to be unique among the many amorphous polymers we have investigated.

It is quite unfortunate that polyisobutylene was chosen in numerous studies[1,5-9] to investigate the validity of GLC-derived polymer–solute interactions as compared to the more conventional static measurements. As reported earlier by Hammers and DeLigny,[5] it is usually necessary to perform extrapolations of retention volumes to zero flow rate, even in the 50–100° temperature range, thereby introducing a certain degree of imprecision. Due to the magnitude of this flow-rate dependence, results obtained below this range are less reliable. Only at a much higher temperature (T_g +150°) can equilibrium measurements be made directly, and these we believe are the only data with sufficient reliability to afford a satisfactory comparison with static data.

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References and Notes

(1) R. N. Lichtenthaler, D. D. Liu, and J. M. Prausnitz, *Macromolecules*, **7**, 565 (1974).
(2) D. M. Ottenstein, *J. Chromatogr. Sci.*, **11**, 136 (1973).
(3) R. H. Perret and J. H. Purnell, *J. Chromatogr.*, **7**, 455 (1962).
(4) J.-M. Braun and J. E. Guillet, manuscript in preparation.
(5) W. E. Hammers and C. L. DeLigny, *Recl. Trav. Chim. Pays-Bas*, **90**, 912 (1971).
(6) W. E. Hammers and C. L. DeLigny, *J. Polym. Sci., Part C*, **39**, 273 (1972).
(7) R. D. Newman and J. M. Prausnitz, *J. Phys. Chem.*, **76**, 1492 (1972).
(8) Y. K. Leung and B. E. Eichinger, *J. Phys. Chem.*, **78**, 60 (1974).
(9) Y. K. Leung and B. E. Eichinger, *Macromolecules*, **7**, 685 (1974).

Some Solution Properties of Poly(bicycloheptene sulfone) (PBCHS)

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The solution properties of poly(bicycloheptene sulfone) (PBCHS) have not been reported in the literature although solution data are available for at least six other fractionated poly(olefin sulfones).[1] The constants in the Mark–Houwink equation ($[\eta] = KM^{-a}$) have been determined for these polysulfones in Θ solvents permitting calculation of the polymer unperturbed dimensions. In this study, we have investigated the solution properties of PBCHS which included refractive index increment measurements and a study of polymer fractions by light scattering, viscometry, and gel permeation chromatography. From these measurements the Mark–Houwink constant, the mean square end to end distance, and the characteristic ratio of the polysulfone chains were estimated.

The free radical initiated copolymerization of bicycloheptene with sulfur dioxide was carried out at −10° in a 2 l. glass lined Parr stirring-type stainless-steel pressure reactor. The yield of polymer ("whole polymer") was 15 g (47.5%). The polymer was fractionated in $CHCl_3$–methyl alcohol. Four fractions and a whole polymer were used for the GPC, refractive index, light scattering, and viscometry measurements.

A modified Waters Associates GPC model 200 with five 4-ft fractionating columns having permeability limits ranging from 5×10^6 to 5×10^3 Å was used in this work.

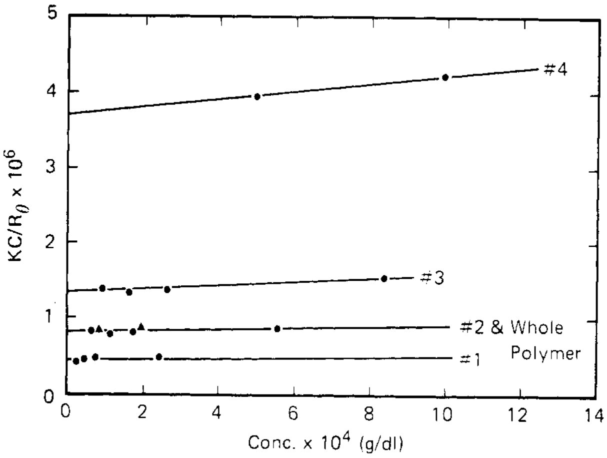

Figure 1. Plot of KC/R_Θ versus concentration of PBCHS in $CHCl_3$ at 25° and at 4° angle of observation.

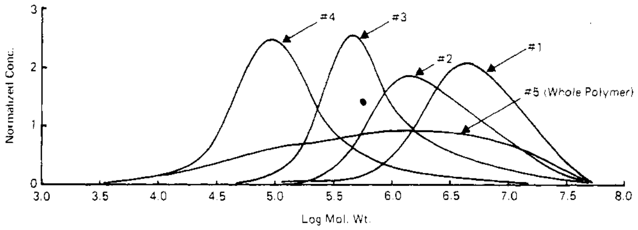

Figure 2. Normalized apparent differential molecular weight distribution (MWD) of the whole PBCHS polymer and its different fractions.

