A Nuclear Magnetic Resonance Study of Poly(ε-caprolactone) and Its Blends with Poly(vinyl chloride)

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ABSTRACT: NMR T_1, T_2, and $T_{1\rho}$ data are reported for poly(ε-caprolactone) (PCL) and its blends with poly(vinyl chloride) (PVC). The relaxation behavior of PCL is similar to that of poly(ethylene oxide) and to that of polyethylene for temperatures below the melting point of PCL. Blends with PVC exhibit small-scale heterogeneity even for component concentrations at which the PCL is recognized as an amorphous material. It is proposed that PCL forms an intimate blend with part of the PVC component through hydrogen bonding and, once mobile, acts as a plasticizer for the PVC. The remaining, excess PVC in the 30/70 and 20/80 PCL/PVC blends studied is unplasticized and remains relatively immobile until temperatures close to the melting point are reached. In the light of these findings, the assignment of a single glass transition temperature to the blends rich in PVC must be reviewed.

I. Introduction

The degree of mixing achieved between component polymers, as monitored on different dimensional scales by a range of experimental techniques, is of central importance in the study of compatible polymer blends. Nuclear magnetic resonance (NMR)[1-4] has provided useful information through exploitation of (i) the short-range character of the dipole–dipole interaction, (ii) an ability to delineate different morphological regions by virtue of their characteristic molecular motions, and (iii) the way in which nuclear spins in these regions can communicate via the mechanism of spin diffusion. Compatibility on a scale ranging typically from molecular dimensions to ~20 nm can often be explored. Here, attention focuses upon the compatible polymer pair poly(ε-caprolactone) (PCL) and poly(vinyl chloride) (PVC), a system which has been investigated extensively but which is not, as yet, fully understood at a molecular level.[5-17] This is not surprising in view of the complex nature of the component homopolymers themselves. The considerable effort expended in attempting to understand PVC has only been partially successful.[3,4,18] Ostensibly, PVC exhibits two transitions: the glass transition and a very broad, β, relaxation at lower temperatures.[19] More recently, DSC measurements by Bair[20] pointed toward two glass transitions in PVC, an observation which was explored further in a subsequent NMR study which showed that the plasticizer diisodecyl phthalate (DIDP) preferentially plasticized only part of the polymer.[3,4] The role of the stabilizer and the small amount of "paracrystalline" PVC material present remained obscure.

PCL also exhibits two relaxations in addition to the first-order melting process: a low-temperature relaxation (~143 K at 110 Hz) which bears close resemblance to the γ relaxation in polyethylene and which is therefore attributed to local CH_2 motions, and the glass transition for which T_g is estimated to be 202 K in wholly amorphous PCL and 218 K in annealed semicrystalline material.[5-7] NMR data on PCL is sparce and relates principally to high-resolution structural studies.[21-23]

PCL is miscible with a number of polymers and it would appear that hydrogen bonding between the polar oxygen in PCL and certain chemical entities in its compatible partner play an important role.[9,14,15,17,21,24-26] Interactions with the methine proton in PVC[9,14,15] or the phenoxy hydroxyl group in poly(hydroxy ether of bisphenol A)[26] are typical examples. According to Olabisi,[9] the strength of hydrogen bonding in PVC/PCL blends is of the same order of magnitude as that between PVC and its commonly used plasticizers. Coleman and Zarian[15] concluded that interactions of C=O with PVC approached saturation for PVC concentrations of the order of 60 wt %. For a wide range of blend compositions a single T_g is observed which systematically increases with increasing PVC concentration.[15] The Fox,[27] Gordon–Taylor,[28] and Bueche–Kelley[29] expressions describe in impressive fashion the T_g behavior in the blend and infer extensive mixing.

On the other hand, the observation of spherulitic morphology in PVC/PCL blends rich in PCL implies at least microscopic heterogeneity. The addition of PVC induces changes in the morphology, crystallinity, and melting behavior of PCL.[10,12,13] Specifically, as the concentration of PVC is increased, the melting point of PCL is depressed, which is, no doubt, related to the parallel decrease in crystallinity toward zero for PVC concentrations in excess of 70 wt %. Brode and Koleske[7] reported, furthermore, that the secondary transition in PCL assigned to local CH_2 motion shifts to lower temperatures by about 15 K with the addition of PVC in concentrations greater than 50 wt %. This again must reflect the concomitant decrease in PCL crystallinity with increase in PVC concentration. It is recalled that in certain cases, the γ relaxation in PE exhibits "doublet" structure and that the loss peak which occurs at the lower temperature is amorphous in origin.[25,30] The secondary transition in PVC also shifts to lower temperatures with the addition of PCL.[7,16] In this case, it has been argued that PCL acts as a plasticizer for the β relaxation in PVC.

In this paper pulsed NMR measurements are presented and analyzed for two blend compositions (PVC ≥ 70 wt %) for which the PCL component is presumed to be amorphous.[5,12] Thus, complications associated with an additional contribution from crystalline PCL to the NMR decay are avoided. A prerequisite study on the PCL homopolymer has been carried out to facilitate data interpretation for the blends.

