Heterogeneity in Polymers as Studied by Nuclear Magnetic Resonance

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A knowledge of the extent to which polymers are heterogeneous is fundamental to a full understanding of their properties. This paper discusses the role of n.m.r. in probing spatial heterogeneity in polymers using two characteristic features of n.m.r.: the short-range nature of the dipole–dipole interaction and the transport of spin energy (spin diffusion) that may occur over many tens of nanometres. The contribution of cross-relaxation is also examined briefly. Several illustrative examples are discussed.

The growing conviction that most, if not all, polymeric systems are heterogeneous is rapidly becoming accepted. Aside from the obvious forms of heterogeneity associated, for example, with morphological differences in partially crystalline polymers, other more subtle manifestations are now emerging. In the context of n.m.r., heterogeneity finds its origins in complexities of both molecular structure and motion. Anisotropy in the molecular motions of polymers can lead to a spread of many orders of magnitude in the distribution of correlation times that characterize the motions. The mere fact that polymer molecules are flexible implies that many degrees of freedom are coupled into the motion of any one segment. Considerable effort has been directed towards the elucidation of the details of these anisotropic motions and while it is virtually impossible to treat all the complexities in any one model, a number of important approaches have been formulated.[1-11] They subdivide crudely into those that represent the gross features of a distribution of correlation times *via* empirical distributions[9-11] and those derived from a more molecular approach.[1-8]

In this paper attention is directed towards the way in which characteristic motions in a polymer may be used to derive information on spatial inhomogeneity. The latter may range from molecular dimensions of nanometres or less (where in fact all materials are heterogeneous) to microns or larger, as in phase separated polymer blends. The contribution of n.m.r. in probing such spatial inhomogeneity has been significant and relies upon two characteristic features of n.m.r. relaxation. The first is the short range nature of the dipole–dipole interaction which predominantly monitors near-neighbour interactions and the second is the transport of spin energy (spin diffusion) that may occur over many tens of nanometres. An extension of the second category, appropriate in a few cases, is the cross-relaxation which occurs between spin systems of different resonant nuclei.[12-14]

In the following sections a number of representative examples that illustrate the role of n.m.r. in the study of heterogeneity in polymers are presented.

PARTIALLY CRYSTALLINE POLYMERS

The three n.m.r. relaxation times, T_1 (spin–lattice), $T_{1\rho}$ (rotating frame) and T_2 (spin–spin), are capable, at least in principle, of distinguishing between local environments characterized by different molecular motions. Under favourable circumstances, T_1 and $T_{1\rho}$ decays are non-exponential while multiple components appear in spectral linewidths. Fig. 1 exhibits typical two-component linewidth and $T_{1\rho}$
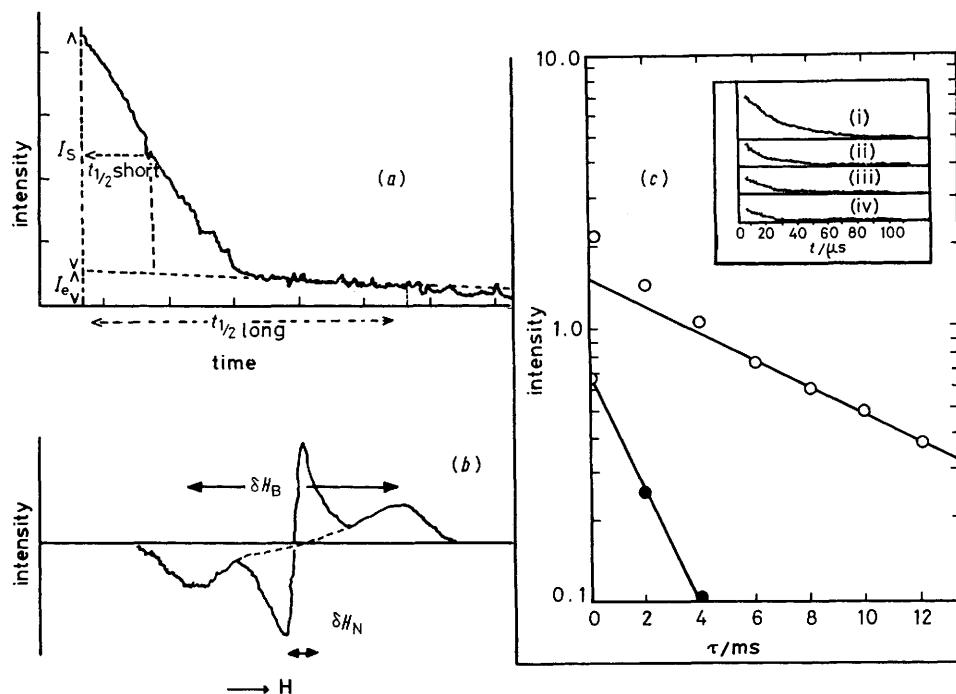
FIG. 1.—Typical two-component linewidth and $T_{1\rho}$ decay observed in a partially crystalline polymer. In part (c) $\bigcirc$ = crystalline, $\bullet$ = amorphous. Inset shows values of τ of (i) 0, (ii) 4, (iii) 6 and (iv) 8 ms.