The instrument used for the weight average molecular weight measurement was a recently developed high precision low angle laser light scattering photometer (LALLS)[2,3] by the Beckman Instrument Co.

The sample solutions were prepared in $CHCl_3$ and also in cyclohexanone (chromatographic grades) and diluted to different concentrations in 25 ml volumetric flasks. The solutions were filtered through a 0.2 μ millipore filter before direct injection into the sample cell. The molecular weight was calculated from the intercept of the plot of KC/R_Θ versus concentration such as that shown in Figure 1. K is the polymer constant which is dependent on the refractive index of the solvent (n) and the refractive index increment, $\Delta n/\Delta c$. In $CHCl_3$, n and $\Delta n/\Delta c$ were determined to be 1.446 and 0.1025 ml/g, respectively. This gives a value of 8.98×10^{-8} for K at 4° angle of observation using a helium–neon laser (6328 Å) light source. The correction due to an interference effect was estimated to be less than 3% ($P(\Theta) > 0.97$) for the highest molecular weight fraction. Consequently, no correction was considered necessary for the lower molecular weight fractions. Light scattering data for sample 2 were also obtained in cyclohexanone; n and $\Delta n/\Delta c$ were found to be 1.451 and 0.112 ml/g, respectively. The $\Delta n/\Delta c$ of PBCHS in $CHCl_3$ and cyclohexanone were measured using the Brice-Phoenix differential refractometer which was calibrated using a potassium chloride solution. The molecular weight obtained in cyclohexanone was 1.10×10^6 compared with 1.25×10^6 in $CHCl_3$. The good agreement in the light scattering data helps support our contention that there is no appreciable association of the polymer with itself.

A Fica Viscomatic viscometer with a Haake temperature controller was used to measure the solution and solvent ef-

Table I
Molecular Weight Averages from GPC Measurement

Sample fraction	$M_n \times 10^{-6}$	$M_w \times 10^{-6}$	$M_v \times 10^{-6}$	$M_z \times 10^{-6}$	H
1	2.7	7.0	6.5	14.5	2.6
2	1.4	4.0	3.6	12.3	2.8
3	0.5	1.8	1.3	10.2	3.6
4	0.1	0.4	0.2	3.5	4.0
Whole polymer	0.1	3.8	2.7	15.2	38.0

Table II
Comparison of GPC Versus Light Scattering Molecular Weight Data

	GPC $M_w \times 10^{-6}$		
Sample fraction	Relative to poly-styrene std	Universal cali-bration	Light-scattering $M_w \times 10^{-6}$
1	7.0	12.9	2.27
2	4.0	7.6	1.25
3	1.8	3.2	0.75
4	0.4	0.7	0.27
Whole polymer	3.8	6.9	1.25

flux times. The intrinsic viscosity was determined from the intercept of both plots of $(\eta_r - 1)/c$ and $\ln \eta_r/c$ versus c.

The intrinsic viscosities of the PBCHS fractions were obtained in both $CHCl_3$ and cyclohexanone at 25 and 40°. The solutions were first passed through a 1 μ millipore filter before charging into the viscometer. This resulted in reproducible efflux time readings within ±0.2%.

The normalized *apparent* molecular weight distribution in Figure 2 shows the very wide distribution of the whole polymer. The *apparent* molecular weight heterogeneity index ($H = M_w/M_n$) of the unfractionated polymer shown in Table I is greater than 27 indicating anomalous GPC retention volume characteristics.

This anomaly seems to persist in the normalized apparent molecular weight distributions of the four fractions also shown in Figure 2. The lower molecular weight fraction contains small quantities of the higher molecular weight fraction as shown by the excessive tailing. This high molecular weight tail was difficult to extract from the low molecular weight fraction by fractional precipitation. As a consequence of this tailing, the heterogeneity index (M_w/M_n) of the fractions increased with decreasing number or weight average molecular weight as indicated in Table I. The KC/R_Θ versus C plot in Figure 1 shows that the virial coefficient (A) is dependent on the molecular weight but is relatively insensitive to the molecular weight distribution. This is indicated by the data points of the whole polymer and fraction 2 which coincide, both having an M_w of 1.25×10^6.

Table II compares the weight average molecular weights obtained from light scattering measurements with those obtained from the GPC chromatograms. It becomes apparent that the M_w's calculated from GPC data using either the relative values or the universal calibration method yield values much greater than those obtained from the light scattering measurement. PBCHS exhibits unusually low retention volumes relative to its true molecular weight (as measured by light scattering). However, this behavior is not unique to PBCHS. It has been observed to occur with other polymers containing highly polar groups, such as polyols,[4] and has been attributed to polymer-solvent interaction,[4] i.e., each sulfone group can associate with two $CHCl_3$ molecules via hydrogen bonding, thereby decreasing its mobility in the solvent and its ability to attain equilibrium between the stationary and mobile phases. This results in a highly skewed chromatogram, the polymer eluting earlier relative to its molecular weight. This could also explain the excessive tailing of the chromatogram and the higher heterogeneity index of PBCHS.