II. Experimental Part

Materials. The commercial sample of PVC, supplied by Solvay, Belgium (PVC RD 258), was purified by a twofold precipitation from tetrahydrofuran into methanol and finally dried under vacuum to constant weight. The molecular weights $\bar{M}_n$ = 43 000 and $\bar{M}_w$ = 80 000 were determined by gel permeation chromatography (GPC).

ε-Caprolactone was polymerized by using di-μ-oxo-bis[bis(1-methylethoxy)aluminum]zinc as catalyst.[31] Polymerization proceeded under anhydrous conditions in toluene at room temperature and was arrested by addition of hydrochloric acid. The solution containing poly(ε-caprolactone) (PCL) was extracted with ethylenediaminetetraacetic acid disodium salt in order to remove completely any aluminum residue. The polymer was finally precipitated into methanol and dried under vacuum to constant weight. Molecular weights were again determined by GPC to be $\bar{M}_n$ = 22 000 and $\bar{M}_w$ = 36 000. The crystallinity of the PCL sample was of the order of 60%.

0024-9297/84/2217-2552$01.50/0

Preparation of Blends. Two blends of respective compositions 30/70 and 20/80 PCL/PVC by weight were prepared as thin films by controlled evaporation of dilute solutions at room temperature. Ideally, the solvent (S) should exhibit the same interaction parameter (χ) with each polymeric partner (P_1 and P_2), that is, $\chi_{P_1S} \simeq \chi_{P_2S}$, and in this respect the choice of solvent is critical.

Furthermore, values of χ_{PS} should be higher than the polymer–polymer interaction parameter. Under these conditions the blending of PVC and PCL is not significantly affected by the presence of the solvent.[32] Interaction parameters, calculated from the data of Small,[33] indicated methyl ethyl ketone (MEK) as a suitable solvent for which $\chi_{PCL/MEK} = 0.027$, $\chi_{PVC/MEK} = 0.0068$, and $\chi_{PVC/PCL} = 0.0068$. Each polymer was separately dissolved in MEK and the resulting solutions (3 wt %) were finally mixed together under vigorous stirring for 12 h. The solutions of PCL/PVC blends were filtered, poured into Petri dishes, and allowed to evaporate slowly under a slight N_2 stream for at least 1 week. The casting films were dried further under vacuum (10^{-4}–10^{-5} mmHg) at 323 K to constant weight. The films were cut into small pieces, packed in NMR sample tubes of 10-mm diameter, and sealed under vacuum.

Experimental NMR. Spin–spin (T_2), spin–lattice (T_1), and roating frame ($T_{1\rho}$) data were recorded on a Bruker SXP spectrometer operating at a proton resonant frequency of 40 MHz. The spectrometer was interfaced to a Commodore PET computer via a Biomation digitizer and signal averaging was possible. T_1 was recorded by using a 180°–τ–90° pulse sequence[34] while the 90°–90°(shift) spin-locking sequence provided $T_{1\rho}$ at an H_1 radio-frequency field of 10 G.[35] Short T_2 relaxation times were recorded by using the $90°–\tau–90°_{90}$ solid-echo sequence;[36] intermediate T_2's were determined directly from the free induction decay following a 90° pulse and long T_2's utilized the 90–τ–180° spin-echo sequence. Methods of data analysis have been described earlier.[37]

III. Results and Discussion

PCL Homopolymer. T_1, T_2, and $T_{1\rho}$ vs. temperature data for PCL are furnished in Figure 1 and 2. The observed behavior bears a remarkable similarity to the T_1 and $T_{1\rho}$ response of poly(ethylene oxide) (PEO),[38,39] a polymer which also has CH_2 groups and a flexible oxygen linkage in the main chain. As with PEO, there is a structural first-order transition in the form of an almost discontinuous break in the NMR data, which heralds the onset of the melting point at ~330 K in PCL and ~338 K in PEO. Glass transition temperatures are also of comparable magnitude: 202–218 and ~206 K for PCL and PEO, respectively.

In the spirit of such comparisons, there is also a close correspondence between the PCL data below the melting point and the NMR response of PE. As already evident in the literature, the γ relaxation in PE and the β relaxation in PCL both find their origins in CH_2 motion.[19,30,40-42] Koleske and Lundberg[5] have commented that as few as two or three CH_2 groups are sufficient to manifest this relaxation. Another point of similarity relates to the T_{2L} behavior between 253 K and the melting point. The plateau of ~70 μs in T_{2L}, indicating the presence of highly mobile material that is nonetheless constrained in some fashion, has been attributed to the motion of folds at the crystalline/amorphous interface in PE.[3,42-44] In fact, T_{2L} represents unresolved contributions from constrained folds and truly amorphous mobile polymer. A similar interpretation is plausible for PCL.

