sufficient data including enough experiments at the appropriate concentrations, reproducibility studies, and studies testing of the calculated ratios by performing a series of copolymerization experiments at alternate starting concentrations. When these criteria are met, and only then, should a mechanism involving charge-transfer complexes in competition with the terminal model for composition–conversion data be assigned.

This study demonstrated that no adequate composition–conversion data currently exists in the literature which can be used to test for a combined terminal charge-transfer polymerization model. Second, this technique provides the guide for what experiments should be performed and how many should be conducted. Third, the method requires accurate composition–conversion data. This necessary accuracy surpasses that which is normally obtainable. However, for certain combinations of reactivity parameters, this is less critical than in other regions. Thus, the method discussed above is a first step in the use of composition–conversion data to probe the importance of charge-transfer complexes in copolymerization processes.

Listings of these programs will be made available upon request.

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References and Notes

(1) H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Beynon, "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience, New York, N.Y., 1966.
(2) G. E. Ham, "Copolymerization," Interscience, New York, N.Y., 1964.
(3) T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "High Polymers," Vol. VIII, Interscience, New York, N.Y., 1952.
(4) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
(5) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
(6) D. R. Montgomery and C. E. Fry, *J. Polym. Sci., Part C*, **25**, 59 (1968).
(7) D. W. Behnken, *J. Polym. Sci., Part A*, **2**, 645 (1964).
(8) G. E. P. Box and H. L. Lucas, *Biometrika*, **46**, 77 (1959).
(9) E. M. L. Beal, *J. Roy. Statist. Soc., B*, **22**, 41 (1960).
(10) P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci., Part A*, **3**, 369 (1965).
(11) P. W. Tidwell and G. A. Mortimer, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4**, 281 (1970).
(12) C. U. Pittman, Jr., and T. D. Rounsefell, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 621 (1973).
(13) E. Merz, T. Alfrey, and G. Goldfinger, *J. Polym. Sci.*, **1**, 75 (1946).
(14) G. E. Ham, *J. Polym. Sci.*, **14**, 87 (1954); **54**, 1 (1961); **61**, 9 (1962).
(15) W. E. Barb, *J. Polym. Sci.*, **11**, 117 (1953).
(16) M. Litt and F. W. Bauer, *J. Polym. Sci., Part C*, **16**, 1551 (1967).
(17) K. Ito and Y. Yamashita, *J. Polym. Sci., Part A-1*, **4**, 631 (1966).
(18) M. Berger and I. Kuntz, *J. Polym. Sci., Part A*, **2**, 1687 (1964).
(19) C. Walling, E. R. Briggs, K. B. Wolfstern, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948).
(20) A. D. Ketley, "Stereochemistry of Macromolecules," Vol. 3, Marcel Dekker, New York, N.Y., 1968, Chapters 1 and 2.
(21) K. Bacon, "New Methods of Polymer Characterization," Interscience, New York, N.Y., 1964.
(22) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N.Y., 1969.
(23) N. C. Yang and Y. Gaoni, *J. Amer. Chem. Soc.*, **86**, 5022 (1964).
(24) G. Henrici-Olive' and S. Olive', *Z. Phys. Chem.* (*Frankfurt am Main*), **48**, 35, 51 (1966).
(25) A. Ledwith, *J. Appl. Chem.*, **17**, 344 (1967).
(26) S. Iwatsuki and Y. Yamashita, *Makromol. Chem.*, **89**, 205 (1965).
(27) R. S. Mulliken and W. B. Person, *J. Amer. Chem. Soc.*, **91**, 3409 (1969).
(28) J. Seiner and M. Litt, *Macromolecules*, **4**, 308, 312, 314, 316 (1971).
(29) D. W. Marquardt, *Chem. Eng. Progr.*, **55**, 65 (1959).
(30) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).