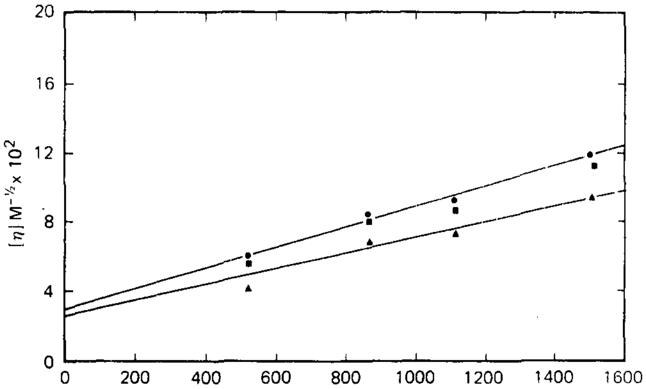

Figure 3. The approximation of K_Θ using the Stockmayer–Fixman extrapolation method: (●) PBCHS in $CHCl_3$ at 25°; (■) PBCHS in $CHCl_3$ at 40°; (▲) PBCHS in cyclohexanone at 25°.

The $[\eta]$-molecular weight relationship was obtained in both $CHCl_3$ and cyclohexanone solvents using a computerized linear regression technique. The Mark–Houwink relationships for the molecular weight range studied in $CHCl_3$ at 25 and 40° are as follows:

$$[\eta]_{25°} = 1.58 \times 10^{-5} M^{0.79} \text{ dl/g} \tag{1}$$

and

$$[\eta]_{40°} = 1.21 \times 10^{-5} M^{0.79} \text{ dl/g} \tag{2}$$

Note that the coefficient and the exponents at two temperatures in $CHCl_3$ have values which are similar.

In cyclohexanone, the Mark-Houwink relationship was obtained at 25°C only.

$$[\eta]_{25°} = 3.05 \times 10^{-5} M_w^{0.73} \text{ dl/g} \tag{3}$$

It should be noted that eq 1–3 are valid only for the molecular weight range studied, i.e., $2 \times 10^5 > M < 3 \times 10^6$.

The unperturbed chain dimension of PBCHS was obtained from the coefficients K_Θ of the Mark–Houwink equation at the Θ condition. K_Θ in Figure 3 is approximated to be 2.90×10^{-4} dl/g using the Stockmayer–Fixman extrapolation.[5] K_Θ was also obtained using the Flory–Fox approximation method[6] as shown in Figure 4 which gave values equal to those obtained by the Stockmayer–Fixman method. The root mean square end to end distance, $\langle r^2 \rangle_0$, is computed from

$$\langle r^2 \rangle_0 = (K_\Theta/\phi)^{2/3} M \tag{4}$$

$$= 0.238 M \tag{5}$$

Likewise, the characteristic ratio, $\langle r^2 \rangle_0/nl^2$, was computed from the known bond lengths of the carbon to carbon and carbon to sulfur bond, and from the molecular weight of the fraction.

The computed $\langle r^2 \rangle_0$, $\langle r^2 \rangle_0/nl^2$, and the molecular weight of the polymer fractions are shown in Table III. The value of the characteristic ratio of PBCHS is much lower than the 6.71 characteristic ratio value reported by Bates and

Table III
Unperturbed Chain Dimension and Molecular Weights[a]

Sample fraction	$M_w \times 10^{-6}$	$\langle r^2\rangle_0^{1/2}$	$\langle r^2\rangle_0/nl^2$
1	2.27	735	4.2
2	1.25	545	4.2
3	0.76	421	4.2
4	0.272	254	4.2

[a] r is in ångströms.

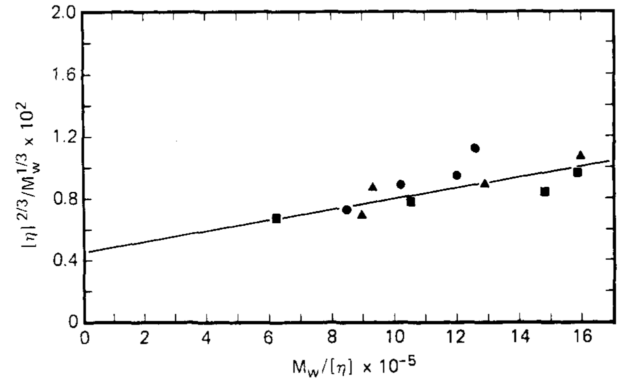

Figure 4. The approximation of K_Θ using the Flory–Fox extrapolation method: (●) PBCHS in $CHCl_3$ at 25°; (■) PBCHS in $CHCl_3$ at 40°; (▲) PBCHS in cyclohexanone at 25°.