(or T_1) decay spectra observed in polymers with crystalline and amorphous regions. Note that it is often possible to assign the $T_{1\rho}$ components to one or other of the regions by observing the way in which the shape of the decay changes as a function of the length of the sustaining r.f. pulse in the usual 90°-90° (90° phase shift) pulse sequence used to determine $T_{1\rho}$.[15] In the data of fig. 1, the long T_2 (mobile component) is observed to decay first which indicates that the short $T_{1\rho}$ manifests amorphous behaviour. The separation of spectra into components that characterize crystalline and amorphous regions constitutes one of the most powerful advantages of n.m.r. over other methods in establishing the overall relaxation behaviour of polymer systems.

Following the first two-component lineshape analysis of Wilson and Pake,[16] many studies of increasing sophistication have been carried out to account for the increasing number of situations for which a description in terms of two components is inadequate. In particular, there are many polymers that require the introduction of a third component, in addition to the usual crystalline and amorphous contributions, in order to achieve a satisfactory interpretation of the data.[7,17-22] This third contribution of intermediate linewidth has been assigned to material at the interface between the crystalline and amorphous regions and may appear explicitly in linewidth or $T_{1\rho}$

data, or may be unresolved in a two component spectrum.   Poor resolution can arise in cases where the fraction of interfacial material is small or when its characteristic motions are not appreciably different from those of the truly amorphous or crystalline components.

Rotating frame and linewidth data for a high molecular weight linear polyethylene are presented in fig. 2.[23]   The presence of three distinct types of material is demon-
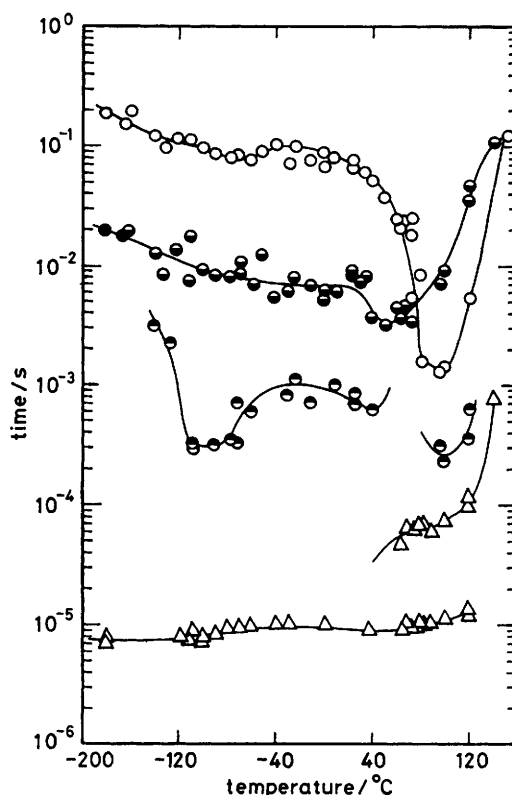

FIG. 2.—$T_{1\rho}(H_1 = 10\,\mathrm{G})$ and $T_2(\triangle)$ data for a high molecular weight linear polyethylene. $T_{1\rho}$ decays are resolved into long ($\bigcirc$), intermediate ($\ominus$) and short ($\obullet$) components as indicated.

strated explicitly in $T_{1\rho}$ and implicitly in T_2.   The observed plateau of $\approx 70\,\mu$s in the long T_2 component near 90 °C represents a weighted average of amorphous material that is near liquid-like in character with interfacial molecules executing fairly vigorous motions that are, nevertheless, constrained compared with the truly amorphous component.