Motional Phenomena and Multiple Pulse Nuclear Magnetic Resonance. Nonisotropic Motion in Natural Rubber

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ABSTRACT: The nonisotropic nature of the motion in *cis*-polyisoprene, both a natural gum sample and a carbon-filled, sulfur-vulcanized sample, has been investigated by a combination of conventional and multiple pulsed nmr studies of the proton resonance at room temperature. The ability of the multiple pulse techniques to remove residual dipolar broadening from the already partially motionally narrowed proton nmr lines confirms the presence of anisotropic or restricted motion within these materials and an order parameter of 0.006 is determined for the natrual gum sample. A phase altered multiple pulse cycle is used to allow separation of chemical shift information from relaxation effects, and the contribution of chemical shift interactions to the second moment of the free induction decay is determined as well as the relaxation rates. All the protons relax with similar rates in the natural gum sample but exhibit relaxation rates differing by an order of magnitude in the carbon-filled sample; this is attributed to the presence of longer correlation times for the backbone protons in the carbon-filled sample.

One of the most useful measurements in a spectroscopic study is the line shape of the resonance. Particularly in nmr studies of liquids, the line width can be related to relaxation processes in the substance being studied.[1] In solids, however, the dipolar Hamiltonian dominates the line width and little information can be gained from line width studies about the relaxation process or smaller static interactions present.[2] Recent developments in pulse nmr[3-9] have furnished means to reduce greatly, or remove, the effects of the dipolar interaction from solid state nmr spectra and have allowed examination of smaller static interactions, such as the chemical shift tensor.[7] In this paper we illustrate the use of the multiple pulse nmr techniques to separate and characterize spin–spin relaxation processes, chemical shift interactions, and dipolar interactions in solids, particularly in systems where the occurrence of restricted or anisotropic motion complicates any attempt to characterize the motional processes by conventional measurements of the temperature and frequency dependence of spin–lattice relaxation times.[10]

The multiple pulse nmr techniques involve the repetitive application of periodic and cyclic pulse sequences to modify the time development of the spin system. Specific pulse cycles have been developed to reduce the effects of the static dipolar interaction.[3,6,8] However, the presence of molecular motion interferes with the averaging effects of the pulse sequence, and, as the rate of molecular motion increases and approaches the time scale of the pulse sequence, the effectiveness of such a pulse cycle is expected to decrease and the line width begins to grow.[5,11] In contrast, the effect of increasing molecular motion on the conventional nmr spectra of solids is to narrow the spectral lines as the time scale of the molecular motion approaches the inverse line width of the dipolar broadened spectra.[12] If the molecular motion is isotropic, further increases in its frequency will effectively average the secular portion of the dipolar Hamiltonian to zero and there is no need for a pulse sequence to remove static dipolar interactions. Consequently, most multiple pulse nmr studies to date have been of rigid solids and there has been no extensive use of the line-narrowing pulse cycles in cases involving molecular motion. However, if the molecular motion is not isotropic, very rapid motions may be present which do not average the secular portion of the dipolar Hamiltonian to zero and substantial benefit can accrue from the use of line-narrowing pulse sequences. The line shape observed in the case of restricted or anisotropic motion can be a complicated function of the effects of the molecular motion on the several contributing Hamiltonians; it will be demonstrated that, by performing several separate but related multiple pulse nmr measurements, it is possible to separate and determine the individual contributions to the line shape of protons in such a sample. This can be of considerable advantage in studies of molecular dynamics of motionally ordered systems such as polymers, liquid crystals, and ordered biological materials, as well as molecules moving on surfaces.

Experimental Section

The preliminary measurements reported here were carried out at room temperature on a spectrometer previously described.[13] Measurements have involved conventional free induction decay and T_1 pulse measurements, multiple pulse measurements using an eight-pulse cycle,[8] and multiple pulse measurements using a modification of the eight-pulse cycle which removes inhomogeneous broadening from such sources as the chemical shift and H_0 field inhomogeneities, as well as dipolar effects.

