N.m.r. relaxation studies of molecular motion in alternating copolymers of styrene and *N*-substituted maleimides

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Spin–lattice and rotating frame relaxation measurements have been made on nine copolymers of styrene with *N*-n-alkyl maleimides in which the alkyl groups are CH_3, C_2H_5, C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ and $C_{18}H_{37}$. Five relaxations have been detected which are correlated with existing relaxation work. The highest temperature ($\alpha\beta$) relaxation is associated with the glass transition and the γ-relaxation results from ring twisting in the ordered (helical) parts of the structure. The δ-relaxation occurs only in the C_1–C_7 polymers and reflects movement in helical stacking within the ordered phase while the ϵ-relaxation occurs only in the C_7–C_{18} homologues and arises from motion of the pendant alkyl chain in both ordered and disordered regions. The lowest temperature minimum in T_1 is associated in all polymers with methyl rotation. Spin diffusion plays a prominent role in the relaxations and this is used to interpret further the morphology of the samples.

INTRODUCTION

Relaxation techniques are a valuable source of information on the detailed motional behaviour of polymers[1], and their combined use (usually dielectric and mechanical) can be a particularly powerful tool in the assignment of relaxations[2]. One of the more serious difficulties of this type of work is concerned with problems of crystallinity, where the specificity of relaxations for the crystalline or amorphous phase is often in doubt. Ambiguities of this nature are enhanced in polymers where distinct crystalline and amorphous phases cannot be identified, but rather where the material comprises short range ordered and disordered regions with an essentially amorphous nature[3]. In these circumstances, the use of X-ray diffraction coupled with diagnostic heat treatments such as quenching or annealing are only of marginal value.

Nuclear magnetic resonance has the distinct advantage over dielectric and mechanical methods that separate relaxation data are often provided for crystalline and amorphous regions throughout a wide temperature interval. This is a particular feature of experiments in the rotating frame, which additionally alleviate one of the disadvantages of the technique, its limited frequency coverage

A further aid towards an understanding of the molecular origin of relaxations lies in the study of similar materials whereby minor structural modifications in their chemistry can be observed for their subsequent effects. The homologous series based on *N*-substituted polymaleimides satisfies these requirements and has formed the basis of previous reports[3,4]. We report here a comprehensive study using pulsed n.m.r. on nine copolymers of styrene and *N*-alkyl maleimides where the pendant n-alkyl chain varies from CH_3 to $C_{18}H_{37}$. The data indicate the existence of five relaxations which (apart from methyl group rotations) we have attempted to correlate with existing dielectric work. The presence of non-exponential decays in the rotating frame has enabled the morphological origin of the relaxations to be established. In addition, the effects of spin diffusion (which is universally present) add further confirmation to, and enlarge our ideas about, the ordering within the amorphous phase.

EXPERIMENTAL

Materials

All the polymers were prepared by the treatment of an alternating copolymer of styrene and maleic anhydride with the appropriate n-alkyl amine[5]. Full details of the preparation and characterization (chemical and physical) have been published[3], and some data relevant to the present study are presented in *Tables 1* and *2*. It should be re-emphasized that none of the samples shows X-ray evidence for the presence of crystallinity although amorphous haloes indicate that extensive short range order is undoubtedly present.

N.m.r.

Measurements were carried out using a Polaron pulsed n.m.r. spectrometer operating at 21 MHz utilizing the 0.5 T magnetic field of a Newport Instruments 7 in (177 mm) electromagnet. A continuous temperature interval, from 120 to 450K, was studied with an additional 'spot' temperature of 77K. T_1 was estimated using the saturation recovery method via 90°–τ–90° pulse sequences. In all polymers at all temperatures, exponential behaviour was observed. Rota-

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Table 1 Transition temperature minima (K) for styrene-*N*-n-alkyl maleimide copolymers