Ivin[7] for poly(hexene 1-sulfone) (PHS). In fact, the characteristic ratio of PBCHS is very close to the value of 4.0 reported for polyoxyethylene[8] and suggests that the PBCHS coil is more dense relative to other polysulfones.

However, the above assertion must be tempered by the relatively rough approximation and long extrapolation used in obtaining the value of $\langle r^2\rangle_0/nl^2$. The data do not represent a wide enough range of molecular weights to allow accurate determination of K_Θ. Additionally, the approximate nature and the limitations of the method used in calculating K_Θ has been recognized early by Orofino and Flory[9] and more recently by Pouchly and Patterson.[10] In fact, Stockmayer[11] has also advocated caution in using the above extrapolation technique.

Based on the unusually low GPC retention characteristics of PBCHS in relation to its true molecular weight (as determined by light scattering), it may be concluded that the PBCHS strongly associates with the $CHCl_3$ solvent perhaps via hydrogen bonding. The increase in the apparent heterogeneity index and the "tailing" of the low molecular weight fraction of PBCHS may be explained by the same above phenomena, i.e., strong solvent interaction can result in lower permeation into the stationary phase, hence lower retention volumes.

The low value of the characteristic ratio of PBCHS suggests a dense polymer coil relative to other polysulfones, i.e., poly(hexene 1-sulfone). However, this conclusion may be subject to errors in the value of K_Θ due to the excessively long extrapolation of the viscosity data. Consequently, confirmation will be required from measurements of K_Θ over a wider range of molecular weights.

References and Notes

(1) W. Pasika, *Adv. Macromol. Chem.*, **1**, 395 (1968).
(2) W. Kaye, *Anal. Chem.*, **45**, 221A (1973).
(3) A. C. Ouano and W. Kaye, *J. Polym. Sci., Part A*, in press.
(4) J. Cazes and D. R. Gaskill, *Sep. Sci.*, **4**, 15, 1969.
(5) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).
(6) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).
(7) T. W. Bates and K. J. Ivin, *Polymer*, **8**, 263 (1967).
(8) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(9) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).
(10) J. Pouchly and D. Patterson, *Macromolecules*, **6**, 465 (1973).
(11) K. Matsuo and W. H. Stockmayer, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **15**, 527 (1974).

A First Step Toward High Resolution ^{13}C NMR Spectroscopy of Intractable Polymers. Epoxies

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High resolution proton NMR is widely employed in polymer characterization studies to yield quantitative measures of microtacticity, functional groups, chain mobility, and, in some cases, molecular weight. NMR of polymers advanced significantly with the advent of carbon-13 Fourier transform (FT) NMR. The FT method overcomes the low sensitivity problem of carbon-13 (1.1% natural abundance and small magnetic moment), while the large chemical shift range and proton decoupling combine to produce spectra in which virtually every type of carbon atom in the polymer backbone is resolved and identifiable.

NMR of intractable polymers is another story, however. Unless such a polymer can be melted or its structure otherwise made mobile (by solvent swelling, or heating above the glass transition temperature, for example), the above NMR techniques are useless. In solids, the chemical shift anisotropy and the dipole–dipole interactions, which are not averaged by rapid molecular tumbling as in mobile systems, produce line widths thousands of times those of liquids. Broadline NMR is of some value for the characterization of polymers, but the broad signals of necessity yield only coarse information, such as phase transition temperatures, or the proportions of crystalline and amorphous regions. Furthermore, low abundance nuclei such as carbon-13 do not give usable signal levels.

The technique of proton-enhanced carbon-13 NMR spectroscopy offers an avenue to high resolution spectra in organic solids,[1,2] including the "intractable" polymers. This technique (a) averages away the dipolar field of the nearby protons, (b) enhances the signal of the rare ^{13}C nuclei by transferring magnetization from the more abundant protons, and (c) allows signal accumulation on a time scale of the proton spin–lattice relaxation time. The overall gain in signal/noise accumulation per unit time[1] can be as great as 10^3, which is sufficient to make the technique a practical and useful tool for the investigation of the chemistry of solids. Unfortunately, the technique cannot remove the chemical shift anisotropy, which randomly oriented aggregates of polymer molecules must necessarily show. The purpose of this note is to exhibit and discuss briefly spectra obtained by application of the technique to epoxy polymers cured with different hardening agents.

The proton-enhanced carbon-13 spectra of three epoxy polymers (the diglycidyl ether of bisphenol A cured with piperidine, hexahydrophthalic anhydride (HHPA), and Nadic methyl anhydride (NMA)) are shown in Figure 1. Also shown are the spectra of the liquid epoxy resin obtained using normal FT technique, and a diagram which represents typical anisotropy patterns expected for the types of carbon atoms in the polymers. The chemical shift positions chosen for the anisotropy diagram (Figure 1e) are