The eight-pulse cycle was modified by introducing a phase error in the P_x pulse in order to remove the effects of the chemical shift and magnetic field inhomogeneities. The effect of such a pulse

$$\overline{H}_p = \frac{2}{t_c}(\phi_{-x} - \phi_x)I_y \qquad (1)$$

error is to introduce the zeroth order Hamiltonian indicated in eq 1[9] which serves as a means of second averaging any small off-resonance Hamiltonians, and, thus, removes chemical shift and magnetic field inhomogeneity effects. Using the quantitative description previously published,[9] it is clear that this scheme is convenient for the small chemical shifts found in proton systems, while an alternative approach of using a pulse cycle which has the proper symmetry to remove both static dipolar and inhomogeneous broadening effects simultaneously might be more appropriate for the larger chemical shifts found in ^{19}F systems, for instance.

The samples of *cis*-polyisoprene $(-CH_2CH{=}CCH_3CH_2-)_n$ were obtained from Dr. J. Schaefer of Monsanto and consisted of a natural gum sample and a carbon-filled, sulfur-vulcanized sample. The filled sample had been prepared with an HAF carbon black and the loading was 60 parts of carbon black to 100 parts of rubber by weight. Electron microscopy of the cross-linked sample indicated that the carbon was in the form of widely dispersed aggregates 500–100 Å in diameter.[14]

Results

In the cases to be discussed here, one can express the Hamiltonian controlling the frequency spectrum of nmr experiments

$$H = H_Z + H_D + H_\sigma + H_{rf} + H_{etc} \qquad (2)$$

where H_Z is the Zeeman interaction, H_D is the pairwise dipolar interaction, H_σ is the chemical shift Hamiltonian, H_{etc} are other small interactions which will be ignored in this treatment, and H_{rf} is the interaction of the spin system with the externally applied radiofrequency fields. In rigid solids the secular portions of the dipolar Hamiltonian normally control the line shape, while in liquids where the secular dipolar interaction is averaged out by rapid molecular motion the chemical shift and spin–spin coupling terms normally control the observed frequency spectrum. However, in cases where several of the terms make significant contributions, such as the case of anisotropic motion under study here, one expects potential contributions from secular dipolar terms, chemical shift terms, and relaxation phenomena. These cases are difficult,[10b,15] and many times impossible, to study with conventional nmr techniques. By making use of the ability of the multiple pulse techniques to alter selectively how each of these Hamiltonians affects the time evolution of the spin system, it is possible to sort out the various contributions and thus determine quantitatively the effects of the separate Hamiltonians.

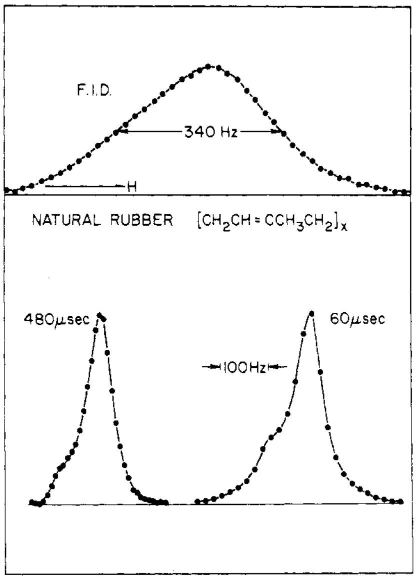

Figure 1. Free induction decay spectrum and eight-pulse spectra of natural rubber. The eight-pulse spectra were taken at two cycle times (the time necessary for application of one full eight-pulse cycle), 60 and 480 μsec.

As a particular example, we describe how use of two multiple pulse cycles together with the conventional free induction decay and T_1 measurements will allow separation of the contributions to the proton spectrum from the dipolar Hamiltonian, the chemical shift Hamiltonian, and homogeneous broadening due to relaxation processes in the two related polymer samples. The free induction decay and multiple pulse spectra of the unfilled rubber at two cycle times are shown in Figure 1. As can be seen, the free induction decay spectrum is slightly asymmetric indicating the presence of fine structure on the line, and its width of 340 Hz indicates that a sizable amount of molecular motion is present. A two-peak spectrum is observed for the multiple pulse spectrum of the natural rubber in which the small shoulder peak can be associated with the chemically shifted proton bonded to the vinyl carbon. The line shape of the multiple pulse spectrum contains contributions from the chemical shift Hamiltonians, relaxation phenomena, and instrumental effects. In order to further separate these, the phase-modified form of the eight-pulse cycle described above is applied and the results for the natural rubber sample are shown in Figures 2 and 3. In Figure 2 is a comparison of the decay observed with the normal eight-pulse cycle and the phase-modified eight-pulse cycle. The normal