Substituent	Polymer T_g[3]	Relaxation assignment				
		$\alpha\beta$	γ	δ	ϵ	CH_3
CH_3 T_1	444	–	–	326	–	<77
$T_{1\rho}$ (long)		–	312	206	–	<77
$T_{1\rho}$ (short)		–	348	273	–	–
C_2H_5	417	–	–	290	–	144
		–	300	184	–	–
		–	–	–	–	100
C_5H_{11}	401	–	–	331	213	147
		413	325	244	116	–
		420	–	–	~110	–
C_7H_{15}	377	–	–	323	218	131
		380	274	197	137	–
		413	–	–	~120	–
C_9H_{19}	378	–	–	–	223	153
		373	287	–	166	–
		392	277	–	~140	–
$C_{12}H_{25}$	356	425	–	–	227	153
		375	276	–	153	–
		393	~285	–	~140	–
$C_{14}H_{29}$	333	390	–	–	233	135
		352	283	–	174	–
		363	287	–	~145	–
$C_{16}H_{33}$	326	417	–	–	236	123
		355	283	–	176	–
		345	283	–	~155	–
$C_{18}H_{37}$	332	389	–	–	237	126
		365	279	–	174	–
		379	281	–	179	–

Table 2 Activation energies (kJ/mol) calculated from *Table 1*

Substituent	$\alpha\beta$	γ*	δ	ϵ
CH_3 Long			29.7 }[51]	
Short			89.2	
C_2H_5			26.7 }[43]	
			–	
C_5H_{11}			49.3	13.5
			–	12.1
C_7H_{15}			26.8	19.6
			–	14.2
C_9H_{19}				34.5
				20.0
$C_{12}H_{25}$	169 }[298]	41.8		24.9
	277	45.9		19.4
$C_{14}H_{29}$	192 }[330]	54.8		36.5
	278	57.7		20.4
$C_{16}H_{33}$	127 }[980]	46.8		36.8
	106	46.8		24.0
$C_{18}H_{37}$	314 }[550]	52.4		34.8
	783	63.7		38.8

Figures in parentheses refer to dielectric data[3].

* Figures derived assuming the T_1 minimum is merged with the higher temperature $\alpha\beta$-relaxation

ting frame data ($T_{1\rho}$) were obtained by the spin-locking $90°–90°_{90°}$ sequence producing information at an effective frequency of 5×10^4 Hz. In most cases the observed decay was non-exponential and was satisfactorily analysed in terms of two components. The receiver recovery time was 8 μsec. Samples were thoroughly purged of oxygen and investigated *in vacuo* as compressed pellets to improve signal/noise ratio. Instrumental details have been reported previously[2].

Results

The n.m.r. behaviour of the nine samples is shown in *Figures 1–9*. A profusion of minima are evident in both T_1 and $T_{1\rho}$ data with the additional complication that the latter can be resolved into long and short components. The temperatures at the minima are recorded in *Table 1* where assignments to various relaxation processes have been made. These assignments are based on a comparison with existing dielectric data where available[3], coupled with such similari-

