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.

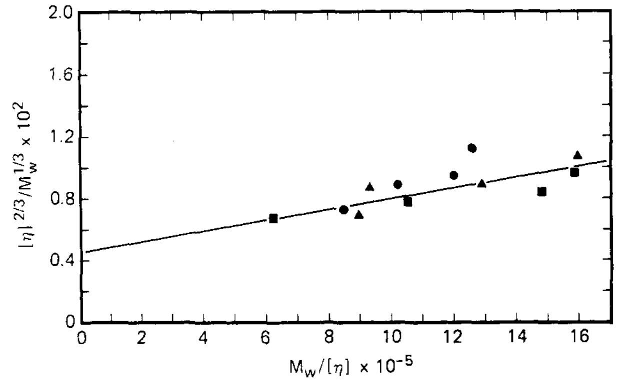

Figure 4. The approximation of K_Θ using the Flory–Fox extrapolation method: (●) PBCHS in $CHCl_3$ at 25°; (■) PBCHS in $CHCl_3$ at 40°; (▲) PBCHS in cyclohexanone at 25°.

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.

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

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Received April 14, 1975

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

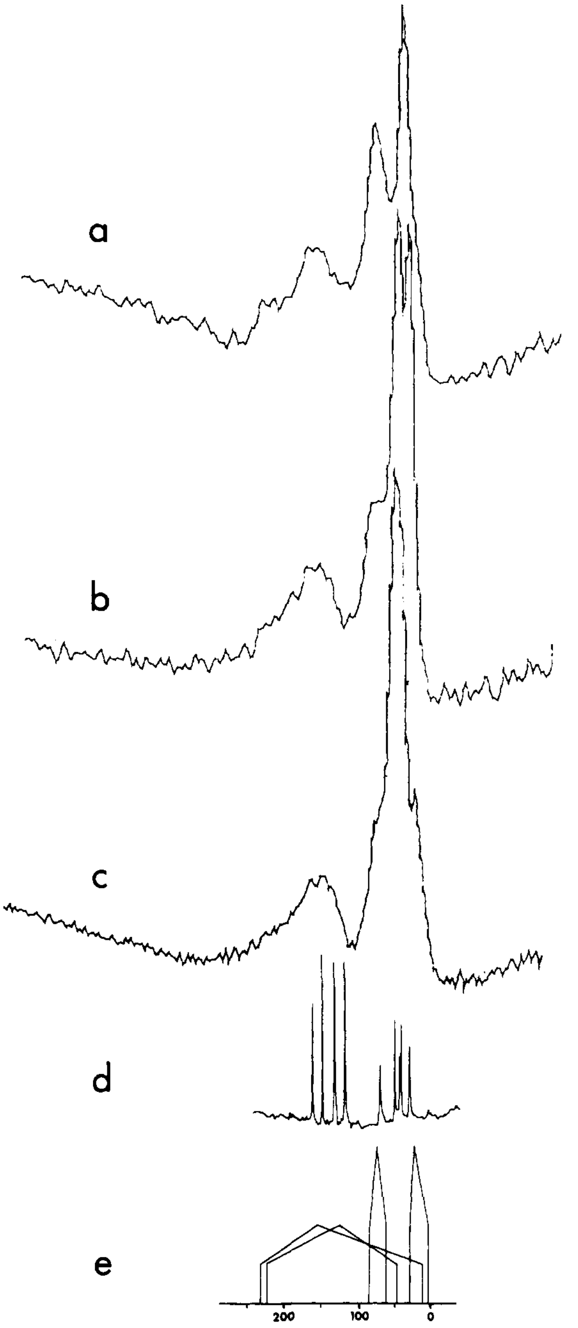

Figure 1. Proton enhanced ^{13}C NMR spectra of epoxy polymers cured with various curing agents: (a) piperidine; (b) hexahydrophthalic anhydride; and (c) Nadic methyl anhydride. In (d) is shown the high resolution ^{13}C spectrum of the diglycidyl ether of bisphenol A, the starting resin for the above. In (e) is depicted the approximate chemical shift anisotropy patterns expected for (left to right) quaternary aromatic carbons, unsubstituted aromatic carbons, methylene carbons, and methyl carbons. The chemical shift scale is in ppm referenced to TMS (tetramethylsilane).

representative of (left to right) a substituted aromatic carbon, an aromatic carbon bearing a proton, a methylene carbon attached to an electronegative atom such as oxygen, and a methyl or methylene group in an aliphatic environment.

The polymer spectra (Figure 1a–c) do indeed contain resolved functional groups, but the broadening due to chemical shift anisotropy is apparent. Narrow, intense signals are seen in the aliphatic region (0–100 ppm), reflecting contributions from methyl and methylene groups. These groups typically show small shift anisotropies of ca. 30 ppm.[1,3] The proportion of curing agent was 5 phr (parts per hundred resin) for piperidine, and 85 phr for HHPA and NMA. The signal contributions of the latter two curing agents in the 0–100 ppm spectral region will therefore be large compared with those of piperidine. In all three cases, a large number of overlapping lines contribute to the spectral envelope in this region, making structure–spectra correlations based on the limited resolution tenuous. The distinctly different character of the three spectra in the aliphatic region may be associated with the rigidity of the polymer as well as the chemical makeup of the curing agent (but see below).

The large anisotropies of ca. 200 ppm observed for aromatic carbon atoms[1,3] limit what can be said about other spectral features. Signals from aromatic carbon atoms are expected over the 30–240 ppm region, as schematically represented in part e of the figure. As predicted, the maxima of the anisotropy broadened lines are observed in the 140–170 ppm region. The anisotropy pattern for the aromatic region appears to be broader in the order piperidine > HHPA > NMA. If it is assumed that motion in the backbone reduces the width of the anisotropy pattern, the predicted rigidities would be piperidine > HHPA > NMA. Taking the heat distortion temperatures as a crude measure of rigidity, an opposite ordering is expected (piperidine 85°, HHPA 135°, NMA 155°). Obviously, useful correlations must await the gathering of a great deal more data.

Although full structural information is not obtainable, the proton-enhanced spectra of these polymers are reproducible and distinct. It is possible to remove the chemical shift anisotropy by "magic angle" rotation of the specimen.[4] When that is done, the effect of the combined techniques on structural studies of solid polymers promises to be truly revolutionary.

Specimens of the polymers were cylindrical pellets 7 mm in diameter, containing about 10^{20} carbon-13 nuclei. Spectra were obtained at room temperature. The spectrometer has been described elsewhere.[5] The single contact proton-enhancement technique was used.[1] This procedure in principle enhances the ^{13}C signal by a factor of 4 by the transfer of proton magnetization to the ^{13}C nuclei, although explicit measurement of this enhancement was not carried out in this work. Contact between the two spin systems was established according to the Hartmann–Hahn criterion with a proton H_1 of approximately 12 G and cross polarization times of 1 to 2 msec. The spectra shown in the figure are fast Fourier transforms of the enhanced free induction decays which were recorded under proton-decoupled conditions at 26.7 MHz. Between 600 and 2000 free induction decays were averaged before Fourier transformation; the time required varied from 15 to 90 min per spectrum.

Acknowledgment. We gratefully acknowledge the generosity of Professor A. Pines of the University of California for allowing us to use his double resonance spectrometer and for provision of helpful advice. We thank Dr. J. J. Chang for his most necessary assistance in gathering data. The study was supported in part by the Naval Air Systems Command.

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