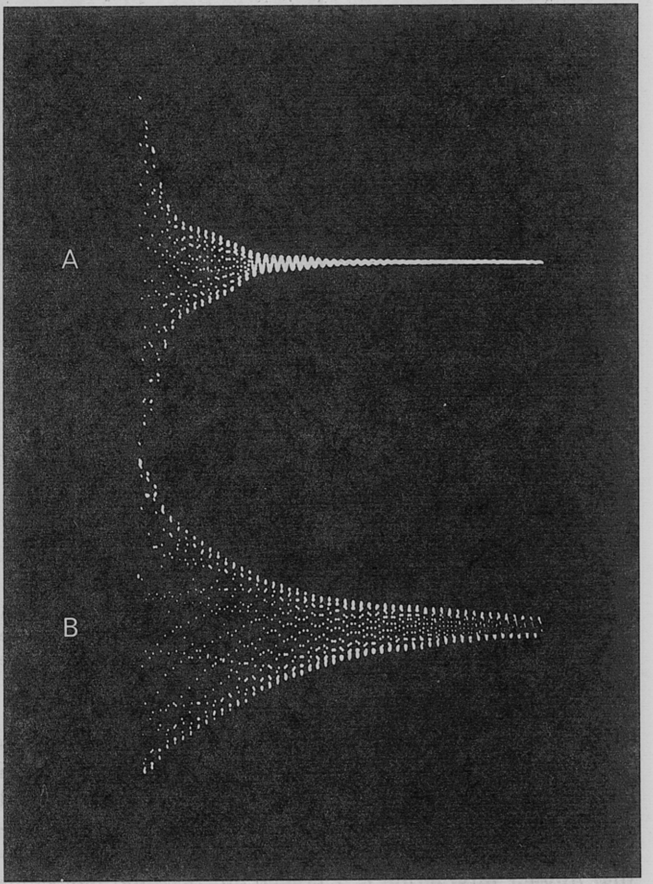

Figure 2. Multiple pulse time domain spectra of natural rubber: (A) eight-pulse decay taken 2 kHz off resonance, 50 msec total sweep; (B) phase-shifted eight-pulse decay taken on resonance, 50 msec total sweep.

eight-pulse spectrum was taken 2 kHz off resonance and Fourier transforms to the spectrum are observed in Figure 1, while the phase-shifted eight-pulse experiment was done at resonance and the observed beat frequency is a measure of the phase shift introduced in the P_x pulse (see eq 1).

Figure 3 shows a plot of the decay envelope for the phase-shifted eight-pulse experiment to be exponential within experimental error with a time constant of 17 msec. This decay is due to relaxation phenomena associated with the complex interaction of the dipolar and radiofrequency Hamiltonians, modulated by the molecular motion present,[15,16] and to instrumental effects. Since the eight-pulse and phase-altered eight-pulse measurements were made under identical conditions, it is possible to deconvolute the line associated with the phase-altered eight-pulse measurement from the normal eight-pulse spectrum observed in Figure 1, and thus isolate the contribution due to the chemical shift Hamiltonian. This deconvoluted eight-pulse spectrum is due to the superposition of partially motionally averaged, chemical shift powder patterns for chemically inequivalent protons present in the sample. Although it will not be discussed in this paper, further detailed analysis can clearly furnish information of the nature of the motional processes present.

It is particularly important to note that by calculating the second moment of the deconvoluted eight-pulse spectrum, one obtains the chemical shift Hamiltonian's contribution to the second moment of the free induction decay. One can obtain the second moment of the deconvoluted spectrum by either deconvoluting and then calculating the second moment of the resulting spectrum, or by subtracting the second moments of the normal eight-pulse measurement and that of the phase-altered eight-pulse measurement. For the case of the natural rubber spectra illustrated in Figures 1 and 3, one obtains values near 1.9 ppm^2 or 11,200 Hz^2 (corrected for the chemical shift scaling factor) for the second moment contribution due to chemical shifts. To obtain the second moment of the broadening function, it was truncated consistent with the signal to noise observed in the spectra.