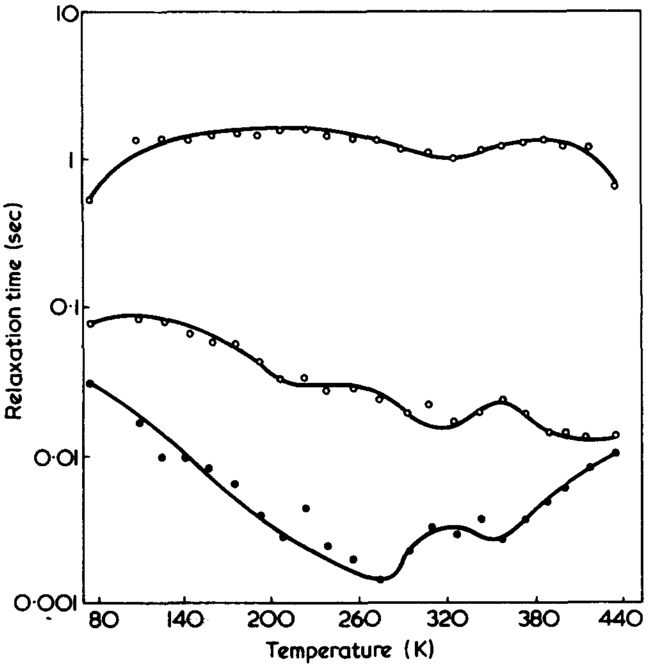

Figure 1 Relaxation data as a function of temperature for the methyl derivative

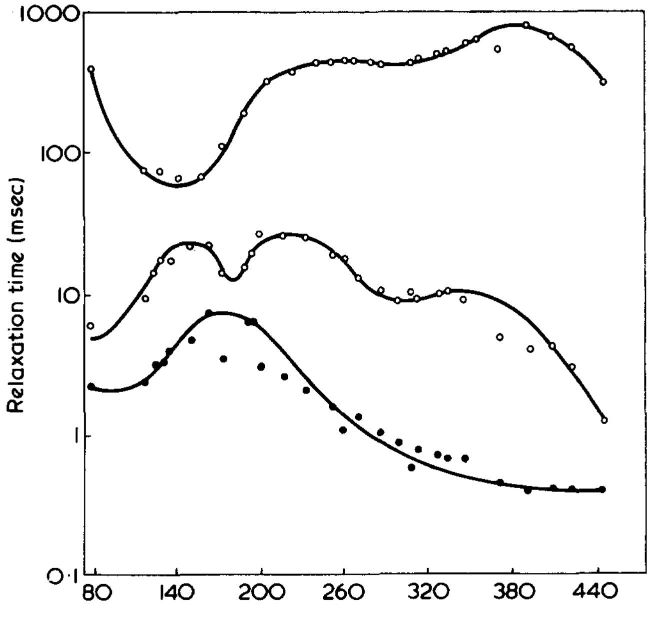

Figure 2 Relaxation data as a function of temperature for the ethyl derivative

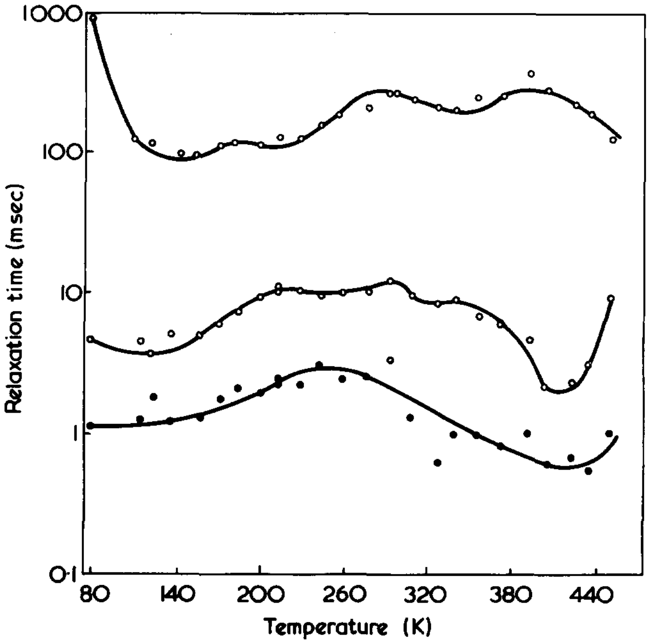

Figure 3 Relaxation data as a function of temperature for the amyl derivative

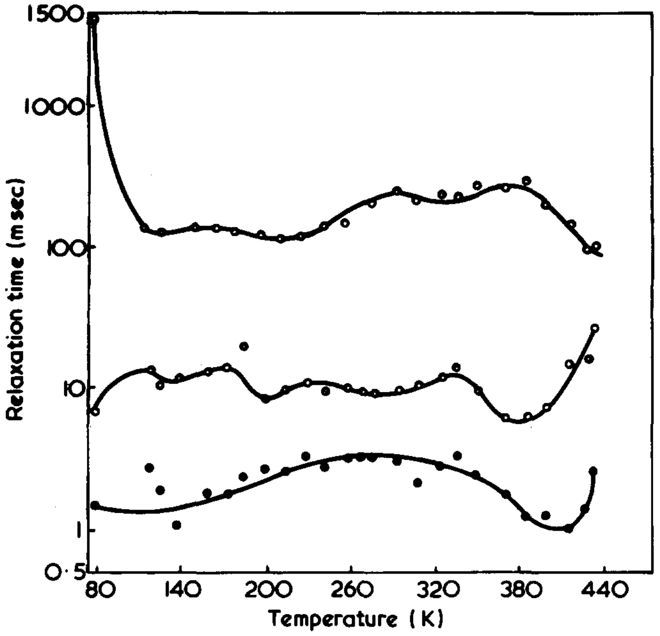

Figure 4 Relaxation data as a function of temperature for the heptyl derivative

ties as are apparent in *Figures 1–9*. Only the methyl, ethyl and dodecyl derivatives have been studied over a sufficiently wide temperature range to include all the relaxations shown in *Table 1*. A relaxation map for these three materials can be constructed using the following relations for the correlation frequencies at the temperature minima:

$\upsilon_c = (2)^{1/2}\upsilon_0$ at a T_1 minimum

$\upsilon_c = \gamma H_1/2\pi$ at a $T_{1\rho}$ minimum

In our case υ_c for T_1 minima is 2.97×10^7 Hz and 5×10^4 Hz for $T_{1\rho}$ minima. Using standard relations for correlating n.m.r. and dielectric frequencies[6], *Figure 10* was constructed. Analysis of this diagram will be deferred until the Discussion section.

