,7,21,22} $\lambda_{ch}\Gamma$, where λ_{ch} is the characteristic material relaxation time and measures the relative "elasticity" of the polymer solutions. It is readily apparent that the HMW and blend solutions possess a much higher degree of memory than the L100 or L120, which are lower molecular weight (than the HMW) and narrower in distribution than the blend. This is reinforced by the rates of stress relaxation shown in Figure 9. It is of interest

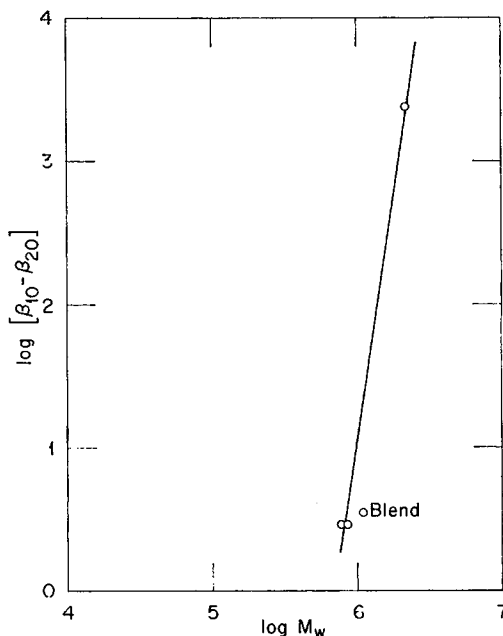


Fig. 11. Zero shear rate normal stress coefficient ($\beta_{10} - \beta_{20}$) as a function of weight-average molecular weight.

to contrast these data with recent results for polyethylene and polystyrene melts.²³ The values of the stress ratio for the polymer solutions are lower than those of the melts at the same shear rate.

Figure 10 plots zero shear viscosity η_0 versus weight-average molecular weight for the HMW, L120, L100, LMMH, and the blend. If we omit the low molecular weight LMMH point, a slope of 3.3 is obtained in agreement with the literature.⁸ The blend data fall in line using a weight-average molecular weight. Such a correlation would not be possible using number-average molecular weights, as is apparent from Table I. This is in agreement with the results of earlier authors.¹² The LMMH sample probably lies below the so-called entanglement transition.^{8,12} Figure 11 plots the zero shear rate normal stress coefficient difference ($\beta_{10} - \beta_{20}$) versus weight-average molecular weight. A slope of 7.5 is obtained. This is reasonable if one considers that, in terms of the second order fluid,^{1,7,21,24}

$$\beta_{10} - \beta_{20} = 2 \left[\int_0^{\infty} sG(s)ds \right] = 2 \left[\frac{\int_0^{\infty} sG(s)ds}{\int_0^{\infty} G(s)ds} \right] \eta_0 = 2J_e \eta_0^2 = \lambda_{cs} \eta_0 \quad (4)$$

where $G(s)$ is the linear viscoelastic relaxation modulus and J_e is the shear compliance. For a box distribution of relaxation times,⁹ λ_{cs} becomes proportional to the maximum relaxation time λ_m . The product $\lambda_m \eta_0$ should be

proportional to the molecular weight to about the seventh power. We should note that the agreement of the blend data point in Figure 11 is somewhat surprising. Higher normal stresses were expected. It is to be noted that J_e may be computed from eq. (4). It seems to depend upon a power of molecular weight of the order 0.5–1.0.

While the weight-average molecular weight in itself was found to correlate with the low shear rate data, this was not the case for the high shear rate data. This is especially seen in Figures 4, 6, and 9. The blend exhibits a significantly higher Weissenberg number, overshoot, and stress relaxation, despite the small difference in weight-average molecular weight. From Table I, we see how very bad will be any correlation based on number-average molecular weight. The M_n for the blend is only 10% of that for the L100 and L120—and despite this, the memory is higher for the former.