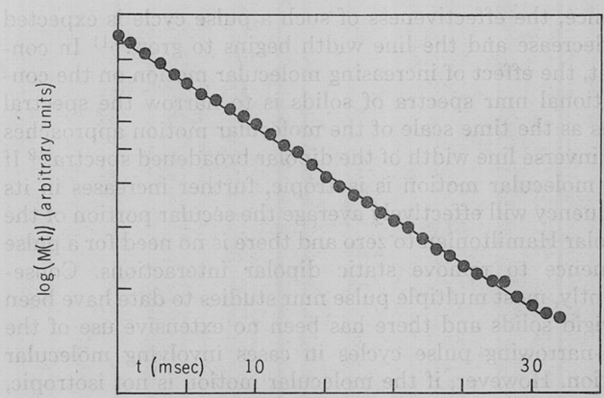

Figure 3. Plot of decay envelope of the phase-shifted eight-pulse spectrum in Figure 2B. The slope of the line placed through the data gives a decay constant of 17 msec.

The contributions to the line shape of the free induction decay spectrum given in Figure 1 are from secular dipolar, chemical shift, and relaxation effects. The relaxation contribution is shown to be small in this case from measured values of the spin–lattice relaxation time (determined for this sample by standard 180–90 pulse measurements to be 95 msec). The experimentally determined second moment of the free induction decay spectrum can then be separated into chemical shift and dipolar contributions since the chemical shift contribution is known from the above analysis of multiple pulse data. The second moment of the free induction decay spectrum in Figure 1 is near 23,700 Hz^2 and when corrected for the chemical shift contribution one obtains a secular dipolar contribution of 12,500 Hz^2. Information on the anisotropic and restricted nature of the molecular motion present in the sample can be obtained from the size of the secular dipolar contribution and the fact that it can be removed by application of the eight-pulse cycle. For instance, the ability to remove the dipolar contribution implies that over the time relevant to eight-pulse cycles used (see Figure 1), it is an effectively static quantity and is thus due to anisotropic or restricted motion. One can, therefore, define an order parameter for this system as the square root of the ratio of the second moment of secular dipolar contribution to the rigid lattice second moment (3.26×10^8 Hz^2)[17] and obtain a value of 0.006 for natural rubber at room temperature. This order parameter is a measure of the freedom of the spins on the polymer to move in the hindering potential of the polymer network.

The results for performing similar measurements on the filled rubber sample at room temperature are illustrated in Figures 4 and 5. The free induction decay (not shown) gives a line of 500 Hz in full width at half-maximum, while the eight-pulse cycle (t_c = 60 μsec, see Figure 4a) furnishes a spectrum ~270 Hz in width (uncorrected for chemical shift scaling factor). The greatest difference between the two samples is exhibited in the results of the phase-altered eight-pulse measurement (Figures 4b and 5). Figure 5 illustrates the non-Lorentzian nature of the decay and also indicates that it is possible to fit the observed decay with a sum of two Lorentzians. The two time constants obtained from such a fit to the data are 1.5 ± 1 and 13.5 ± 2 msec