Computed activation energies based on these assignments are compiled in *Table 2* together with comparison values from ref 3. A glance at *Figure 10* shows quite clearly that at the high temperatures necessary to observe the γ-relaxation in the T_1 data, this relaxation will have merged with the $\alpha\beta$-minimum and be unresolved. This forms the basis of the calculation for the γ-activation energy in *Table 2*.

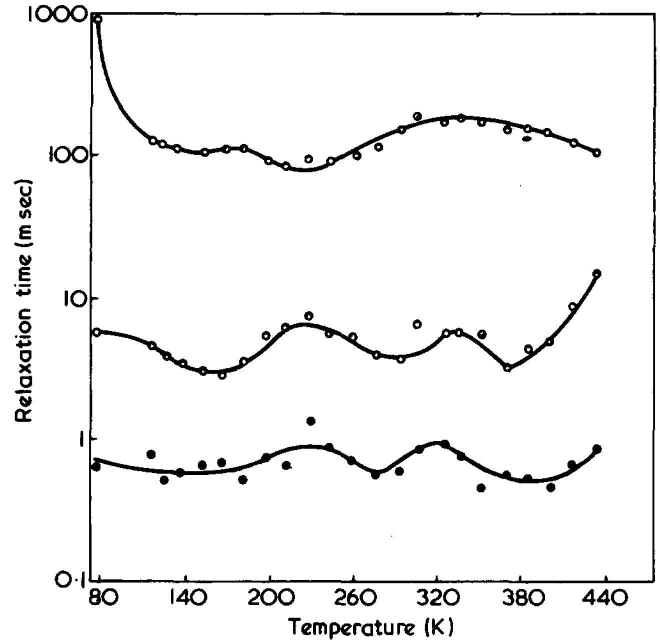

Figure 5 Relaxation data as a function of temperature for the nonyl derivative

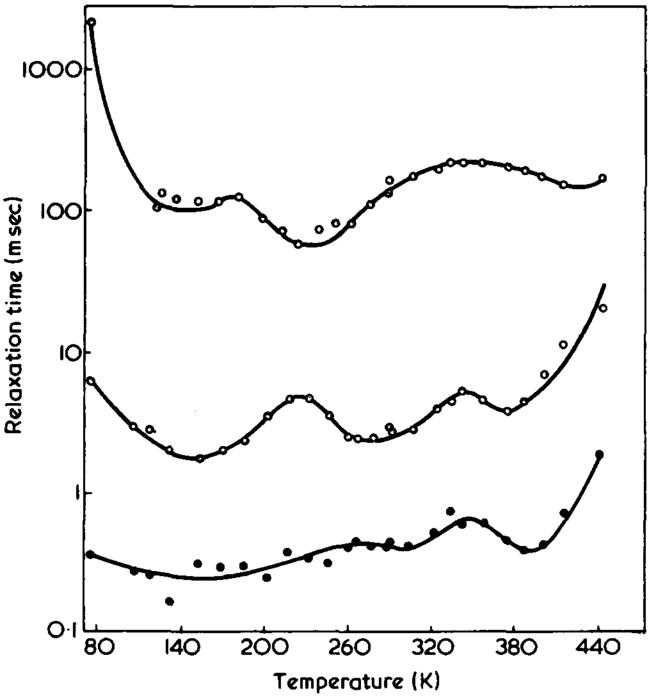

Figure 6 Relaxation data as a function of temperature for the dodecyl derivative

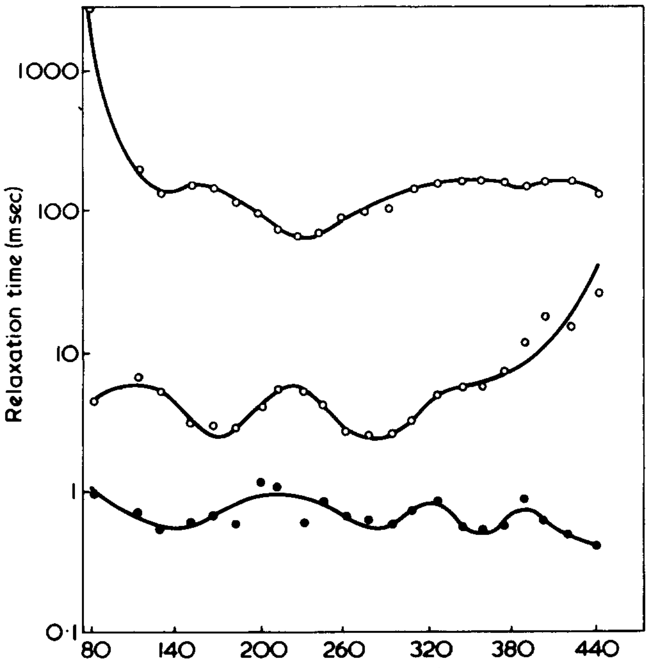

Figure 7 Relaxation data as a function of temperature for the tetradecyl derivative

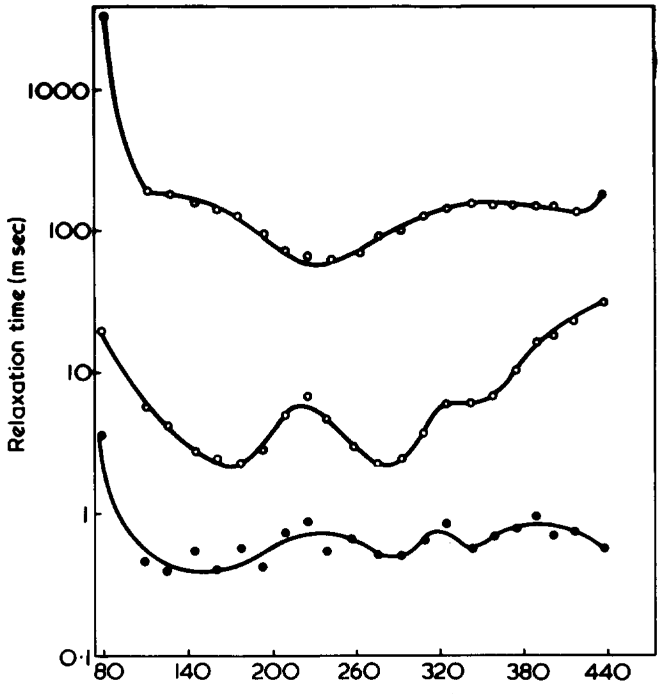

Figure 8 Relaxation data as a function of temperature for the hexadecyl derivative

The relative contributions of the long and short $T_{1\rho}$ components are of interest since it might be supposed that the relative abundances of the molecules contributing to them could be determined. The data for