# 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 tem-

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perature 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 $\bar{M}_n$ = 22000 and $\bar{M}_w$ = 36000. The crystallinity of the PCL sample was of the order of 60%.

**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 ($\chi$) 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 $\chi_{PS}$ 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°–$\tau$–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–$\tau$–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 $\gamma$ relaxation in PE and the $\beta$ 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.

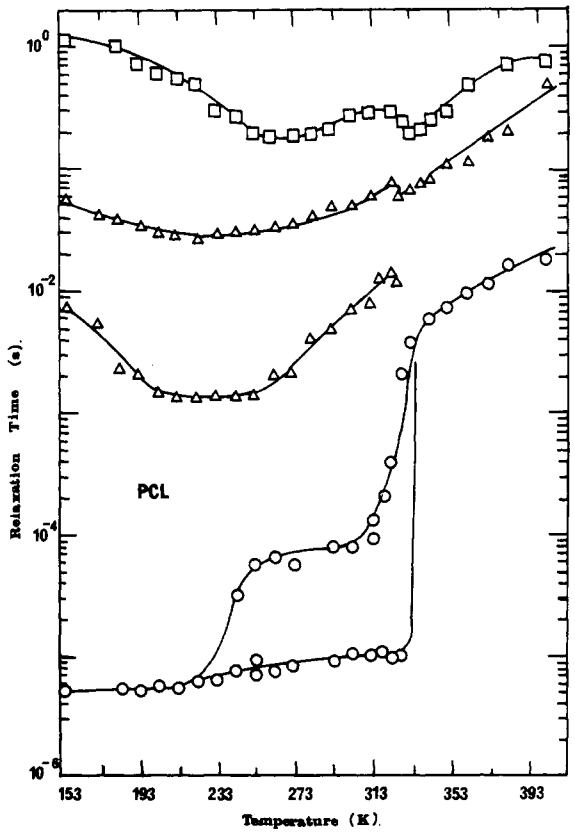


**Figure 1.** $T_1$ (□), $T_2$ (○), and $T_{1\rho}$ (△) vs. temperature data for PCL.

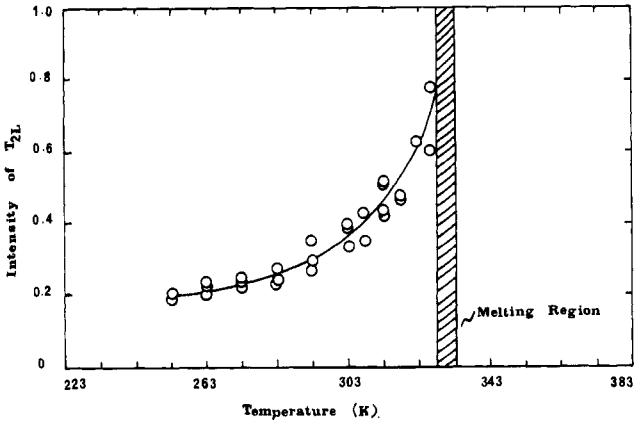


**Figure 2.** Intensity of the long $T_2$ component for PCL as a function of temperature.

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 $\gamma$ relaxation, alluded to in section I, shows up in the thermally stimulated depolari-

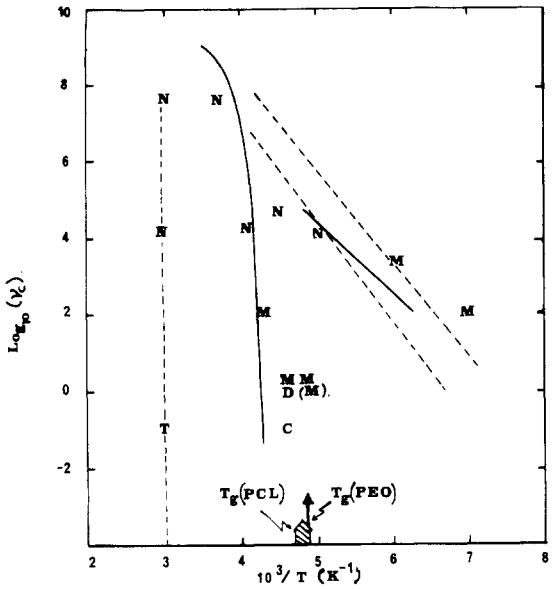


**Figure 3.** Transition map for PCL, where N denotes NMR data, M, dynamic mechanical relaxation, D, dielectric relaxation, T, DSC measurements, and C, thermally stimulated current depolarization measurements. The two dashed lines at low temperatures denote the $\gamma$ relaxation in PE[19] and the solid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