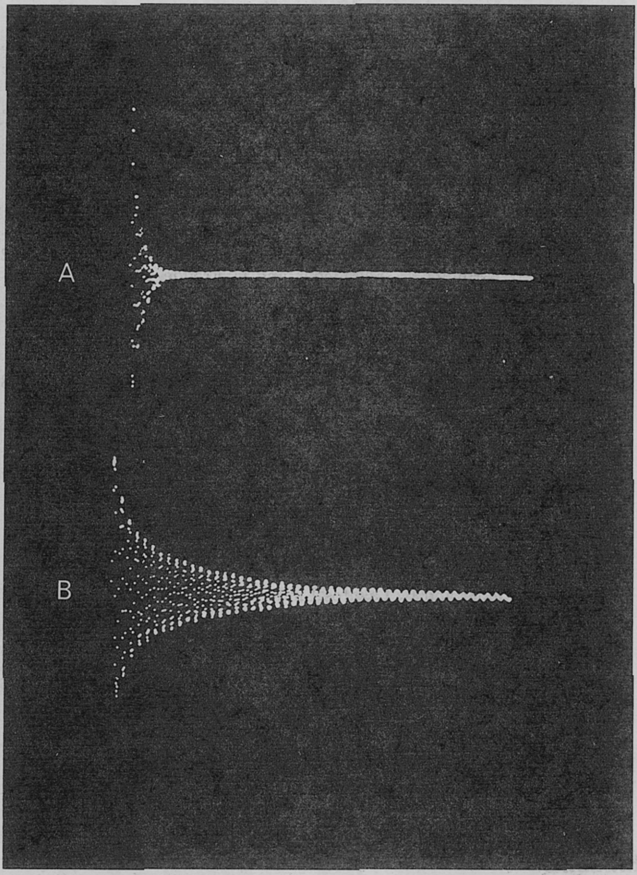

Figure 4. Multiple pulse time domain spectra of filled rubber sample: (A) eight pulse decay taken 2kHz off resonance, 50 msec total sweep; (B) phase-shifted eight-pulse spectrum decay taken on resonance, 50 msec total sweep.

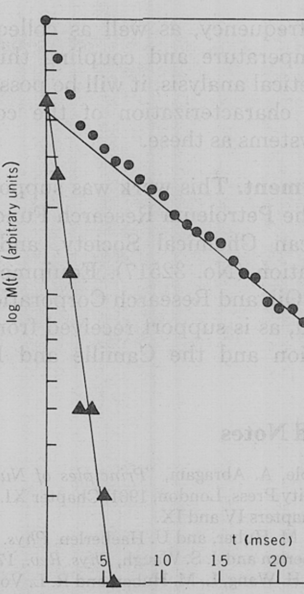

Figure 5. Plot of decay envelope of the phase-shifted eight-pulse spectrum in Figure 4B. The slopes of the two lines placed through the data give decay constants of 1.5 and 13.5 msec, with the 1.5-msec decay accounting for 60% of the intensity and the 13.5-msec decay accounting for 40% of the intensity.

and their relative intensities, 60% for the 1.5-msec decay and 40% for the 13.5-msec decay, correspond within experimental error to the relative fraction of methyl protons, 37.5%, and backbone protons, 62.5%. While the simple correspondence of the relative intensities of the two decays to the ratio of methyl to backbone protons is not alone justification to associate the observed decay constants with these groups, there are other reasons to expect the methyl and backbone protons to behave in the observed fashion. The damping constant under the influence of the multiple pulse sequence is expected to be particularly sensitive to motions near the cycle frequency, $2\pi/t_c$, and the cooperativity associated with cross linking is expected to enhance the power spectrum in this region.[15,17,18] The methyl groups are attached to the molecular frame at only a single point and thus have substantially more freedom of motion than the backbone protons (which are on carbons which are an integral part of the molecular frame), and the frequency spectrum would be altered less by the cross-linking process. Thus one would expect a larger decrease in the decay constant for backbone protons than for the methyl protons under the influence of the multiple pulse sequence. The correspondence of the experimental fractions to the calculated fractions supports this argument. A quantitative treatment of this behavior is in preparation.[16]

As in the case of the unfilled natural rubber sample one can associate the differences between the eight-pulse and phase-altered eight-pulse measurements (see Figure 4) with the partially motionally averaged chemical shift tensors of the protons in the sample and can obtain the secular dipolar contribution to the second moment of the free induction decay by subtracting off the chemical shift component (again as T_1 is 60 msec the relaxation contribution is very small). Because of the complication introduced by the existence of the two decay constants in the phase-altered eight-pulse measurement a quantitative treatment will be delayed.[16] However, it is clear that, as in the case of the natural gum sample, nonisotropic motion is present and at least a portion of the dipolar broadening is removable by use of the multiple pulse techniques.

