Nuclear Magnetic Resonance Relaxation Time Studies of Photoconductive Polymers. Poly(*N*-ethyl-2-vinylcarbazole) and Poly(*N*-ethyl-3-vinylcarbazole)

M. F. Froix,* D. J. Williams, and A. O. Goedde

Xerox Webster Research Center, Webster, New York 14580. *Received September 11, 1975*

ABSTRACT: Proton nuclear spin-lattice (T_1) and spin-spin (T_2) relaxation times have been measured for the series of structurally related polymers poly(*N*-vinylcarbazole) (PVK), poly(*N*-ethyl-2-vinylcarbazole) (P2VK), and poly(*N*-ethyl-3-vinylcarbazole) (P3VK). Correlation frequencies derived from these measurements were used in conjunction with dielectric data (ref 11) to construct transition maps which exhibit details of molecular dynamics in these polymers. P2VK and P3VK exhibit a very efficient T_1 minimum at low temperatures which is attributed to ethyl group rotation (δ relaxation). The T_1 minimum associated with torsional libration (γ relaxation) is more intense and well defined for P2VK and P3VK than PVK, indicating a larger amplitude motion and narrower distribution of correlation frequencies in the former. This is also substantiated by a gradual increase in T_2 in P2VK and P3VK below T_g. Somewhat lower activation energies for the α relaxation (main chain motions) in P2VK and P3VK indicate a looser polymeric structure than in PVK. The implications of the nature, frequency, and amplitude of the various motions for charge transport are discussed.

There has been considerable interest in recent years in establishing correlations between the structural features of organic polymeric photoconductors and their electrical properties. In the absence of a detailed microscopic model of electronic transport in these materials a considerable amount of guesswork is necessarily involved in determining the most important structural and dynamical features. It is intuitively obvious, however, that the detailed ground and excited state energetics, charge distributions, relative nuclear coordinates, and overlap between neighboring chromophores must be important considerations for transport in molecular solids.

The most thoroughly characterized polymeric solid in this context is poly(*N*-vinylcarbazole) (PVK). Because of its electron donor properties holes can be photogenerated or photoinjected and transported through the material. Numerous papers have appeared on transport,[1] photogeneration,[2] spectroscopy,[3,4] and morphology[5-7] in PVK. Considerable progress has been made in the theoretical aspects of transport by Scher and Montroll[8] who have developed a stochastic theory of transport in disordered solids. The physical interactions responsible for electron transfer between neighboring chromophores or "sites" are of necessity treated phenomenologically and are still not well understood. Structural characterizations by proton NMR have been reported for the series of structurally related polymers PVK, poly(*N*-ethyl-2-vinylcarbazole) (P2VK), and poly(*N*-ethyl-3-vinylcarbazole (P3VK).[9] In this study a variation in chemical shift of the aromatic protons was attributed to differences in steric interactions in the three polymers and a qualitative correlation with transport was observed. It is clear however that a much more detailed understanding of the relationship between local time dependent spacial interactions and transport is needed.

Studies of the dynamical features of polymer structure by NMR[10] and dielectric[11] techniques have been undertaken in order to characterize the nature, frequency, and activation energies of local molecular motions in PVK. Internal molecular motions can cause fluctuations in electronic overlap, electronic energy levels, and dielectric fluctuations within the polymer and depending on their frequency and amplitude may be expected to influence the charge-transport process. The γ relaxation in PVK was found to correspond to a low amplitude torsional libration about the backbone C to N bond.[10,11] At room temperature the correlation frequency for this motion is $\sim 10^7$ Hz which is of the order of the inverse residence time of a positive carrier (hole) on a carbazole group based on transit time measurements.[12] Although there is a very wide distribution of hopping times according to the Scher-Montroll analysis[8] (time between arrival of hole on carbazole group and time of arrival on the next) the transit time characterizing the motion of the fastest carriers probably describes the motion of the remaining carriers when they are not influenced by an extremely long hopping time. As the temperature is lowered this motion will become slow compared to the residence time of the carrier and if the modulation of the overlap by this mechanism is appreciable a slight variation in activation energy for the process might be expected. The other molecular motions in PVK are too low in frequency to be of interest. In this paper correlation frequencies for internal motions in P2VK and P3VK are reported and compared with dielectric data on the same samples.[13] These polymers differ from PVK in that two molecular motions with correlation frequencies either comparable to or greater than the increase residence time are expected, i.e., torsional libration and ethyl group rotation. The influence of these various types of motion on transport properties will be the subject of a future report.