the dodecyl and octadecyl derivatives are illustrated in *Figure 11* which shows behaviour typical of the longer alkyl chains in the series. Comparison with *Figures 6* and *9* reveals a remarkable similarity in that the fractional proportion of the long component follows the relaxation behaviour very closely and appears to approach minima at the same temperatures as does the relaxation time. Since it is thus clearly inappropriate to assign the long and short contributions to the total magnetization in terms of molecular populations, a more satisfactory explanation in terms of spin diffusion must be invoked[7]. This work will be explored in detail later. The technique of non-exponential curve resolution and the determination of relative component magnitudes follows that discussed in ref 8. The errors in the determination of the short component parameters are necessarily greater than those for the long component and the errors in the decomposition become larger as the difference in the two relaxa-

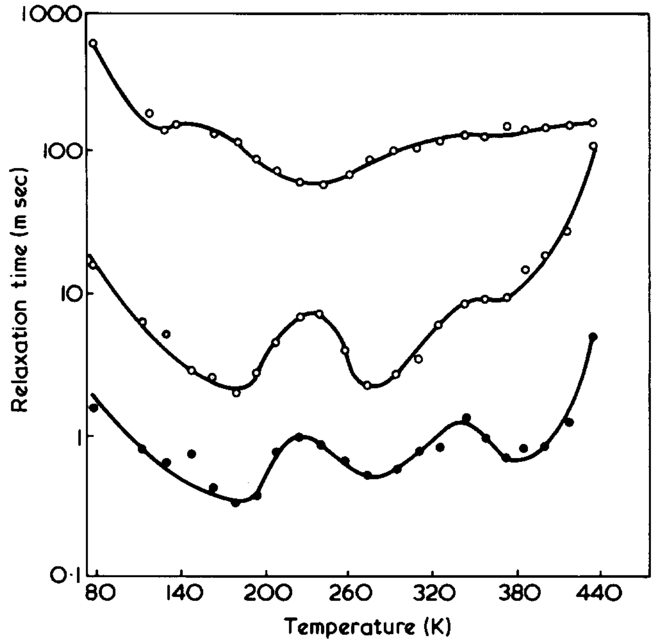

Figure 9 Relaxation data as a function of temperature for the octadecyl derivative

