tions in swelling behavior. (4) Because of these aberrations and the inability to predict from polymer structure and T_g alone swelling profile magnitudes (particularly the all-important glassy portions of these) it is not possible currently to predict the solvent crazing resistance of a hitherto untested polymer across the whole spectrum of organic liquids. (5) Resistance to crazing in the absence of organic liquids correlates with two quantities: (a) T_g (the higher the better) and (b) the existence of low-temperature relaxations that reduce yield stress and make homogeneous creep occur more easily.

References and Notes

(1) Plastics Department, Pittsfield, Mass.

(2) (a) G. A. Bernier and R. P. Kambour, *Macromolecules*, 1, 393 (1968). (b) R. P. Kambour, E. E. Romagosa, and C. L. Gruner, *Macromolecules*, 5, 335 (1972).

(3) R. P. Kambour, C. L. Gruner, and E. E. Romagosa, *J. Polym. Sci., Polym. Phys. Ed.*, 11, 1879 (1973).

(4) R. P. Kambour, F. E. Karasz, and J. H. Daane, *J. Polym. Sci., Part A-2*, 4, 327 (1966).

(5) A. Eisenberg and B. Cayrol, *J. Polym. Sci., Part C*, 35, 129 (1971).

(6) L. M. Robeson and J. H. Faucher, *J. Polym. Sci., Part B*, 7, 35 (1969).

(7) K. H. Illers and E. Jenckel, *Rheol. Acta*, 1, 322 (1958).

(8) K. H. Illers and H. Breuer, *Kolloid-Z. Z. Polym.*, 176, 110 (1961).

(9) F. N. Kelley and F. J. Bueche, *J. Polym. Sci.*, 50, 549 (1961).

(10) P. I. Vincent and S. Raha, *Polymer*, 13, 283 (1972).

(11) With acetone as the swelling agent crystallization reduces the degree of swelling in polycarbonate by 40%; that is, solubility is not proportional to the noncrystalline fraction of polymer.[4] Effects of this kind could be expected to vary from one swelling liquid to the next, depending on the degree to which each allows crystallinity to develop.

(12) G. W. Miller, S. A. D. Visser, and A. S. Morecroft, *Polym. Eng. Sci.*, 11, 73 (1971).

(13) In the molding of the sheets polymer pellets were usually piled up in the center of the mold so that, upon closing the press, a degree of flow would occur that would improve the knitting together of the pellets and the elimination of air bubbles. The flow thus tended to be radial; consequently, orientation is likely to have varied from point to point in the sheet both in direction and magnitude. Orientation in the direction in which the crazing stress is subsequently applied tends to produce increased resistance to crazing while orientation transverse to the applied stress tends to produce a decreased crazing resistance.[14] For a given *degree* of orientation, however, the *decrease* produced by transverse orientation is known to be considerably smaller than the *increase* produced by parallel orientation.

(14) R. P. Kambour, *J. Polym. Sci. Macromol. Rev.*, 7, 1 (1973).

(15) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand-Reinhold Co., New York, N. Y., 1970, p 85.

(16) Evidence from which polymer-polymer miscibility may be inferred is found in ref 17.

(17) B. P. Barth, U. S. Patent 3,365,517, Jan 23, 1968.

(18) F. P. Price, unpublished data.

(19) These latter T_g's were measured on swollen-but-still amorphous polymer in torsion pendulum tests at 1 Hz;[4] since the maximum in log decrement for the dry amorphous polymer occurred at 151°—7° lower than the T_g determined by scanning calorimetry—the torsion pendulum T_g's have been adjusted by arbitrarily adding 7° to each. The crosses in Figure 2 are plotted from these adjusted values.

(20) This discrepancy points up one of the difficulties inherent in the procedures leading to the kind of correlation attempted here. The time scales for the various measurements and observations are not the same. With dry polymer the crazing measurement is complete in about 24 hr but with liquids like acetone crazing and cracking do not proceed beyond a minute or so. Calorimetric glass temperatures are all measured at the same scan rate but the completion of crystallization requires times of the order of a minute to a day depending on the degree of swelling.

(21) J. C. Bauwens, *J. Mater. Sci.*, 7, 577 (1972).

(22) R. E. Robertson and A. Patel, *Polym. Eng. Sci.*, 12, 346 (1972).

Notes

Infinite-Dilution Viscoelastic Properties of Randomly Branched Polystyrenes

NORIO NEMOTO, YUTAKA MITSUDA, JOHN L. SCHRAG, and JOHN D. FERRY*

Department of Chemistry and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706.