Experimental Section

The preparation of P2VK and P3VK used in these experiments was reported elsewhere.[14] GPC analysis for these polymers gave the following results (P2VK, $\bar{M}_n \sim 330\,000$, $\bar{M}_w/\bar{M}_n \sim 3.0$; P3VK, $\bar{M}_n \sim 202\,000$, $\bar{M}_w/\bar{M}_n \sim 5.1$). Evacuated samples were obtained by pumping the samples to $\sim 10^{-5}$ mm at 100°C for 12 hr. The 8 mm O.D. NMR tubes were attached to nylon valves so that samples could be re-equilibrated with oxygen or ambient at a later time.

The NMR relaxation times were obtained on a Bruker SPX-90 NMR spectrometer at 90 MHz. The magnetic field was generated by a 12-in. Bruker current regulated, shimmed electromagnet. The temperature was controlled by a gas flow system thermostated with a copper-constantan thermocouple and controlled to an accuracy of ±1°.

Spin-lattice relaxation times were measured by the 180-τ-90 degree pulse technique.[15] Values of the T_1 were derived from a least-squares analysis of plots of ln $[A(\infty) - A(\tau)]$ as a function of the interval τ between 180 and 90° pulses, where $A(\tau)$ is the amplitude of the free induction decay following the 90° pulse and $A(\infty)$ is the value of $A(\tau)$ for the infinite time interval.

Spin-spin relaxation times (T_2) were obtained from the free induction decays following the 90° pulse. T_2 was taken as $t_{1/2}/\ln 2$

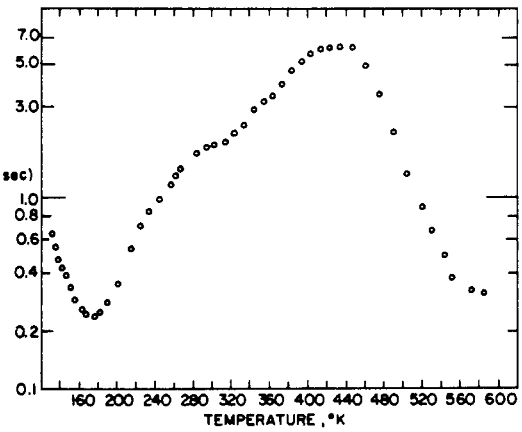

Figure 1. Plot of T_1 vs. temperature for P2VK.

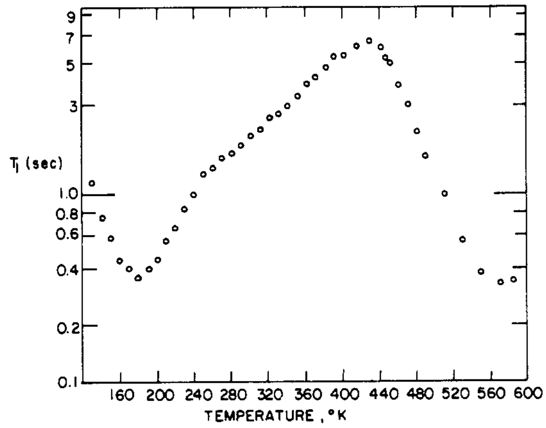

Figure 2. Plot of T_1 vs. temperature for P3VK.

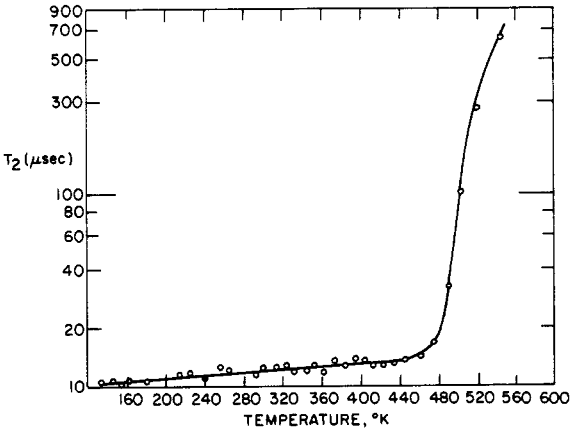

Figure 3. Plot of T_2 vs. temperature for P2VK.

where $t_{1/2}$ is the time for the magnetization to decay to one-half of its original value.