Folds and cilia are deemed to be the principal morphological entities in the interfacial region.   Models developed to describe their constrained motions treat the fold or cilium as a chain of N connected segments.[7]   Specific character is injected into the model by specifying the mutual orientation of successive polar axes of the chain segments in a particular way.   By way of illustration, if one assumes that a cilium is internally rotating and that successive elements of the molecule can rotate about the previous element, then T_2 for each element, neglecting inter contributions, takes the simple form:

$$T_2^2 = e^{3N\beta^2}\, T_{2\mathrm{RL}}^2;\tag{1}$$

T_{2RL} is the intra rigid lattice T_2; β is the bend angle between successive elements and N is the element number where $N = 1$ denotes the element anchored to the crystal surface. For $N\beta^2$ small, T_2 does not differ appreciably from T_{2RL}. As $N\beta^2$ increases, however, T_2 correspondingly increases, implying the development of considerable flexibility for elements progressively removed from the point of constraint.

The model developed for fold motions adopts a configurational probability approach based upon Gaussian statistics.[7] From the total ensemble of unconstrained configurations of an assumed wormlike chain,[24] only those that are consistent with the imposed constraints of the fold, such as specification of the points of entry and exit from the crystal surface, are selected. The constrained probabilities so derived are used to compute the averages required in the calculation of the overall T_2 for the fold.

Both models provide adequate descriptions of the available linewidth data as indeed is the case with other molecular models.[25] From a macroscopic viewpoint, lineshape studies have also resulted in gratifying consistency with experiment. Not only have the lineshapes been computed with remarkable accuracy, but inconsistencies in the determination of the degree of crystallinity by n.m.r. have been reconciled with independent assessments over a wide temperature range.[22]

While interfacial studies such as these have found primary motivation in the area of partially crystalline polymers, it is pertinent to mention that the model calculations discussed above also provide a description of n.m.r. data from a totally different class of heterogeneous material, namely, carbon black-filled elastomers.[26] N.m.r. reveals the presence of three distinct types of rubber distinguishable by their characteristic motions.[26,27] There is a layer of relatively immobile rubber in the immediate vicinity of the filler particle surrounded by an annular region of considerably more mobile, though still constrained, material. This structure is consistent with the distribution of T_2 values predicted by eqn (1). The third unconstrained component exhibits motions comparable with the pure gum.

T_2 component intensity data can provide estimates of the relative amounts of each type of material present.[16] The following *caveat* must, however, be borne in mind: while it is customary to discuss complex lineshapes or decays in terms of discrete components this does not necessarily imply a sharp discontinuity between regions; there may well be a more gradual transformation from one type of material to another, described by a distribution of relaxation times. Although the decay is formally resolved into two or three discrete components, in such cases this only represents an approximation to the true physical state of the polymer.

POLYMER BLENDS

The range of properties achieved in blends of two or more component polymers is controlled in large measure by the extent of micro- or macro-phase separation in the composite. Blends of chemically dissimilar polymers have been fabricated such that intimate mixing occurs on a scale of molecular dimensions.[28-31] On the other hand, there are polymer systems where phase separation occurs on a scale of microns or larger.[28,32] The full exploitation of the properties of these heterogeneous systems requires a knowledge of the degree of compatability achieved and in this respect n.m.r. has been particularly revealing.

Consider the polymer pair, poly(styrene-co-acrilonitrile) (PSAN) and poly(methyl methacrylate) (PMMA), for which T_1 and $T_{1\rho}$ data are presented in fig. 3.[31] The broad T_1 minimum in neat PMMA centred at 0 °C manifests relaxation due to α-methyl reorientation. At these temperatures the resonant protons in PSAN are only weakly coupled to the lattice. Note, however, that the blends of PSAN and PMMA

all exhibit exponential decay rather than a weighted superposition of component decays. Thus, within the experimental limits of the measurement, it may be deduced that the α-methyl protons are not only relaxing other protons in PMMA but also those in PSAN through the mechanism of spin diffusion.[33] The maximum diffusive path length $\langle r \rangle$ to the relaxation sites may be estimated from the approximate expression