One of the interesting developments among researchers developing molecular models of polymer flow has been the development of *master curves* to bring together viscosity, shear data at different temperatures, and molecular weights. Notable here is the work of Bueche²⁵ and Graessley.²⁶ Figure 12 contains a master curve of the sort described by Graessley and Segal¹⁰ for all the polymer solutions investigated. With the exception of the blend, all of the data fall on the same curve, which is close to the "theoretical" curve. The data for the blend fall on a separate curve, as indicated by Graessley and Segal.¹⁰

Figures 3, 4, and 8 may be interpreted in terms of a perennial problem which harasses polymer processors. The blend polymer is a material that meets a single-point viscosity specification (say, that of L100 or L120). The differences in molecular weight distribution cause variations in rheolog-

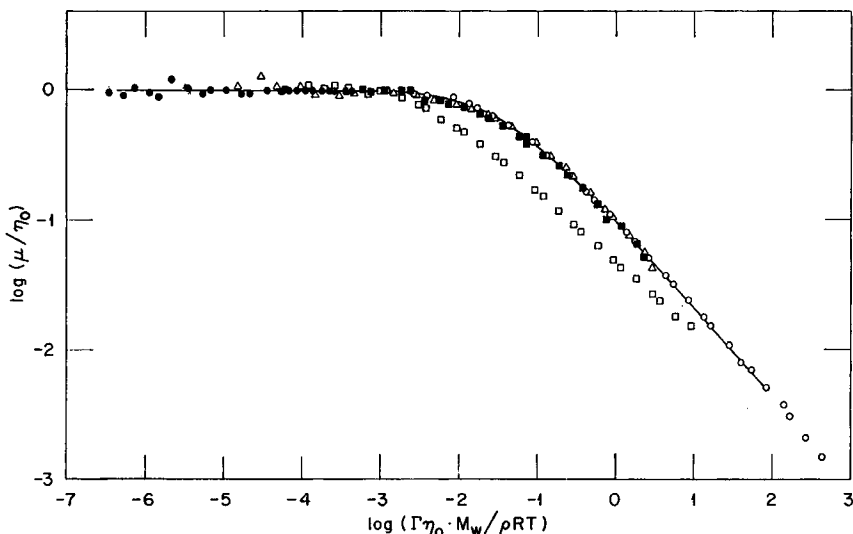


Fig. 12. Non-Newtonian viscosity master curve. PIB, 5%, in decalin, 25°C: (O) HMW; (Δ) L120; (\bullet) L100; (\blacksquare) LMMH; (\square) blend.

ical properties which are seen to be enormous and would certainly affect processing.^{1,7}

CONCLUSIONS

1. The concept that elution volume is a unique function of extended chain length was found to work well in calibrating a gel permeation chromatograph for polyisobutylene with polystyrene standards. This may well, however, be due to similar polymer-solvent interaction.
2. The molecular weight distributions of a series of commercial and laboratory-prepared polyisobutylenes were evaluated.
3. Transient and steady-state shear stress and normal stresses were evaluated for these polymers in 5% decalin solutions at 25°C.
4. The zero shear viscosity was found to increase with the 3.3 power of the weight-average molecular weight. The zero shear normal stress coefficient $(\sigma_{11} - \sigma_{22})/\Gamma^2$ increases with the 7.5 power of the weight-average molecular weight.
5. Relative elastic memory as measured by $(\sigma_{11} - \sigma_{22})/\sigma_{12}$ or the inverse rate of stress relaxation following a steady shear flow increases with molecular weight and with breadth of distribution at constant number- or weight-average molecular weight.

Dr. W. Philippoff of Esso Research and Engineering kindly made a sample of very high molecular weight polyisobutylene available to us. Mr. I. Jen Chen was very helpful in advising us on operation problems with the Weissenberg Rheogoniometer. Dr. T. Homma of Japan Synthetic Rubber Company kindly corresponded with us on the calibration of gel permeation chromatographs, especially with regard to ref. 16. The authors thank Prof. M. Yamamoto for his helpful comments.

This research was supported in part by NSF Grant GK-11035.

All communications should be addressed to James L. White.