Results

Plots of log T_1 vs. temperature for degassed samples of P2VK and P3VK (Figures 1 and 2) exhibit three relaxation regions. Minima in T_1 are observed at ~180°K (δ relaxation) and ~580°K (α relaxation) and a diffuse minimum is centered at approximately 320°K (γ relaxation). Plots of log T_2 vs. temperature (Figures 3 and 4) exhibit a gradual increase in T_2 beginning at ~200°K in P2VK and 220° in P3VK and a sharp increase in T_2 at ~460°K. T_1 was measured for P3VK in the presence of air and oxygen (Figure 5). As with PVK,[10] values of T_1 are lowered in air and O_2 environments with the most substantial effect observed at

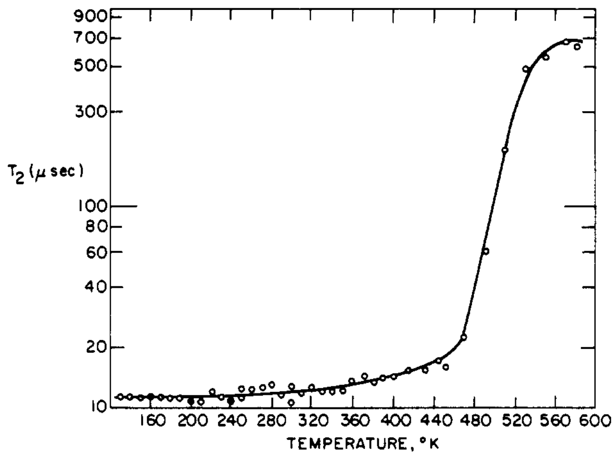

Figure 4. Plot of T_2 vs. temperature for P3VK.

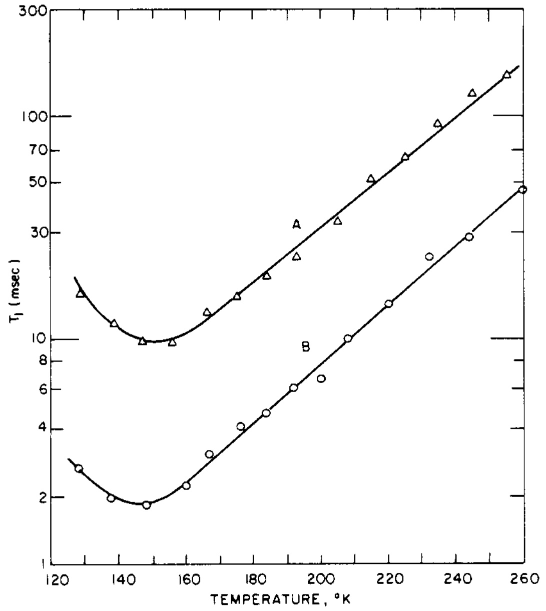

Figure 5. Plot of T_1 vs. temperature for P3VK in ambient (A) and 1 atm of O_2 (B).

low temperatures. The low-temperature δ relaxation observed in the degassed samples is shifted to or replaced by a new relaxation at ~150°K in air or O_2. The enhancement of this effect at 1 atm of O_2 indicates that this is indeed a paramagnetic impurity effect rather than a plasticization or some other effect of the gas.

Discussion

Correlation frequency maps constructed from NMR and dielectric data[13] for P2VK and P3VK are shown in Figures 6 and 7. The NMR correlation frequencies ν_c were obtained from the T_1 minima and T_2 transitions and the relationships[16]

$$\nu_c \simeq \sqrt{2}\nu_0 \simeq 10^8\ \text{Hz} \tag{1}$$

at the temperature of the T_1 minimum where ν_0 is the spectrometer frequency and

$$\nu_c = \frac{1}{\pi T_{2\text{LT}}} \simeq 5 \times 10^4\ \text{Hz} \tag{2}$$

at the temperature of a T_2 transition where $T_{2\text{lT}}$ is the transverse relaxation time on the low-temperature side of the transition.