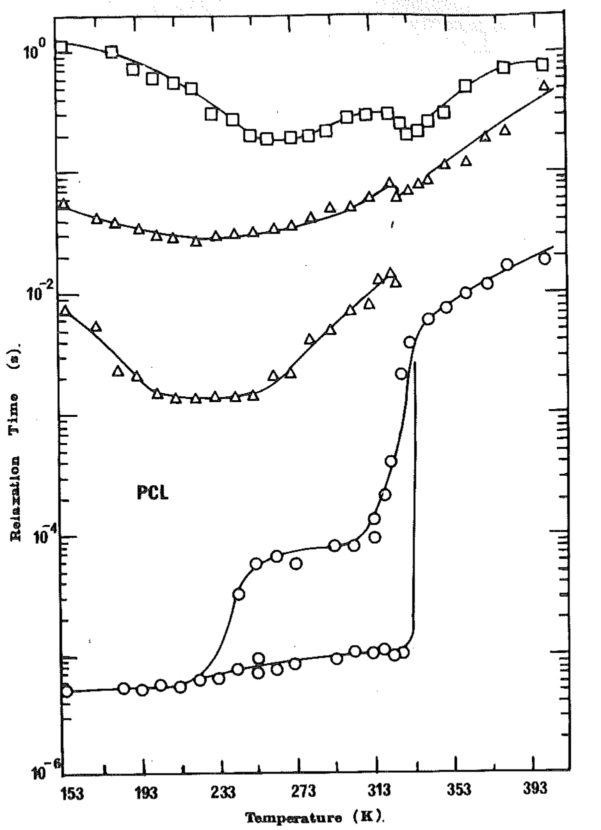

Figure 1. T_1 (□), T_2 (○), and $T_{1\rho}$ (△) vs. temperature data for PCL.

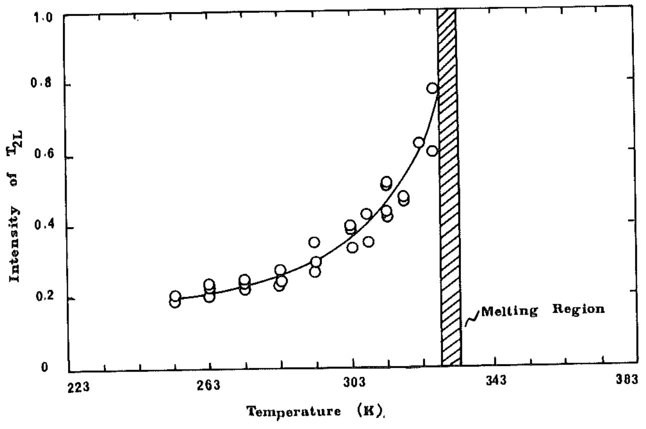

Figure 2. Intensity of the long T_2 component for PCL as a function of temperature.

The abrupt increase in T_{2L} and the tendency for T_1 and $T_{1\rho}$ to decrease as the melting point is approached indicates the onset of general motions. Reference to Figure 2 shows that an increasing amount of PCL material is participating in these motions. Whereas these observations can be rationalized in terms of the molecular weight distribution in PCL, the possibility that the onset of such motions "triggers" the structural transition cannot be ruled out.

Note, too, that T_1, T_2, and $T_{1\rho}$ for PCL (and PEO) are appreciably different above the melting point, which indicates that liquid-like motions are not attained in the melt of either polymer.

The similarity between PCL and PEO and, in a more limited sense, PE is clearly apparent in the transition map of Figure 3, where established techniques have been used to extract correlation frequency/temperature data from T_1 and $T_{1\rho}$ minima and T_2 transitions.[19,37] Note that the doublet structure in the PE γ relaxation, alluded to in section I, shows up in the thermally stimulated depolari-

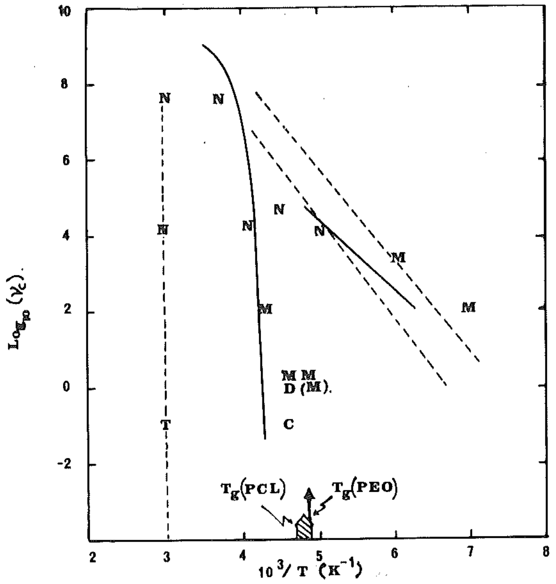

Figure 3. Transition map for PCL, where N denotes NMR data, M, dynamic mechanical relaxation, D, dielectric relaxation, T, DSC measurements, and C, thermally stimulated current depolarization measurements. The two dashed lines at low temperatures denote the γ relaxation in PE[19] and the solid lines are the relaxation loci for PEO.[19,38,39] (M) signifies wholly amorphous PCL.