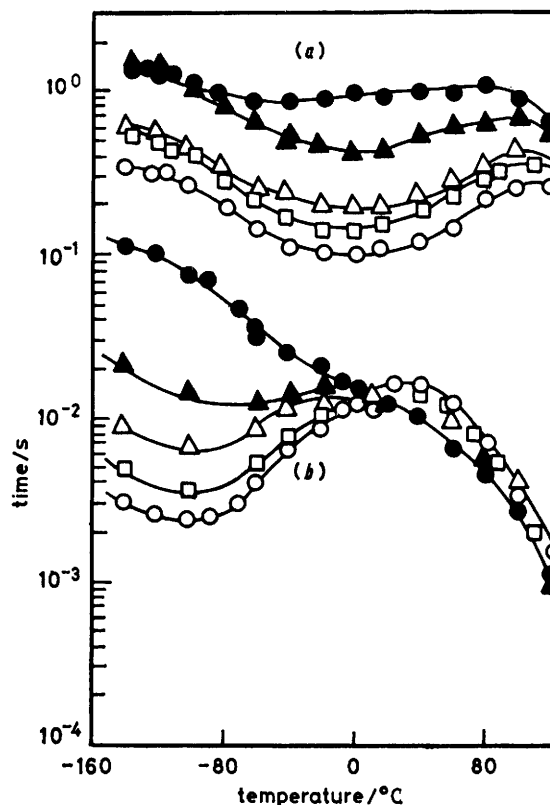$$\langle r \rangle = [6D\tau]^{\frac{1}{2}}. \qquad (2)$$

FIG. 3.—(a) T_1 (40 MHz) and (b) $T_{1\rho}$ ($H_1 = 10$ G) data for PMMA ($\bigcirc$), PSAN ($\bullet$) and PSAN/ PMMA blends in the following proportions by weight: 75/25 ($\blacktriangle$), 50/50 ($\triangle$) and 25/75 ($\square$).

The time over which diffusion occurs, τ, is of the order of 0.5 s (fig. 3). The diffusion coefficient is typically 10^{-12} cm^2 s^{-1} and therefore $\langle r \rangle \approx 17$ nm, which represents an upper limit to the size of PSAN or PMMA aggregates, if present in the blend. The results of simple spin diffusion, in addition, predict the magnitudes of the T_1 minima for the three blends on the assumption of strong coupling between the spins.

$T_{1\rho}$ also exhibits exponential decay, with the exception of the 75/25 PSAN/ PMMA blend which shows marginal, though significant, departure from exponential behaviour. Furthermore, the magnitudes of the $T_{1\rho}$ minima for the blends are not in accord with the results of simple spin diffusion theory, in contrast to the T_1 data. These differences in the $T_{1\rho}$ response may be rationalized on the basis that the spin systems are not tightly coupled on the much shorter timescale, 10^{-2} s, of the $T_{1\rho}$ experiment. The maximum diffusive path length in this case in ≈ 2 nm. Thus it may be concluded from these, albeit approximate, calculations that there is spatial inhomogeneity in the PSAN/PMMA blends on a scale between 2 and 17 nm.[31]

Detailed n.m.r. studies have also been carried out on blends of polyvinylidene fluoride (PVF_2) and PMMA.[14] In addition to conventional T_1, T_2 and $T_{1\rho}$, cross-relaxation measurements between the ^{19}F and ^1H nuclei may also be performed in this blend through application of the transient Overhauser effect.[12-14,34] One of the processes that leads to an Overhauser effect involves an exchange of energy between the ^{19}F (I) and ^1H (S) spin systems as evidenced by the spectral density term $-J_0(\omega_I - \omega_S)$ in the expression for the cross relaxation rate, σ. Such an exchange will only conserve energy, however, when there is additional interaction with a lattice undergoing motions at the difference frequency ($\omega_I - \omega_S$). These motions provide the necessary energy balancing.[13] Comparison of σ as a function of temperature in neat PVF_2 and a 40/60 blend of PVF_2/PMMA indicates that there is additional cross-relaxation near -40 °C in the blend. It follows that there are additional motions in the blend at the difference frequency (1.6 MHz) and reference to the transition map for PMMA[35] shows that α-methyl motion is the most likely candidate. From these observations, supported by T_1, T_2 and $T_{1\rho}$ data, it is concluded that a substantial fraction of the amorphous PVF_2 molecules are in intimate contact with PMMA in the blend.

While this section has concentrated exclusively upon composites of essentially compatible polymers, it is pertinent to recall again that there are many examples in the literature such as SBS block copolymers[32] and polyethylene/polypropylene blended fibres prepared by the surface growth technique,[23] to name but two, where n.m.r. has demonstrated almost complete segregation of the component polymers.