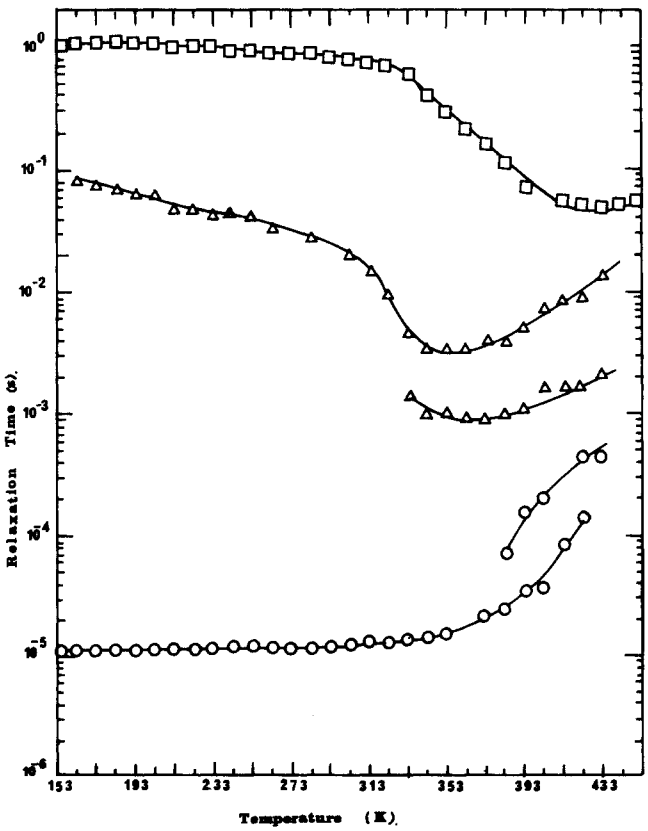


**Figure 4.** $T_1$ (□), $T_2$ (○), and $T_{1\rho}$ (△) vs. temperature data for PVC.

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

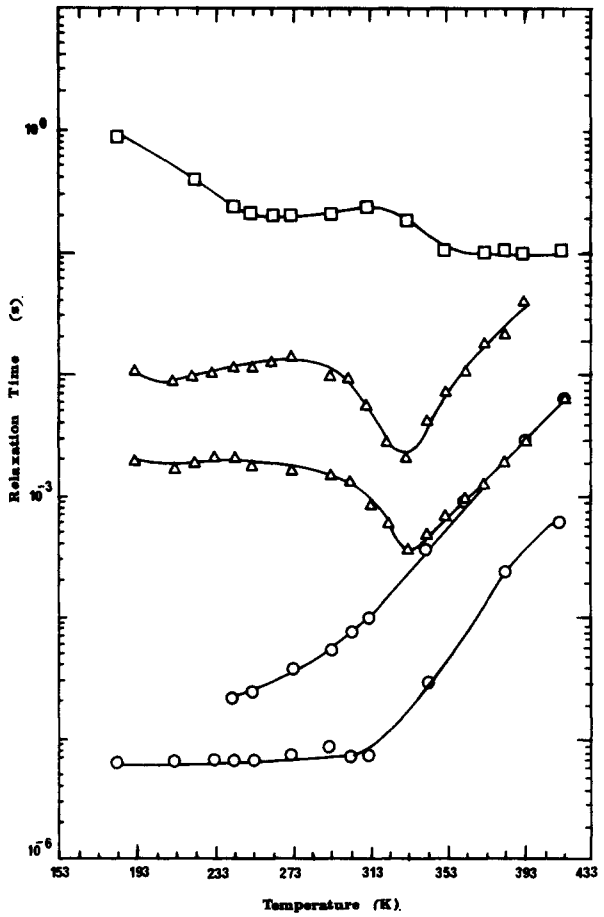


**Figure 5.** $T_1$ (□), $T_2$ (○), and $T_\rho$ (△) vs. temperature data for the 30/70 PCL/PVC blend.

$T_{1\rho}$ 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 $\beta$ relaxation is weak and does not always appear in relaxation measurements on PVC. There is no overt indication of the $\beta$ 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 $\beta$ 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 $D \simeq 10\text{–}12$ cm$^2$