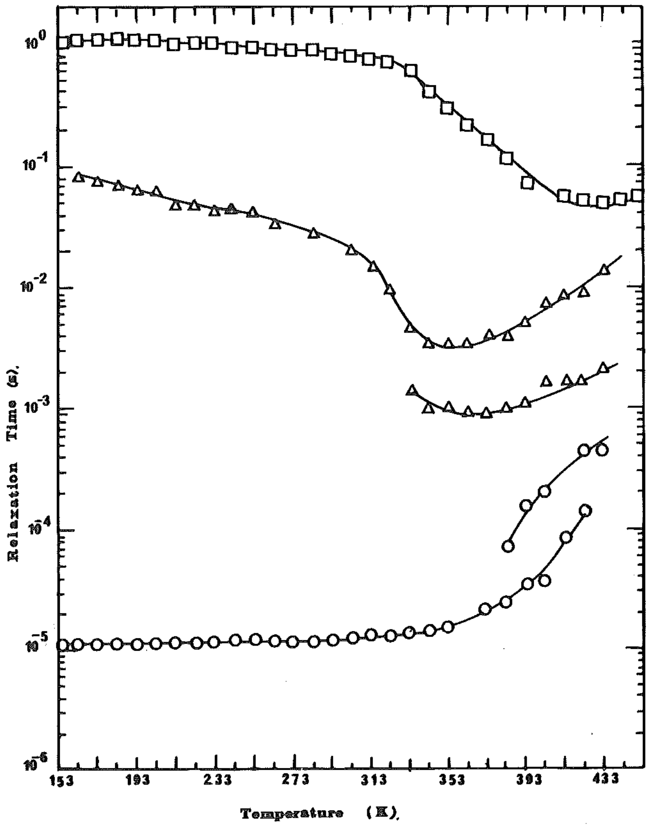

Figure 4. T_1 (□), T_2 (○), and $T_{1\rho}$ (△) vs. temperature data for PVC.

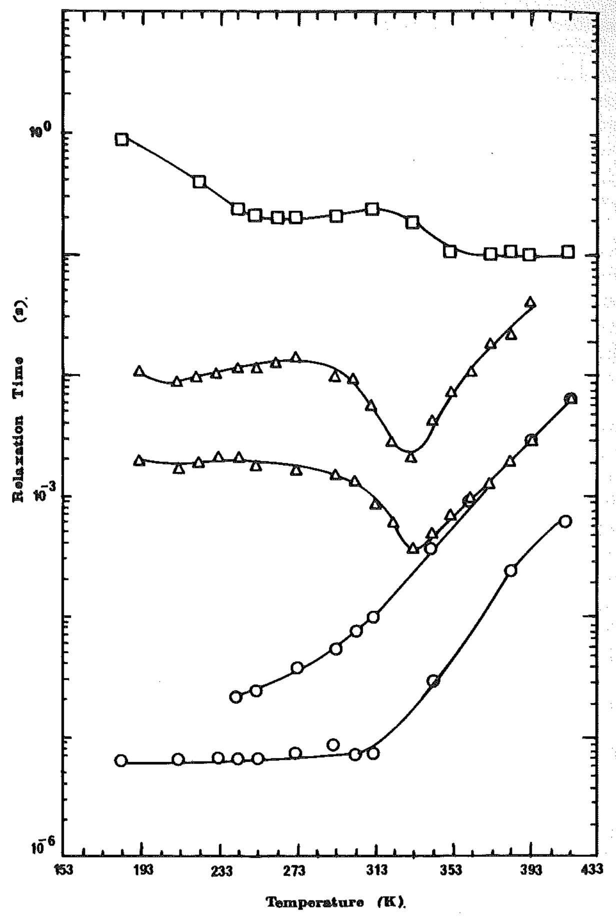

Figure 5. T_1 (□), T_2 (○), and T_ρ (△) vs. temperature data for the 30/70 PCL/PVC blend.

zation current (TSDC) measurements on PCL[25] (labeled C in Figure 3).

In summary, PCL behaves in remarkably similar fashion to PEO and exhibits some of the relaxation characteristics of PE at temperatures below the melting point.

PVC Homopolymer. NMR data for the PVC homopolymer, presented in Figure 4, are broadly consistent with earlier results.[3,4] Briefly, the T_1 minimum at ~430 K, the $T_{1\rho}$ minima near 370 K, and the abrupt increase in T_2 in the vicinity of 380 K are all manifestations of the glass transition. The β relaxation is weak and does not always appear in relaxation measurements on PVC. There is no overt indication of the β relaxation in our data. The observation of two-component decay for $T_{1\rho}$ and T_2 reflects significant microscopic heterogeneity in PVC as discussed in detail in the earlier report.[3,4]

With this preparatory examination of PVC and PCL in mind, we now consider the blends, recalling that PCL is presumed to be amorphous in the two samples studied.

Blends of PCL with PVC. NMR data for the two blends are presented in Figures 5 and 6. In general terms, the results reflect an inhomogeneous system at a molecular level and, in many respects, are reminiscent of the small-scale heterogeneity observed in plasticized PVC.[3,4] We shall return to this point after a discussion of specific relaxations.