Received December 18, 1973

Measurements of storage and loss shear moduli of dilute polymer solutions, taken in a frequency range near the reciprocal of the terminal relaxation time and extrapolated to infinite dilution, provide data which are sensitive to long-chain branching and should clearly distinguish even one branch point per molecule provided the molecular weight distribution is fairly narrow.[1-5] Studies of certain ethylene-propylene terpolymers[4] have provided estimates of the degree of branching which were plausible in the light of their compositions, but could not be compared with quantitative information from an independent source. In the absence of theory for randomly branched polymers, the reduced intrinsic steady-state compliance was compared with that calculated for comb polymers of regular structure by the method introduced by Osaki,[6] modified from the theory of Zimm and Kilb.[7] In this calculation, the steady-state compliance is found to be a monotonically decreasing function of the number of branch points per molecule and of the fraction of molecular mass present in the branches. It is assumed that the randomly branched polymer will correspond roughly to a comb in which the branch lengths and the backbone spacings between branches are equal, and the value of f (branch points per molecule) is chosen which matches the experimentally determined steady-state compliances after correction for molecular weight heterogeneity.

In the present report, data are given for three randomly branched polystyrenes whose average degrees of branching were known from a kinetic analysis of the polymerization mechanism.[8] These samples were generously given us by Professor S. Onogi and Dr. T. Masuda of Kyoto University, together with data for their characterization, which are presented in Table I. The number of branch points per molecule from the polymerization kinetics, denoted by $\bar{M}_n/M_b$, ranged from 1.9 to 17. The number-average molecular weight $\bar{M}_n$ was determined by osmometry, and the ratio $\bar{M}_w/\bar{M}_n$ by gel chromatography.

Aroclor 1232 was used as a solvent for all three samples, and *o*-xylene was also used for RB-24, which had the highest molecular weight, to extend the measurements into the terminal zone. Their viscosities, η_s, at 25.0° were 0.1005 and 0.00753 P, respectively; their densities 1.2686 and 0.8760, respectively. Intrinsic viscosities, $[\eta]$, were obtained from the viscoelastic measurements at low frequencies, and in one case $[\eta]$ was also measured by capillary viscometry and found to be in reasonable agreement. These values are also given in Table I. For sample RB-24 the difference between the intrinsic viscosities in the two solvents indicates that *o*-xylene is a slightly better solvent. All viscoelastic measurements were made at 25.00°

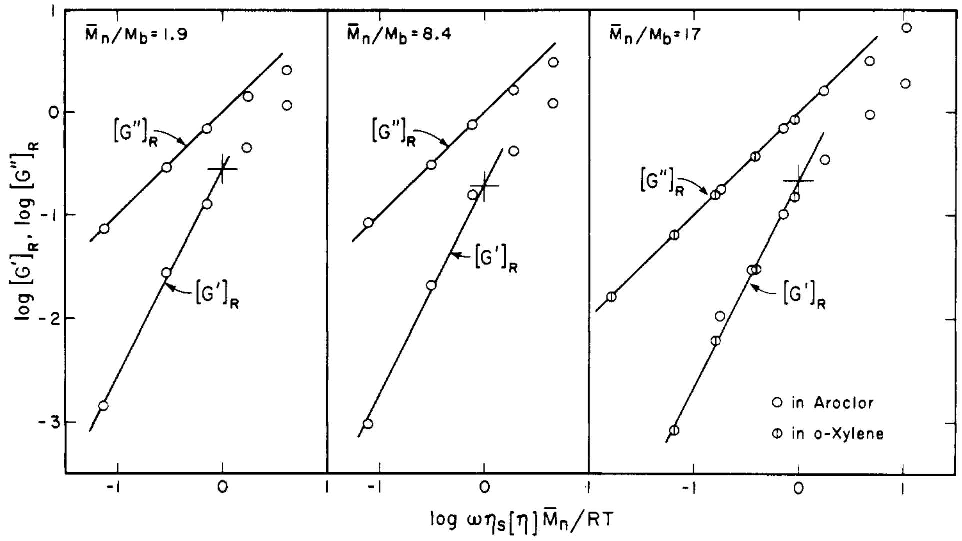

Figure 1. Reduced intrinsic storage and loss shear moduli plotted logarithmically against $\omega\eta_s[\eta]M/RT$ for samples with branch points per molecule (deduced from polymerization kinetics) as indicated. Cross denotes intersection of low-frequency segment of $[G']_R$ with ordinate axis.