References

1. J. L. White and N. Tokita, *J. Appl. Polym. Sci.*, **11**, 321 (1967); *ibid.*, **12**, 1589 (1968); J. L. White, *Rubber Chem. Technol.*, **42**, 257 (1969).
2. J. C. Moore, *J. Polym. Sci.*, **A2**, 835 (1964); J. C. Moore and J. G. Hendrickson, *ibid.*, **C8**, 233 (1965); *ibid.*, **4**, 167 (1966).
3. Goodyear Tire and Rubber Company, *Rubber Chem. Technol.*, **38** (3), 26 (1965); *ibid.*, **38** (4) 26 (1965).
4. H. Benoit, Z. Grubsic, P. Rempp, D. Decker, and J. G. Zilliox, *J. Chim. Phys.*, **63**, 1507 (1966); *J. Polym. Sci.*, **B5**, 753 (1967).
5. J. L. White and G. Kingry, *J. Appl. Polym. Sci.*, **14**, 2723 (1970).
6. A. S. Lodge, *Elastic Liquids*, Academic Press, New York, 1964.
7. D. C. Bogue and J. L. White, *Engineering Analysis of Non-Newtonian Fluids*, NATO Agardograph, 1970; J. L. White, *Rubber Chem. Technol.*, **42**, 257 (1969).
8. T. G. Fox, S. Gratch, and S. Loshaek, in *Rheology*, Vol. 1, F. Eirich, Ed., Academic Press, New York, 1956.
9. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960; K. Ninomiya and H. Fujita, *J. Colloid Sci.*, **12**, 204 (1957); S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).
10. W. W. Graessley and L. Segal, *Macromolecules*, **2**, 49 (1969).
11. H. Endo, T. Fujimoto, and M. Nagasawa, Normal and Shear Stress in a Visco-

elastic Liquid Under Steady Shear Flow (Effect of Molecular Heterogeneity), unpublished manuscript.

12. V. R. Allen and T. G. Fox, *J. Chem. Phys.*, **41**, 337 (1964).
13. H. Leaderman, R. G. Smith, and L. C. Williams, *J. Polym. Sci.*, **36**, 233 (1959).
14. T. Masuda, K. Kitagawa, T. Inoue, and S. Onogi, *Macromolecules*, **3**, 116 (1970).
15. F. Danusso and G. Moraglio, *Rend. Accad. Naz. Lincei.*, **25**, 509 (1958).
16. M. Iwama, M. Abe, and T. Homma, *Kogyo Kagaku Zasshi*, **72**, 931 (1969); T. Homma, private communication, Sept. 8, 1970.
17. H. Markovitz and R. B. Williamson, *Trans. Soc. Rheol.*, **1**, 23 (1957); J. G. Brodnyan, F. H. Gaskins, and W. Philippoff, *ibid.*, **1**, 109 (1957).
18. R. F. Ginn and A. B. Metzner, *Proc. 4th Int. Rheol. Congr.*, **2**, 538 (1964).
19. J. D. Huppler, I. F. MacDonald, E. Ashare, T. W. Spriggs, R. B. Bird, and L. A. Holmes, *Trans. Soc. Rheol.*, **11**, 181 (1967).
20. D. C. Bogue, *Ind. Eng. Chem., Fundam.*, **5**, 253 (1966).
21. J. L. White, *J. Appl. Polym. Sci.*, **8**, 2339 (1964).
22. D. C. Bogue and J. Doughty, *Ind. Eng. Chem., Fundam.*, **5**, 243 (1966).
23. T. F. Ballenger, I. J. Chen, J. W. Crowder, G. E. Hagler, D. C. Bogue, and J. L. White, *Trans. Soc. Rheol.*, **15**, 195 (1971).
24. B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, **35**, 1 (1964).
25. F. Bueche and S. W. Harding, *J. Polym. Sci.*, **32**, 177 (1958).
26. W. W. Graessley, *J. Chem. Phys.*, **43**, 2696 (1965).

Received October 27, 1970

Revised January 19, 1971