The β relaxation in the PCL component is responsible for minima in $T_{1\rho}$'s at ~210 and ~200 K in the 30/70 and 20/80 blends, respectively, and is also reflected in the broad T_1 minimum centred on ~270 K. Because of the relatively small concentration of PCL in the blends, the relaxation is not evident in T_2. Even in ideal circumstances the change in T_2 is small (see Figure 1). The shift of the transition to lower temperatures with increased PVC concentration is in keeping with the observations of Brode and Koleske.[7]

The corresponding minimum in $T_{1\rho L}$ almost certainly signals partial relaxation, via spin-diffusion coupling, of PVC protons in the blend. It is recalled that the root-mean-square diffusive path length, $\langle r^2\rangle^{1/2} = [6D\tau]^{1/2}$, is only 1.4 nm where the diffusion coefficient $D \simeq 10^{-12}$ cm^2 s^{-1} and the time for diffusion $\tau = T_{1\rho} \simeq 5 \times 10^{-3}$ s.[1-4] On the other hand, the time scale of the T_1 experiment, $\tau \simeq 0.25$ s, permits efficient relaxation of the PVC protons by the CH$_2$ protons in PCL by virtue of the longer diffusive path length of ~12 nm. Hence the observation of a single T_1. In fact, 12 nm can be viewed as an upper limit on the size of PVC domains in the blend, if present. On the basis of intimate mixing[4,45]

$$K = K_1^0\frac{N_1}{N_T} + K_2^0\frac{N_2}{N_T} \qquad (1)$$

where K is the observed relaxation rate, N_1 is the number of PCL methylene protons with an intrinsic relaxation rate K_1^0, N_2 is the number of PVC protons with an assumed, albeit small, intrinsic relaxation rate K_2^0, and N_T is the total number of protons in the blend. Equation 1 may be written in terms of the weight, W, of PCL in the blend.

$$(W + 1.2)K = (2.2K_1^0 - 1.2K_2^0)W + 1.2K_2^0 \qquad (2)$$

The plot of $(W + 1.2)K$ vs. W, shown in Figure 7, is linear over the limited range of blend compositions available. The intrinsic relaxation time T_1 $(=(K_1^0)^{-1})$ for the PCL methylene protons is estimated to be 0.11 s, which is marginally shorter than the measured value of 0.19 s for the semicrystalline PCL homopolymer. This difference can be rationalized when it is recalled that the γ relaxation sets in at different temperatures in the crystalline and amorphous regions of PCL. Thus, at any given temperature the region which is more efficiently coupled to the lattice is also relaxing the second region by spin diffusion. Consequently, the relaxation time in semicrystalline PCL is expected to be higher than that for wholly amorphous PCL.

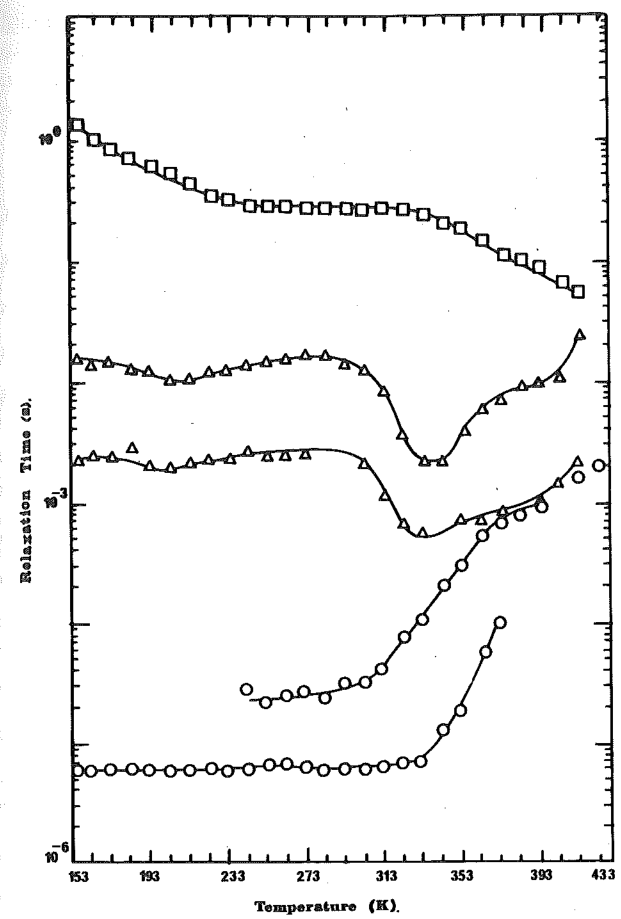

Figure 6. T_1 (□), T_2 (○), and T_ρ (△) vs. temperature data for the 20/80 PCL/PVC blend.

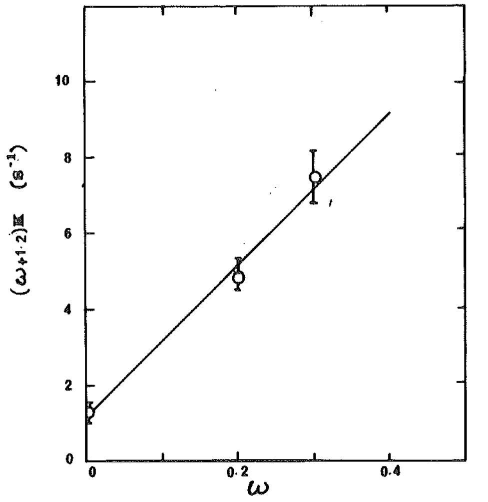

Figure 7. Plot of $(W + 1.2)K$ vs. W (see text).