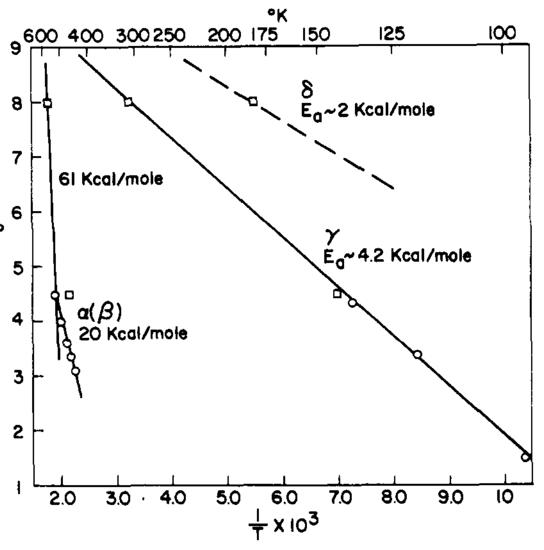

Figure 6. Transition map for P2VK: (□) NMR, (○) dielectric.[13]

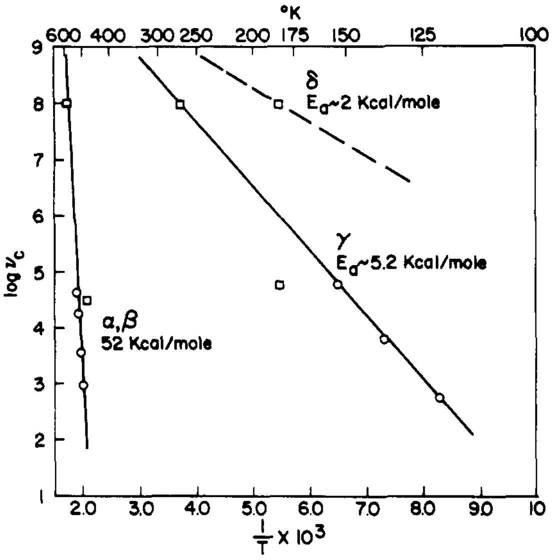

Figure 7. Transition map for P3VK: (□) NMR, (○) dielectric.[13]

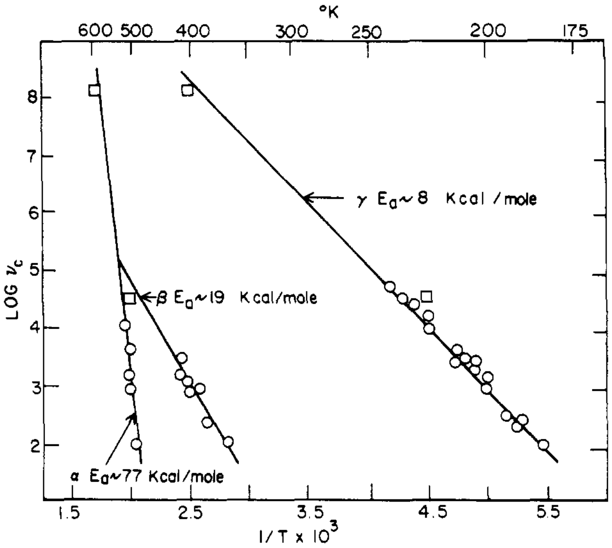

Figure 8. Transition map for PVK: (□) NMR, (○) dielectric.[13]

Degassed samples of P2VK and P3VK exhibit a low-temperature δ relaxation which is not observed in similarly treated PVK samples. Aside from the position of attachment of the pendant group to the backbone, the main difference between these polymers and PVK is the ethyl group attached to the nitrogen. Methyl and ethyl side groups require very little excess free volume and the activation energies associated with reorientation of these groups are small. These groups have been observed to exhibit minima in T_1 due to reorientation at temperatures ranging from below 77 to 300°K, depending on the steric factors which facilitate or hinder their reorientation.[19,22] In view of these observations the δ relaxation is probably associated with reorientation of the ethyl group. The activation energy for this relaxation (2 kcal/mol) was determined from the slope of a log T_1 vs. $1/T$ plot on the high-temperature side of T_1 minima at $\simeq$170°K.[17] Although this method of determining activation energies for molecular motions is not generally applicable it has been found to be in reasonable agreement with those determined by other methods for methyl and ethyl group rotations.[18]

The overall lowering of T_1 in P2VK and P3VK reflects the influence of the spin diffusion mechanism to the ethyl group on the overall relaxation times. It has been shown by NMR[10] and dielectric data[11] that PVK (data shown in Figure 8 for reference) has a rigid backbone with very little thermal motion at room temperature. Similarly, P2VK and P3VK have very rigid backbones[13] so that the enhanced relaxation cannot be due to extensive internal motion in the polymers but rather the very efficient spin diffusion to the ethyl groups.