The results obtained here can be compared with previous results of ^{1}H nmr studies of natural rubber,[17,19,20] where it was only possible to speculate on the presence of nonisotropic motional phenomena, and with ^{13}C studies,[10,14,21] where some indication of nonisotropic motion was suggested. It is tempting to suggest that results such as these combined with current theoretical developments[22] may lead to an understanding of local motion within such systems.

Summary and Conclusions

Room-temperature measurements on two polymer samples have been used to illustrate the ability of the multiple pulse techniques to increase the information obtainable from nmr measurements. By furnishing a means to control the form of the effective Hamiltonian, the multiple pulse techniques make it possible to sort out and determine the size and nature of the various interactions contributing to the shape of the frequency spectrum. In the particular examples considered here it was possible to characterize the secular dipolar broadening as being due to anisotropic or restricted motion and to associate an order parameter characteristic of the degree of anisotropy within the natural rubber sample. The size of the chemical shift anisotropy could be determined and separated from relaxation effects, and finally the relaxation under the multiple pulse sequences could be accurately characterized. This was accomplished with a minimum of experimental results, and these results have been subjected to only a crude analysis at this point. Thus, these preliminary results will primarily serve as a guide to more detailed work. By performing the indicated measurements as a function of the various experimental parameters, particularly those which determine the time domain in which motional processes are studied, the pulse cycle time, the radiofrequency field levels, and the resonance frequency, as well as collecting data as a function of temperature and coupling this with a more complete theoretical analysis, it will be possible to obtain a more complete characterization of the complex motion found in such systems as these.

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References and Notes

(1) See, for example, A. Abragam, "*Principles of Nuclear Magnetism,*" Oxford University Press, London, 1961, Chapter XI.
(2) Reference 1, Chapters IV and IX.
(3) J. S. Waugh, L. M. Huber, and U. Haeberlen, *Phys. Rev. Lett.*, **20**, 180 (1968); U. Haeberlen and J. S. Waugh, *Phys. Rev.*, **175**, 453 (1968).
(4) J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, *J. Chem. Phys.*, **48**, 662 (1968).
(5) U. Haeberlen and J. S. Waugh, *Phys. Rev.*, **185**, 420 (1969).
(6) P. Mansfield, *J. Phys. C.*, **4**, 1444 (1971).
(7) L. M. Stacey, R. W. Vaughan, and D. D. Elleman, *Phys. Rev. Lett.*, **26**, 1153 (1971); R. W. Vaughan, D. D. Elleman, W.-K. Rhim, and L. M. Stacey, *J. Chem. Phys.*, **57**, 5383 (1972).
(8) (a) W.-K. Rhim, D. D. Elleman, and R. W. Vaughan, *J. Chem. Phys.*, **59**, 3740 (1973); (b) *ibid.*, **58**, 1772 (1973).
(9) W.-K. Rhim, D. D. Elleman, L. B. Schreiber, and R. W. Vaughan, *J. Chem. Phys.*, **60**, 4595 (1974).
(10) See, for example: (a) J. Schaefer, *Macromolecules*, **6**, 882 (1973); (b) F. A. Bovey, "High Resolution NMR of Macromolecules," Academic Press, New York, N.Y., 1972.
(11) H. Schmiedel, D. Freude, and W. Grunder, *Phys. Lett. A*, **34**, 162 (1971); W. Grunder, H. Schmiedel, and D. Freude, *Ann. Phys. (Leipzig)*, **27**, 409 (1971).
(12) E. R. Andrew and R. G. Eades, *Proc. Roy. Soc., Ser. A*, **218**, 537 (1953).
(13) R. W. Vaughan, D. D. Elleman, L. M. Stacey, W.-K. Rhim, and J. W. Lee, *Rev. Sci. Instrum.*, **43**, 1356 (1972).
(14) J. Schaefer, S. H. Chin, and S. I. Weissman, *Macromolecules*, **5**, 798 (1972).
(15) J. P. Cohen-Addad, *J. Chem. Phys.*, **60**, 2440 (1974).
(16) C. R. Dybowski and R. W. Vaughan, to be published.
(17) H. S. Gutowsky, A Saika, M. Takeda, and D. E. Woessner, *J. Chem. Phys.*, **27**, 534 (1957).
(18) J. L. Ericksen, *Arch. Ration. Mech. Anal.*, **4**, 231 (1960).
(19) W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **34**, 998 (1963).
(20) D. W. McCall and D. R. Falcone, *Trans. Faraday Soc.*, **66**, 262 (1970).
(21) J. Schaefer, *Macromolecules*, **5**, 427 (1972).
(22) (a) R. I. Cukier and K. Lakatos-Lindenberg, *J. Chem. Phys.*, **57**, 3427 (1974); (b) R. I. Cukier *ibid.*, **60**, 734 (1974).