As in the case of neat PCL, a second, T_{2L}, component is resolved above 230 K. The shallow minimum in $T_{1\rho s}$ centered about 270 K also manifests this transition. The absence of a parallel minimum in $T_{1\rho L}$ is due to the reduced effects of spin diffusion as a consequence of the higher T_{2L} magnitudes involved (to a reasonable approximation, $D \propto T_2^{-1}$). The observed magnitudes of T_{2L} are lower than T_{2L} for PCL, implying more restricted motion in the blend. The effect is most pronounced in the 20/80 sample. The formation of a plateau in T_{2L}, clearly evident in the 20/80 sample, is puzzling in view of the absence of crystalline PCL in the blend. So also is the persistence to high temperatures of T_{2s}, which manifests relatively immobile material. Note that T_{2s} begins to rise at progressively higher temperatures as the concentration of PVC is increased in the blend.

The corresponding $T_{1\rho}$ behavior at high temperatures is complex. The dominant minimum, evident in both $T_{1\rho}$ components, shifts modestly to lower temperatures as the PCL concentration is increased in the blend. T_1 behaves in similar fashion. There is an indication of a second minimum, nearly coalescent with the first, on the high-temperature side of the principal minimum in both $T_{1\rho}$ components of the 20/80 blend. This second $T_{1\rho}$ minimum is reminiscent of the response of neat PVC. The effect is much less pronounced in the 30/70 blend and can only be inferred from the skewness of the $T_{1\rho}$ minimum on the high-temperature side.

As mentioned earlier, the high-temperature NMR behavior of the blends bears a remarkable similarity to plasticized PVC data. The analogy that the plasticizer DIDP selectively plasticizes certain regions of PVC and not others, as concluded in the earlier NMR study,[3,4] can be sustained in the present case where PCL, once mobile, plasticizes only part of the PVC component. Of course, this conclusion is consistent with the deduction that C=O interactions with PVC approach saturation in blends with PVC concentrations greater than ~60 wt %.[15] This leads us to visualize a blend where the available PCL interacts with PVC via methine proton/C=O chemical linkages and plasticizes it when the PCL becomes mobile, leaving the excess PVC as a second unplasticized phase. On the assumption that interactions are saturated at 60 wt % PVC, it is estimated that the excess unplasticized PVC phase contributes 20% and 43% to the intensity of the FID in the 30/70 and 20/80 blends, respectively. These order-of-magnitude estimates may be compared with experimental intensities of T_{2s} of 24% and 50%, determined from FID's recorded at 348 K, a temperature at which neat

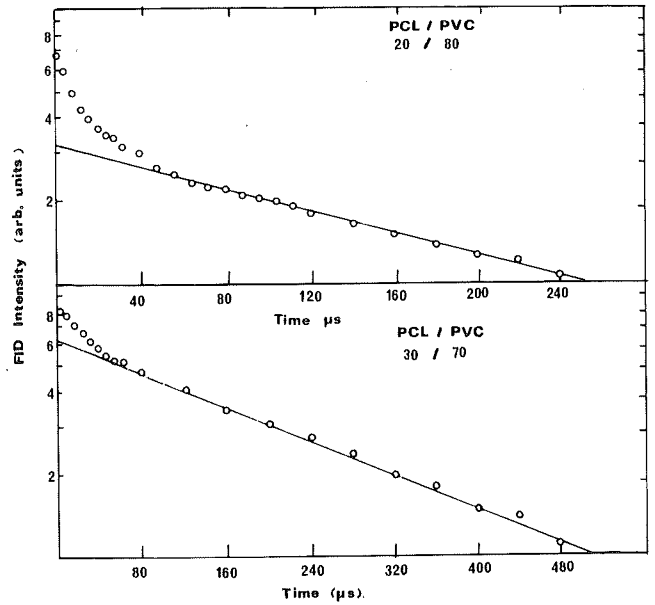

Figure 8. FID decays for 20/80 and 30/70 PCL/PVC blends recorded at 348 K.

PCL exhibits near-liquid-like mobility (Figure 8). The agreement is satisfactory in view of the uncertainties involved.

Turning to the finer details of the T_2 data, it is evident that the two phases in the blend are coupled. The onset of general motions in the mobile, plasticized, phase is responsible for the premature increase in T_{2s}, not unlike the way in which the mobile butadiene component in SBS copolymers induces premature motion in the styrene component.[46] At lower temperatures the rigid phase, in turn, places restrictions upon the motions availablie to the mobile phase. The plateau in T_{2L} may well arise from polymer chains pinned at one or both ends by C=O/methine proton linkages or by small domains of rigid-phase material possibly acting as crude cross-links. The size of such domains was estimated to be of the order of 3–4 nm in plasticized PVC.[3,4] The upper limit on their size in PCL/PVC blends is 12 nm.

IV. Conclusions

The relaxation behavior of PCL is closely similar to that of PEO and to that of PE for temperatures below the melting point of PCL. Blends with PVC, even for component concentrations at which the PCL component is presumed to be amorphous, are heterogeneous at a molecular level. Drawing upon earlier NMR results on PVC plasticized with a conventional plasticizer, it is proposed that PCL forms an intimate blend with part of the PVC component and, once mobile, acts as a plasticizer for the PVC. The remaining, excess, PVC is unplasticized and remains relatively immobile until temperatures close to the melting point are reached. Again by analogy with conventionally plasticized PVC, a description in terms of two glass transition temperatures would appear to be appropriate for the 30/70 and 20/80 blends examined herein.