The γ relaxation in PVK has been assigned to low-amplitude torsional oscillation of the carbazole group about the backbone to ring C–N bond. This assignment was based on dielectric and NMR data for PVK in the presence and absence of O_2 and also with comparative data for poly(3-chloro-*N*-vinylcarbazole) where the γ relaxation is dielectrically active.[10,11] Contrary to PVK the γ relaxation for P2VK and P3VK was found to be dielectrically active. If the γ relaxation is due to torsional oscillation, the lack of coincidence of the dipole moment and the axis of the oscillation would produce a dielectrically active relaxation which has been observed.[13] Examination of molecular models for P2VK and P3VK reveals a much less sterically hindered pendant group than in PVK so that side group motion of this sort would be expected to have lower activation energies and larger amplitudes than the corresponding relaxation in PVK. The T_1 minimum corresponding to the γ relaxation is more intense and appears at lower temperatures than in PVK. A gradual increase in T_2 with increasing temperature is seen for P2VK and P3VK over the temperature range 200 to 450°K which is not seen in PVK. This indicates a gradually increasing amplitude for the torsional oscillation due to the lesser degree of steric hindrance in these polymers. The activation energies for the γ relaxation are 7.6, 4.2, and 5.2 kcal/mol for PVK, P2VK, and P3VK, respectively, which also substantiates the above arguments and the assignment of the γ relaxation.

The α and β relaxations associated with main chain and localized segmental motion are not sufficiently different in frequency in the accessible frequency range to be resolved in either the dielectric or NMR data. The large increase in T_2 and the corresponding efficient T_1 relaxation in the vicinity of 600°K reflect extensive motion in the backbone of these polymers. The activation energies for the α relaxation are somewhat lower than the 77 kcal/mol observed previously for PVK[10] and when viewed with the above observations and the discussion of the γ relaxation indicate somewhat looser structures for these polymers. The significance of the variation in activation energy for the $\alpha(\beta)$ relaxation in P2VK is unclear but may be related to the overlapping α and β relaxation in the dielectric data.

The T_1 values for P3VK are suppressed by the presence of oxygen. A new minimum appears at 150°K and that at 180°K due to ethyl reorientation disappears. In the presence of paramagnetic oxygen the observed relaxation rate can be written as the sum of two contributions,

$$R = (1/T_1) + (1/T_{1\mathrm{p}}) \tag{3}$$

where $1/T_1$ is the relaxation rate due to the intrinsic molecular processes, $1/T_{1\mathrm{p}}$ is the relaxation rate due to interaction with the paramagnetic oxygen. From eq 1 one can calculate the paramagnetic contribution to the overall relaxation rate knowing T_1 for the degassed sample and R for the sample in the presence of oxygen. Taking values of 360 msec for T_1 of the degassed sample and 18 msec for P3VK in air at 180°K, the minimum in T_1 for ethyl reorientation, the paramagnetic contribution to T_1 ($T_{1\mathrm{P}}$) is 19 msec. Thus the overall relaxation is completely dominated by the paramagnetic contribution and the contribution from ethyl group rotation is totally obscured.

Conclusions

NMR T_1 and T_2 measurements were made on P2VK and P3VK and compared with NMR and dielectric data for PVK. The measurements reveal an additional efficient relaxation (δ) in these polymers due to ethyl group rotation. This relaxation is extremely efficient and leads to a general lowering of the T_1 values via spin diffusion over those observed for degassed PVK. The γ relaxation corresponding to torsional oscillation of the pendant group has a considerably lower activation energy in P2VK and P3VK than in PVK (4.2, 5.2, and 7.8 kcal/mol, respectively). The T_1 minima corresponding to this relaxation are more intense and occur at lower temperature than in PVK indicating a narrower distribution of correlation frequencies. The gradual increase in T_2 below the glass transition temperature in conjunction with the well defined T_1 minima indicate a gradual increase in amplitude for the γ process. These observations and examination of molecular models are consistent with a lower degree of steric hindrance in these polymers than in PVK. The lower activation energies for the α relaxation are also consistent with this interpretation.