PLASTICIZED POLY(VINYL CHLORIDE)

Considerable insight into the heterogeneous nature of PVC has been derived through observation of the effects of plasticization. Fig. 4 presents $T_{1\rho}$ and T_2 data for neat material, designated PVC(0), and for samples with 1% PVC(1), 5% PVC(5) and 17% PVC(17) by weight of the plasticizer di-isodecylphthalate (DIDP).[36] The T_2 data support the view that there are three types of material distinguished by their characteristic motions; a mobile fraction (M), a less mobile, intermediate fraction (I) and a fraction which remains essentially rigid (R) below ≈ 120 °C on the T_2 time-scale. The M and I components are both contained in the long T_2 component; the initial rise corresponds to the M fraction and the subsequent rise, following the point of inflection, corresponds to the I fraction.

· Following the procedures described in fig. 1 for the assignment of $T_{1\rho}$ components, it may be concluded that the minima in the short $T_{1\rho}$ in the ranges 85-95 °C and 95-115 °C are associated with M and I material, respectively. While the R material has a long intrinsic $T_{1\rho}$, its relaxation rate is indistinguishable from the I component due to the effects of spin diffusion.

The addition of plasticizer produces dramatic effects on the relaxation behaviour of the I and M fractions. The I fraction shows a somewhat greater dependence on the presence of plasticizer than the M fraction while the R material remains almost totally insensitive to it. This behaviour again demonstrates the heterogeneous nature of the system.

Returning to the $T_{1\rho}$ data, the appearance of the high temperature minimum in the long component manifests partial spin diffusion coupling between the I and M regions.[37] Note that the depth of the minimum decreases with increasing plasticizer content since the spin diffusion coupling becomes less efficient with increasing amounts of plasticizer: T_{2I} and T_{2M} increase and therefore the effects of spin diffusion decrease.

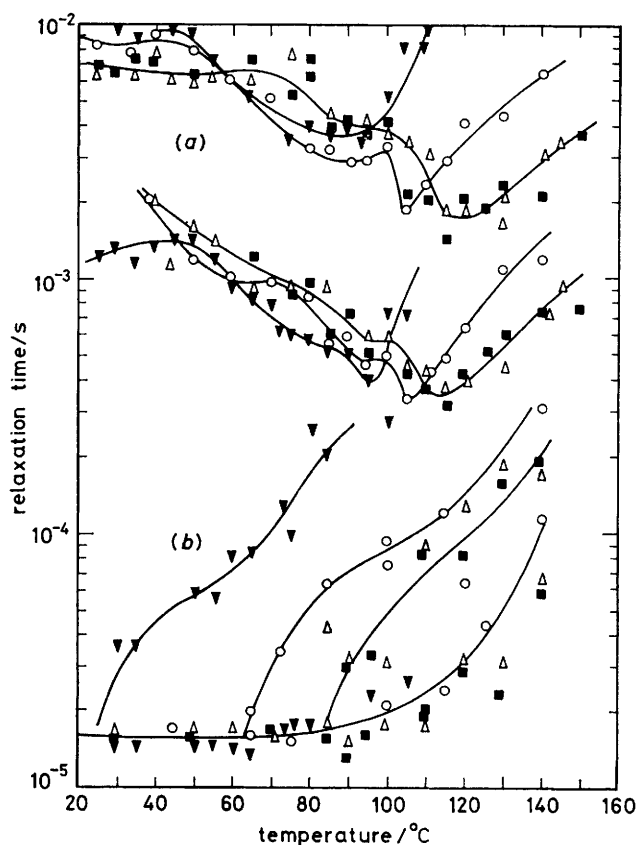Since the $T_{1\rho}$ and T_2 data demonstrate that there is some fundamental inhomo-

FIG. 4:.—(a) $T_{1\rho}(H_1 = 10$ G) and (b) T_2 data for PVC (■) and samples containing △, 1; ○, 5 and ▼, 17% plasticizer by weight.