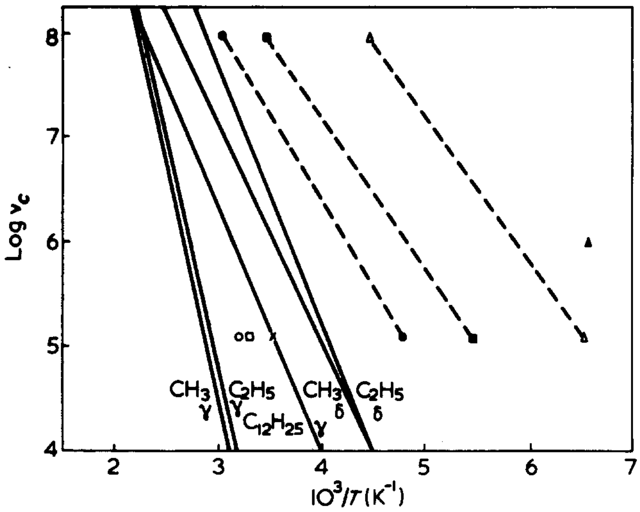

Figure 10 Arrhenius plot of log ν_c against $1/T$ for the methyl, ethyl and dodecyl derivatives. The solid lines refer to dielectric data[3], with the following code for the remaining points: ○, methyl derivative, γ-relaxation (n.m.r.); ●, methyl derivative, δ-relaxation (n.m.r.); □, ethyl derivative. γ- relaxation (n.m.r.); ■, ethyl derivative, δ-relaxation (n.m.r.); X, dodecyl derivative, γ-relaxation (n.m.r.); △, dodecyl derivative, ε- relaxation (n.m.r.); ▲, dodecyl derivative, ε-relaxation (dielectric). Only the long component of the rotating-frame data is represented

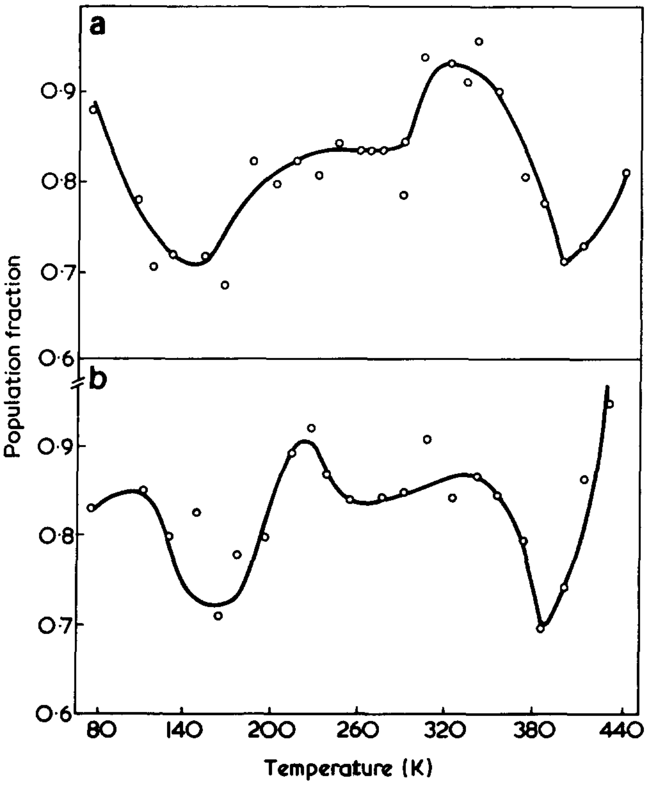

Figure 11 Relative intensity of the long component of the rotating-frame data as a function of temperature. (a) dodecyl derivative; (b) octadecyl derivative

tion times becomes smaller. For the shorter chain lengths in the series (methyl, ethyl and amyl) the errors in $T_{1\rho}$ (short) are particularly large and the population fractions subject to such scatter that no discernible trends can be ascertained.