The implications of the above observations for charge transport in these materials are necessarily speculative at this point. The two main differences between P2VK, P3VK, and PVK are the presence of ethyl group rotation and the larger amplitude ring motion. The ethyl group rotation will not produce any significant π overlap modulation and has very little influence on the energy of the carbazole HFMO. It is therefore not expected to influence the transport process to any appreciable extent regardless of temperature. The γ process which involves relative motion of the π systems will produce a fluctuation in overlap which can be slow or fast compared with the residence time of a carrier on a site depending on temperature and the activation energy for transport. If the activation energy for transport is different than that for the γ relaxation a crossover temperature will exist where the relative time scales of the γ motion and the molecular transport process are interchanged. On one side of this crossover π overlap modulation (presumably the high side if the activation energy for transport is larger than for the γ relaxation) will be slow compared with the residence time of the carrier while on the other side the two processes will interchange time scales and we might therefore expect a decrease in activation energy for transport. Detailed transport data for these polymers is sparce. Pai[12] has reported transit time data for PVK samples at various fields and thicknesses and as a function of temperature. At a field of ~10^5 V/cm the transit time is ~10^{-2} sec. Ignoring the statistical nature of the residence times, the time a carrier is associated with a carbazole group can be estimated to be ~5×10^{-6} sec assuming an average intersite distance of ~10 Å. The activation energy for transport was measured as ~8.3 kcal/mol. A close examination of the data appears to indicate a changing activation energy with ~11 kcal/mol at high temperatures and ~7 kcal/mol at low temperatures. The break occurs at about 260°K. At this temperature the correlation frequency for the γ relaxation is about 10^6. The apparent lowering of the activation energy may indicate that below 260°K (i.e., when carrier motion and the period for the γ relaxation become the same) the motion of the carrier may become correlated with fluctuating overlap in the system. This conclusion is speculative and subject to closer examination of the temperature dependence for transport in the low-temperature region. If this correlation can be verified we anticipate a similar correlation with the γ relaxation in P2VK and P3VK.

References and Notes

(1) J. Mort, I. Chen, R. L. Emerald, and J. H. Sharp, *J. Appl. Phys.*, **43**, 2285 (1972).
(2) G. Pfister and D. J. Williams, *J. Chem. Phys.*, **61**, 2416 (1974).
(3) W. Klopffer, *J. Chem. Phys.*, **50**, 2337 (1969).
(4) G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(5) A. Kumura, S. Yoshimoto, Y. Akana, H. Hirata, S. Kusaboyashi, M. Mikawa, and N. Kasai, *J. Polym. Sci., Part A-2*, **8**, 643 (1970).
(6) R. G. Crystal, *Macromolecules*, **4**, 379 (1971).
(7) C. H. Griffiths, *J. Polym. Sci.*, **13**, 1167 (1975).
(8) H. Scher and E. Montroll, *Phys. Rev. B*, **12**, 2455 (1975).
(9) D. J. Williams, A. O. Goedde, W. W. Limburg, and J. M. Pearson, *J. Chem. Phys.*, **62**, 1501 (1975).
(10) M. F. Froix, D. J. Williams, and A. O. Goedde, *J. Appl. Phys.*, **46**, 4166 (1975).
(11) J. M. Pochan and D. D. Hinman, *J. Appl. Phys.*, **46**, 4155 (1975).
(12) D. Pai, *J. Chem. Phys.*, **52**, 2285 (1970).
(13) J. M. Pochan and D. D. Hinman, submitted for publication.
(14) W. W. Limburg and D. J. Williams, *Macromolecules*, **6**, 787 (1973).
(15) E. L. Hahn, *Phys. Rev.*, **80**, 580 (1950).
(16) D. W. McCall, *Acc. Chem. Res.*, **4**, 231 (1971).
(17) E. O. Stejskal, D. E. Woessner, T. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **31**, 55 (1959).
(18) D. W. McCall, *Natl. Bur. Stand. (U.S.), Spec. Publ.*, **No. 310**, 475 (1969).
(19) W. P. Slichter, *J. Polym. Sci., Part C*, **14**, 33 (1966).
(20) N. Bloembergen, *Physica*, **15**, 386 (1949).
(21) A. Abragham, "Principles of Nuclear Magnetism", Oxford University Press, London 1961, p 382.
(22) B. I. Hunt, J. G. Powles, and A. E. Woodward, *Polymer*, **5**, 339 (1964).