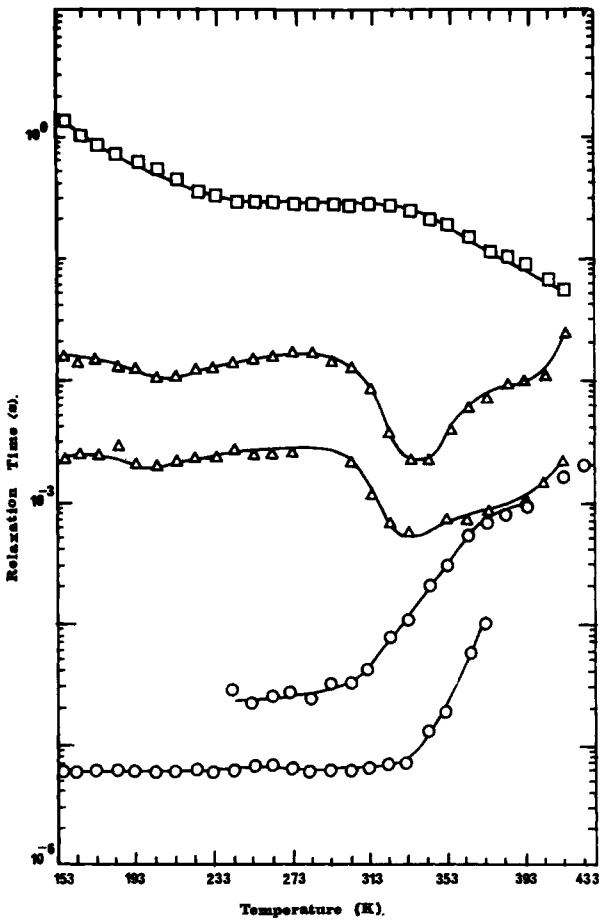


**Figure 6.** $T_1$ (□), $T_2$ (○), and $T_\rho$ (△) vs. temperature data for the 20/80 PCL/PVC blend.

$s^{-1}$ 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]

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

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.

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

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 $\gamma$ 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.

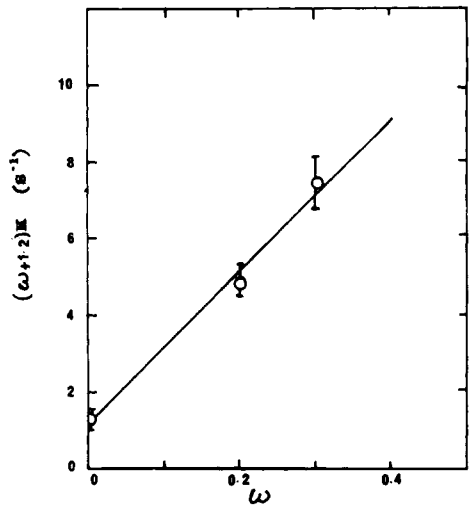


**Figure 7.** Plot of $(W + 1.2)K$ vs. $W$ (see text).

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

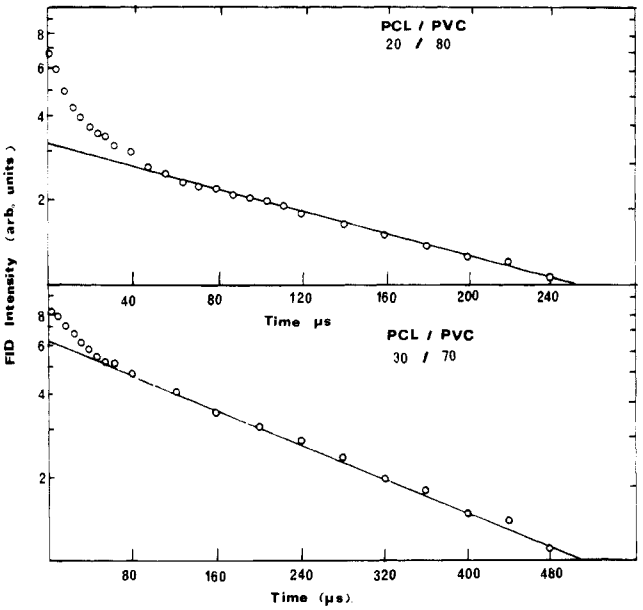


**Figure 8.** FID decays for 20/80 and 30/70 PCL/PVC blends recorded at 348 K.

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.

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