Acknowledgment. It is a pleasure to acknowledge helpful discussion with A. Brazier. B.A. is indebted to SPPS (Services de la Programmation de la Politique Scientifique) for financial support in connection with her Ph.D. thesis work in Liège and to FRNS (Fonds National de la Recherche Scientifique) for funding to undertake advanced training in NMR in Trinity College, Dublin. Support from the National Board for Science and Technology of Ireland is also gratefully acknowledged.

References and Notes

(1) McBrierty, V. J.; Douglass, D. C. *Macromol. Rev.* **1981**, *16*, 295.
(2) McBrierty, V. J.; Douglass, D. C. *Phys. Rep.* **1980**, *63*, 61.
(3) McBrierty, V. J. *Faraday Discuss Chem. Soc.* **1979**, *68*, 78.
(4) Douglass, D. C. *ACS Symp. Ser.* **1980**, *No. 142*, 147.
(5) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Part A-2* **1969**, *7*, 795.
(6) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Part A-2* **1972**, *10*, 323.
(7) Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1109.
(8) Robeson, L. M. *J. Appl. Polym. Sci.* **1973**, *16*, 3607.
(9) Olabisi, O. *Macromolecules* **1975**, *8*, 316.
(10) Khambatta, F. B.; Warner, F.; Russell, T.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1391.
(11) J. V. Koleske In "Polymer Blends"; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978, Chapter 22.
(12) Ong, C. J.; Price, F. P. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 63*, 45; **1978**, *No. 63*, 59.
(13) Stein, R. S.; Khambatta, F. B.; Warner, F. P.; Russell, T.; Escala, A.; Balizer, E. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 63*, 313.
(14) Olabisi, O.; Robeson, L. M.; Shaw, M. T. "Polymer–Polymer Miscibility", Academic Press: New York, 1979.
(15) Coleman, M. M.; Zarian, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 837.
(16) Aubin, M.; Prud'homme, R. E. *Macromolecules* **1980**, *13*, 365.
(17) Augin, M.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1245.
(18) Hjertberg, T. Thesis, Chalmers University of Technology, Goteborg, Sweden, 1982.
(19) McCall, D. W. *Natl. Bur. Stand. Spec. Publ.* **1968**, *No. 301*, 475.
(20) Bair, H., private communication.
(21) Perret, R.; Skoulios, A. *Makromol. Chem.* **1972**, *156*, 143.
(22) Newmark, R. A.; Runge, M. L., Chermack, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1329.
(23) Hammerich, A. D.; Willeboordse, F. G. *Anal. Chem.* **1973**, *45*, 1696.
(24) Cousin, P. Prud'homme, R. E. *Eur. Polym. J.* **1982**, *18*, 957.
(25) Vanderschueren, J. *Ladang*, M.; Heuschen, J. M. *Macromolecules* **1980**, *13*, 973.
(26) Coleman, M. M.; Mosala, E. J. *Polymer* **1983**, *24*, 251.
(27) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *2*, 123.
(28) Gordon, M. Taylor, T. S. *J. Appl. Chem.* **1952**, *2*, 493.
(29) Kelley, F. N.; Bueche, F. *J. Polym. Sci.* **1961**, *50*, 549.
(30) Illers, K. H. *Rheol. Acta* **1964**, *3*, 202; *Kolloid Z. Z. Polym.* **1969**, *231*, 622.
(31) Hamiltou, A.; Ouhadi, T.; Jerome, R.; Teyssie, P. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 865.
(32) Zeman, L.; Patterson, D. *Macromolecules* **1972**, *5*, 513.
(33) Small, P. A. *J. Appl. Chem.* **1953**, *3*, 71.
(34) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1962**, *128*, 2042.
(35) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.
(36) Powles, J. G.; Mansfield, P. *Phys. Lett.* **1962**, *2*, 58.
(37) McBrierty, V. J. *Polymer* **1974**, *15*, 503.
(38) Connor, T. M. *J. Polym. Sci., Part A-2* **1969**, *7*, 1005.
(39) Connor, T. M. *J. Polym. Sci., Part A-2* **1970**, *8*, 191.
(40) McCall, D. W.; Falcone, D. R. *Trans. Faraday Soc.* **1970**, *66*, 262.
(41) Fujimoto, K.; Nishi, T.; Kado, R. *Polym. J.* **1972**, *3*, 448.
(42) McBrierty, V. J.; Douglass, D. C.; Barham, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1561.
(43) Douglass, D. C.; McBrierty, V. J.; Weber, T. A. *J. Chem. Phys.* **1976**, *64*, 1533; *Macromolecules* **1977**, *10*, 178.
(44) Packer, K. J.; Pope, J. M.; Yeung, R. R.; Cudby, M. E. A. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(45) McBrierty, V. J.; Douglass, D. C.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1265.
(46) Wardell, G. E.; McBrierty, V. J.; Douglass, D. C. *J. Appl. Phys.* **1974**, *45*, 3441.