The Resonance Raman Spectrum of Thermally Degraded Poly(vinyl chloride)

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ABSTRACT: The bands which appear in the Raman spectra of poly(vinyl chloride) samples after thermal degradation are shown to be the result of a resonance Raman effect from conjugated polyene sequences formed during the degradation. This is demonstrated by the band intensities, their dependence on the wavelength of the exciting line in relation to the visible absorption spectra of the degraded polymers, the appearance of strong harmonic and combination bands, and the systematic variation of their half-widths. Intensity measurements on the two strongest resonance lines for a series of samples degraded to known extents at 160 and 190° indicate that the average sequence length of the conjugated polyenes increases with increasing time and temperature of degradation.

Liebman, Foltz, Reuwer, and Obremski[1] have recently found bands at 1124 and 1511 cm^{-1} in the Raman spectra of poly(vinyl chloride) samples subjected to various heat treatments. The intensities of these two bands were greater the higher the temperature to which the samples were taken and, for a given temperature, were more intense for slow cooling than for quenching. They concluded that the appearance of the two bands was indicative of a degradation process rather than a predegradative structural reorientation, and they suggested that conjugated polyene sequences were responsible. They did not give quantitative information on the extent to which conjugated polyene sequences were formed but it is evident that, with the conditions employed and in the light of the results reported below, the level must have been below 0.01%. They refer to work by Rimai, Kilponen, and Gill[2] on intense bands at 1158 and 1527 cm^{-1} for β-carotene and at 1158 and 1515 cm^{-1} for lycopene, which were shown to be of enhanced intensity because of the resonance Raman effect, and conclude[1b] that resonance enhancement is the reason why the 1124- and 1511-cm^{-1} bands appear so strongly in degraded PVC samples containing rather low levels of conjugated polyene sequences.

The purpose of the present study has been twofold. The first objective has been to demonstrate unequivocally that the 1124- and 1511-cm^{-1} bands arise from a resonance Raman effect involving the conjugated polyene sequences formed during the thermal degradation of PVC. Second, in view of the high intensity of the two resonance bands it is clearly of interest to study the feasibility of estimating low levels of degradation and, possibly, of obtaining information on the nature of the conjugated polyene sequences.

Experimental Section

The degraded poly(vinyl chloride) samples were prepared from a commercial polymer made by a mass polymerization process. Two series of materials, degraded at 160 and 190° for varying times, were examined. The methods used to degrade the polymer and to estimate the amount of hydrogen chloride evolved, to obtain a quantitative value for the degree of degradation, were improvements on the procedure of Marks, Benton, and Thomas[3] and were introduced to increase the precision of the measurements on lightly degraded materials. The degradation apparatus was flushed with dry nitrogen until the pH titrating–recording system showed no further change, indicating that any atmospheric carbon dioxide admitted with the sample had been expelled. The nitrogen flow was continued for a further 10 min during which time the pH remained constant, indicating the absence of zero drift. The sample well of the heating furnance contained a small quantity of thermally stable oil, to ensure rapid equilibration when the tube containing the polymer was introduced. The hydrogen chloride evolved was carried by the nitrogen stream into a slightly alkaline trap liq-