DISCUSSION

Spin diffusion

That spin diffusion relaxation mechanisms are a major factor in this series has already been demonstrated in *Figure 11*. Further evidence for the existence of spin diffusion can be found from the magnitude of the relaxation time at the various minima illustrated in *Figures 1–9*. According to established formulae[9] for those magnitudes it is clear that, because of their high value, they are substantially affected by spin diffusion.

Spin diffusion effects occur because excess energy can remain in the spin system for a long time (compared to T_2) before being transferred to the lattice via preferred relaxation sites. Although a number of such sites may exist in a typical lattice[10], only two need concern us for this series of purified amorphous, oxygen-free polymers. The first of these is the well established sink for spin energy provided by rapidly rotating methyl groups[11]. Two sites for methyl groups exist in this series, at the termination of the alkyl chain and as end groups on the main chain (a consequence of azobisisobutyronitrile initiation in the synthesis of the precursor styrene–maleic anhydride copolymer). With the exception of the methyl derivative, where it occurs at a very low temperature, all the polymers exhibit substantial methyl group minima in the T_1 data. This mechanism is responsible for relaxing the spin energy along the whole polymer chain and results in the anomalously high values of the relaxation times at the minima. This phenomenon is well known and almost universal in materials containing methyl groups. Since the polymers in the series are so similar, it would be expected that this preferential relaxation would affect all the polymers in the same way. However, we have to account for the increasing dominance of spin diffusion as the alkyl chain length increases – an influence which is sufficiently powerful to produce the anomalous intensity variations depicted in *Figure 11*. The cause for this is the presence of a second important site for spin diffusion interactions.

Temperature-dependent $T_{1\rho}$ component intensities, unrepresentative of the number of contributing nuclei, have been observed on several occasions[12] and attributed to spin diffusion between different phases within a polymer. A similar influence is observed between water and protein molecules resulting in cross-relaxation in hydrated collagen[13]. We suggest the following argument to account for the importance of spin diffusion in our substrates.

It has been established that, in these and similar materials[3,4] there is no X-ray-observable crystalline phase. However, the present $T_{1\rho}$ data, existing dielectric work[3,4] and X-ray evidence[5,14] all indicate the presence of ordered regions within an amorphous phase. In particular, the X-ray results show two amorphous haloes in favourable cases, which have been interpreted as originating in local order in both main chain (helical) and side chain. It was proposed that for alkyl chain lengths up to and including C_5 the main chain conforms to a 3_1 helix while the increasing side chain influence above this length begins to dominate the structure. The spin diffusion behaviour exhibited by this series is consistent with this morphology. For the lower numbers of the series *Figures 1–3* show that the relaxation behaviour of the two regions is essentially independent with little correlation between the two. Indeed, the assignments to similar relaxations proposed in *Table 1* must be regarded as tentative. The morphology is determined by main-chain conformations and spin diffusion effects arise principally from the CH_3 'sink'. In the C_7 derivative and above we see that the relaxation behaviour of the two regions becomes increasingly similar with increasing chain length. The stacking of side chains is now the principal structure-determining factor and there is consequently a close physical interaction between the two phases allowing cross-relaxation by spin diffusion. This results in the appearance of relaxation minima which do not necessarily reflect the true motional characteristics of a phase but rather the coupling of spins. Thus anomalous intensity patterns are generated as shown in *Figure 11*. That methyl rotation is still a potent factor in spin diffusion is apparent from *Figures 4–9*. Support for this structure variation is also to be found in the characteristics of the other relaxations.

αβ-relaxation

Existing relaxation work[3] indicates that the α- and β-relaxations are very closely associated, even at very low frequencies ($\sim 10^{-3}$ Hz), and their resolution is often unsatisfactory. It is clear from such data that these two relaxations will have merged at the frequencies employed in this investigation and are represented by the high temperature relaxation minima found here which should be considered as a combined αβ process.

There is little doubt that this relaxation is associated with the micro-Brownian motion accompanying the glass–rubber transition. *Table 1* shows a strong correlation between the dielectric and n.m.r. observations and we suppose that, where no minimum has been observed, this is due to temperature limitations on the part of the apparatus. The calculated activation energies reveal much lower values than the corresponding dielectric evidence. This is not surprising in view of the combined nature of the relaxation and the relative efficiency of the relaxation process in the two cases. In the dielectric case, the chain dipole resides principally in the maleimide ring and the observation of this relaxation requires the substantial motion of a relatively rigid entity. Contrastingly the n.m.r. experiment is responding to the motion of protons in the more facile aspects of the complex variety of modes contributing to the overall behaviour. There is evidence in the Figures and *Table 2* that this relaxation is both more prominent and more difficult in that area associated with the short $T_{1\rho}$ component, particularly in later members of this series. This suggests, in common with other materials exhibiting non-exponential decays[7], that the short component is associated with the more disordered regions in the polymers.