geneity in PVC, it is desirable to determine the extent of these regions in the polymer. Goldman and Shen[38] have developed the pulse sequence shown in fig. 5(a) that may be used to monitor spin diffusion between regions of a heterogeneous system described by significantly different T_2 values.   The first 90° pulse orients the total magnetization transverse to the steady laboratory magnetic field.   After a time $\tau_1 = 30$ μs, the short T_2 component has decayed essentially to zero (see fig. 4) and leaves the long T_2 little altered.   The second 90° pulse, out of phase with the first, returns the remaining magnetization along the laboratory field direction.   A third 90° pulse is used to examine subsequent effects of spin diffusion at suitably chosen intervals τ_2. It is convenient to label the decay following the third pulse as $S(\tau_2)$.   When τ_2 is short, say 0.1 ms, there is insufficient time for spin diffusion to equilibrate the rigid and mobile regions and one observes the long component shown in fig. 5(b) (ii). When spin energy transfers out of the short into the long component the shape of $S(\tau_2)$ changes.   This change is conveniently monitored as the difference signal $S(\tau_2) - S(0.1)$, [fig. 5(b)].   The change in magnetization of the mobile and rigid material due to spin diffusion redistribution of energy within the spin system is easily visualized by the graphic decomposition of this difference signal [fig. 5(c)].   For times $\ll T_1$, the absence of a redistribution would in fact lead to a zero difference signal.

   Returning to the experimental data, the difference signal of fig. 5(b) (iv) shows a

partial recovery of the less mobile material, with a corresponding heating of the mobile component for $\tau_2 = 1$ ms. At $\tau_2 = 10$ ms it is obvious that the entire mobile component is communicating with the less mobile material and that recovery of a uniform spin temperature is more or less complete. Using this time of ≈ 10 ms, in conjunction with eqn (1), it is concluded that the regions of inhomogeneity are of the order of ≈ 10 nm.
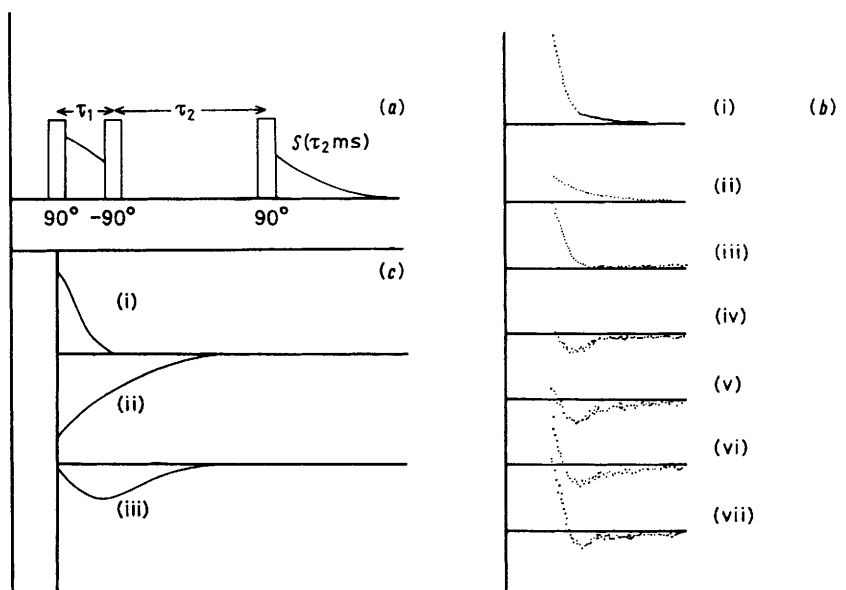

Fig. 5.—(a) Goldman–Shen pulse sequence (see text). (b) Diagrams which illustrate the change in shape of the decay curve $S(\tau_2)$ in the G–S experiment on PVC(5) at 85 °C. (iii)–(vii) show the behaviour of the difference signal $S(\tau_2)$–$S(0.1)$. Note that (ii) and (iii) denote the mobile and rigid components, respectively. (i) FID, (ii) $S(0.1)$; (iii) $S(400)$–$S(0.1)$; (iv) $4 \times [S(1) - S(0.1)]$; (v) $4 \times [S(10) - S(0.1)]$; (vi) $4 \times [S(30) - S(0.1)]$; (vii) $4 \times [S(70) - S(0.1)]$. (c) Diagram which presents the difference signal in terms of the (i) short and (ii) long component change in time τ_2; (iii) shows the combined difference signal.

One interpretation of the observed inhomogeneity in PVC suggests the presence of ordered or " paracrystalline " regions associated with short segments of syndiotactic material.[39] There are a number of other possible candidates. Structures may be present analogous to those induced in ionomers[40] that may conceivably result from the presence of stabilizers such as lead phthalate or zinc stearate commonly used in these systems. Though less likely in this polymer, molecular weight distributions may also contribute.

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