Table I
Characterization and Viscoelastic Data

Polymer Code No.	RB-15	RB-26	RB-24
$\bar{M}_n \times 10^{-5}$	3.27	3.84	7.9
$\bar{M}_w/\bar{M}_n$	1.25	1.31	1.37
$\bar{M}_n/\bar{M}_b$	1.9	8.4	17
$[\eta]$, MLR, ml/g	82	58	83[a] 101[b]
$[\eta]$, capillary		64	
κ_h	1.80	2.04	2.30
j_{eR}^0	0.28	0.19	0.21
S_2/S_1^2	0.155	0.09	0.09
f	2.5	>6	>6

[a] In Aroclor 1232. [b] In *o*-xylene.

except that sample RB-26 was run at 20.00°, where the viscosity of Aroclor 1232 was 0.1312 P.

The storage and loss shear moduli, G' and G'', of the solutions were measured by the Birnboim-Schrag multiple-lumped resonator (MLR)[9] with computerized data acquisition and processing system.[10] One resonator was used with five frequencies from 100 to 6000 Hz. The range of concentration (c) was from 0.003 to 0.013 g per ml.

The quantities $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$, where ω is radian frequency, were plotted against c and extrapolated to zero c at each frequency as described in previous studies[1-4] to give the corresponding intrinsic quantities $[G']$ and $[G'']$. These were reduced to $[G']_R = [G']\bar{M}_n/RT$ and $[G'']_R = [G'']\bar{M}_n/RT$ and plotted logarithmically against $\omega\eta_s[\eta]\bar{M}_n/RT$ in Figure 1. These coordinates are convenient for comparison with theory.[4] Linear plots are obtained at low frequencies as expected from theory; for sample RB-24 the data in the two solvents agree well and indicate that the hydrodynamic interaction parameter h^* is not noticeably different for these two. At low frequencies, log $[G']_R$ has a slope of 2, and its intercept on the ordinate axis, denoted by a cross, is log j_{eR}^0, where j_{eR}^0 is the reduced intrinsic steady-state compliance. This quantity is sensitive to both branching and molecular weight distribution; if the latter is reasonably narrow so that the degree of branching is fairly uniform, it may be expressed by the product $j_{eR} = \kappa_h S_2/S_1^2$, where κ_h is a heterogeneity coefficent and S_2 and S_1 are sums over relaxation times ratios which are characteristic of the branching geometry. For a Lansing-Kraemer distribution[11] of molecular weights, $\kappa_h = (\bar{M}_w/\bar{M}_n)^{(a+1)^2}$, and for relatively narrow distributions, κ_h is not very sensitive to the form of the distribution. Values of j_{eR}^0, κ_h, and S_2/S_1^2 are given in Table I.

For a linear molecule with h^*, the hydrodynamic interaction factor, chosen as 0.15, which is appropriate to a relatively good solvent, S_2/S_1^2 is 0.25.[4] The experimental values are all much smaller, as expected for branching. They can be compared with predictions for branched polymers with a regular comb structure,[4,6] *i.e.*, one with the comb arm lengths and the backbone spacings between arms all equal. This procedure provides the values of f, branch points per molecule, given in the last row of Table I. For sample RB-15, the result agrees satisfactorily with the value deduced from polymerization kinetics. For the others, the result is consistent but it can only be concluded that f is greater than 6, because S_2/S_1^2 becomes insensitive to the degree of branching beyond that point.

Additional evidence is thus provided that viscoelastic measurements in very dilute solution can serve to detect and gauge small degrees of long-chain branching.

Acknowledgment. This work was supported in part by the Army Research Office (Durham), The National Institutes of Health, and the National Science Foundation.

References and Notes

(1) K. Osaki, Y. Mitsuda, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 17 (1972).
(2) Y. Mitsuda, K. Osaki, J. L. Schrag, and J. D. Ferry, *Polym. J.*, **4**, 24 (1973).
(3) Y. Mitsuda, J. L. Schrag, and J. D. Ferry, *Polym. J.*, **4**, 668 (1973).
(4) Y. Mitsuda, J. L. Schrag, and J. D. Ferry, *J. Appl. Polym. Sci.*, in press.
(5) Y. Mitsuda and J. D. Ferry, *Kobunshi Kagaku*, in press.
(6) K. Osaki, Y. Mitsuda, J. L. Schrag, and J. D. Ferry, *Trans. Soc. Rheol.*, in press.
(7) B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).
(8) T. Masuda, Y. Nakagawa, Y. Ohta, and S. Onogi, *Polym. J.*, **3**, 92 (1972).
(9) J. L. Schrag and R. M. Johnson, *Rev. Sci. Instrum.*, **42**, 224 (1971).
(10) D. J. Massa and J. L. Schrag, *J. Polym. Sci., Part A-2*, **10**, 71 (1972).
(11) W. D. Lansing and E. O. Kraemer, *J. Amer. Chem. Soc.*, **57**, 1369 (1935).