γ-relaxation

As stated previously, we have supposed that at the high temperatures necessary to observe T_1 minima in these polymers, the γ-relaxation has merged with the *αβ*-process. Justification for this is derived from comparisons with dielectric data illustrated in the relaxation map of *Figure 10* where we observe the $T_{1\rho}$ γ-relaxations in close proximity to the dielectric γ-position.

The γ-relaxation is present in all members of the series but the short $T_{1\rho}$ component is much less prominent and even missing in the short chain polymers. Furthermore, this relaxation is probably the least susceptible to spin diffusion and cross relaxation in that it only gradually becomes more prominent as the chain length increases and in consequence its intensity component behaviour is not so clearly anomalous. We suggest that this relaxation originates in the ordered phase only and its appearance in the short $T_{1\rho}$ data is entirely due to spin diffusion. It is worthwhile recollecting that the dielectric γ-relaxation was the most susceptible to quenching treatments and in the ethyl derivative particularly it was virtually removed from the spectrum[3]. The activation energies (*Table 2*), although approximate, are consistent with a mechanism that is quite independent of the length of the alkyl side chain and similar to those recorded by dielectric relaxation[2–4] and by both electrical and mechanical techniques, in the precursor styrene–maleic anhydride copolymer[15]. The molecular mechanism is therefore a property of the helical nature of the ordered parts of the structure and is consistent with a ring-twisting process in the maleimide ring.

δ-relaxation

This relaxation is observed only in the short alkyl chain length members of the series. As with the γ-relaxation for these polymers, the short $T_{1\rho}$ component is relatively structureless and the δ-relaxation appears to be absent (the assignment in the methyl derivative is tentative). The minima in both T_1 and the long $T_{1\rho}$ components are relatively shallow and the appearance temperatures are somewhat erratic. The relaxation map (*Figure 10*) reveals that this relaxation occurs at lower temperatures in the n.m.r. data compared with the available dielectric results, particularly at the $T_{1\rho}$ frequency which also leads to a lower activation energy. Again contrasting with this n.m.r. work, the dielectric δ-relaxation is relatively prominent, being nearly an order of magnitude more than the γ-process.

The molecular origin is obscure; it must occur in the ordered regions of the structure and be specific to the main-chain dominance present in the lower members. However, it does not depend on helical order since this is present in all polymers, albeit in a modified form for the longer side-chain materials[3]. We tentatively suppose that it is related to chain-stacking or ordering for 3_1 helices, its increased motional facility in n.m.r. *vis-à-vis* the dielectric mode again reflecting the relative ease of proton motion compared with that for dipole orientation in these materials.

ε-relaxation

This is, in a sense, the complement of the δ-process since it makes its appearance as the latter relaxation disappears and the two are coexistent in the C_5 and C_7 members. Both the appearance temperature and activation energy increase as the chain length increases. This relaxation is prominent in both $T_{1\rho}$ components with similar relative efficiencies. No doubt this is partly due to the influence of spin diffusion but the consistently lower activation energy appropriate to the short component suggests that such a mechanism is not the principal factor governing the appearance of this minimum in the disordered regions. Clearly the motion responsible is occurring in chain dominated areas of the structure, becoming more hindered as chain entanglement increases, but always more facile in disordered areas where the steric hindrances are less severe. The low activation energy (12–40 kJ/mol) is less than would be expected for the crankshaft-type motion that is known to occur in polymers containing methylene chains[16], but some related mechanism is appropriate. It must be pointed out that dielectric work has revealed the existence of a very small relaxation in the C_{12} derivative [3] which correlates quite well with the n.m.r. data (*Figure 10*). The results were admittedly sparse and insufficiently well documented to quote an activation energy, but the existence of a dipolar component indicates that a simple methylene group motional mode is too naive a picture. However, in regions of alkyl chain entanglement, even such a mechanism must be transmitted to the backbone and will result in a dipole movement. In contrast, a relaxation with similar appearance temperature and activation energy (19.5 kJ/mol), occurs in poly(*N*-vinyl succinimide)[17]. This has been assigned to the motion of methylene units in the side chain and is dielectrically inactive.

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