Determination of Short-Chain Branching up to C_6 in Low-Density Polyethylenes by High-Resolution Pyrolysis–Hydrogenation Gas Chromatography

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ABSTRACT: Short-chain branching up to hexyl in low-density polyethylenes (LDPE) has been studied by pyrolysis–hydrogenation fused-silica capillary gas chromatography. The branch content was estimated from the relative peak intensities of the characteristic key isoalkanes in the C_{11} region by comparing the data of reference model ethylene–α-olefin copolymers with known content of methyl, ethyl, butyl, amyl, and hexyl branches, respectively. The results obtained are in fairly good agreement with those found by ^{13}C NMR spectroscopy. In general, the short-chain branches in a given LDPE exist in order of abundance butyl > ethyl > amyl > methyl > hexyl branches, regardless of the total branch content. Further, the presence of pair and/or branched branches is also suggested in addition to isolated branches.

The type and concentration of short-chain branching (SCB) in low-density polyethylenes (LDPE), which vary according to the polymerization conditions, affect many properties of the polymer. Therefore, the characterization of the SCB is required. In recent years, quantitative analyses of the SCB have been primarily performed by ^{13}C NMR spectroscopy.[1]

On the other hand, pyrolysis–hydrogenation gas chromatography (PHGC) methods, which require minimal sample size and a simple operating procedure, have also been utilized for the study of the SCB. In earlier work, Michailov et al.[2] identified some of the isoalkane peaks on the hydrogenated pyrograms of LDPE's and pointed out that ethyl and butyl branches predominate. Seeger and Barall,[3] using ethylene–1-butene and ethylene–1-hexane copolymers as standards, detected about 20 ethyl and 10 *n*-butyl branches per 1000 carbons from the high yields of 3- and 5-methylalkanes. The resolution of the pyrograms, however, was insufficient because of the use of packed columns. Ahlstrom and Liebman[4] demonstrated the presence of ethyl and butyl branches from increases in the size of the 3-methylalkanes and *n*-butane peaks, respectively, although 5-methylalkanes were not resolved.

Later, Mlejnek,[5] employing a more effective open tubular column and Curie-point pyrolyzer, obtained high-resolution pyrograms of PE's. On the basis of the relative peak area of isoalkanes, he concluded that the presence of methyl, ethyl, and butyl groups was equally probable in LDPE's. In our recent work,[6-8] glass capillary PHGC was applied to the quantitative analysis of the SCB. Relating the relative peak intensities of characteristic isoalkanes for LDPE's to those of reference model copolymers, we determined methyl, ethyl, and butyl branch contents in LDPE's. Liebman et al.[9] reported a comparable study on the SCB in PE's by fused-silica capillary PHGC and ^{13}C NMR spectroscopy. In order to extend the interpretative capabilities of PHGC, a computer simulation method was applied to reproduce the fragmentation pattern of the pyrogram of LDPE's using the data of known references. They[9] suggested that PHGC can estimate contents of SCB as low as one branch per 10 000 CH_2. Recently, Haney et al.[10] proposed a new PHGC method at relatively low pyrolysis temperature (360 °C). By this method, enhanced yields of the products pertaining to the branch points were observed on the resulting pyrograms of PE's. The observed excess amount of 3-methylpentane from PE's was qualitatively attributed to the existence of Willbourn-type branches such as 2-ethylhexyl (branched branch) and 1,3-paired ethyl (pair branch).

Table I
Type and Content of Branches in the Reference Ethylene–α-Olefin Copolymers

sample	α-olefin comonomer	branch type	branch content[a]
EP	propylene	methyl	20
EB	1-butene	ethyl	24
EHX	1-hexene	butyl	18
EHP	1-heptene	amyl	12
EO	1-octene	hexyl	20

[a] Branch content/1000 C determined by IR spectroscopy.

However, the existence of amyl branches and branches longer than hexyl, which has been confirmed by ^{13}C NMR spectroscopy,[11-15] has not been clearly characterized by PHGC mainly because of the lack of well-defined model polymers and of insufficient resolution for the associated isoalkanes on the pyrograms. In this work, PHGC methods for determining the SCB in LDPE's are extended up to hexyl branches using a high-resolution fused-silica capillary column and well-characterized model copolymers. Branch content thus estimated is compared with that obtained by ^{13}C NMR spectroscopy. In addition, the possible existence of pair and branched branches is also discussed on the basis of theoretical and observed yields for 5-ethylnonane, which is characteristic of the ethyl branch.

Experimental Section

Samples. The four representative commercial high-pressure LDPE samples studied are identical with those in ref 15. The five kinds of ethylene–α-olefin copolymers used as references are listed in Table I. The branch content was determined by IR spectroscopy using the corrected absorbance at 7.25 μm.[16] The conversion coefficients from the absorbance to the degree of branching were established from the relationship between the IR absorption intensity and the radioactivity for each type of copolymer of ethylene and α-olefin labeled with ^{14}C.[17,18] Both the reference copolymers and their IR data were kindly supplied by Sumitomo Chemical Industry Co., Ltd., through the courtesy of M. Kakugo.

Conditions for PGC. The pyrolysis–hydrogenation capillary gas chromatographic system utilized in this work is basically the same as that described previously.[8] A vertical microfurnace-type

0024-9297/84/2217-2557$01.50/0