

Molecular Motions in Bisphenol A Polycarbonates as Measured by Pulsed NMR Techniques. II. Blends, Block Copolymers, and Composites

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Synopsis

Molecular motions in several polyblends and composites based on bisphenol A polycarbonate were investigated over a wide temperature range by means of two pulsed nuclear magnetic resonance methods: the spin-lattice relaxation time T_1 and the spin-lattice relaxation time in rotating frame $T_{1\rho}$. Characteristic changes in the transitions of the polyblends and composites with respect to the transitions of unmodified homopolymers and copolymers were observed. By selecting different types and quantities of materials to modify the matrix (bisphenol A polycarbonate) these changes were analyzed. It was found that the multiple transitions in the composites and polyblends were not always combinations of the transitions present in the constituent materials, but depended on compatibility of the polymers and the type of molecular motions of the individual components. Unlike other methods of investigating polymers in bulk, nuclear magnetic relaxation methods are sensitive to supramolecular structure or morphology. Supplemented with transmission and scanning electron micrographs, the results from these experiments led to the postulation of interaction domains or zones between the two phases in certain nonhomogeneous polymer systems in which the motions in one phase (usually the continuous phase) were affected by the motions in the other phase (usually the dispersed phase). Information on the nature and extent of this interaction was obtained by the NMR relaxation methods. The experimental results reflect not only the presence of separate phases in the nonhomogeneous materials, but also the complex heterogeneity of such systems. The results suggest correlations between internal molecular motions and physical properties of the materials examined. Based on the above concepts, a mechanism of rubber reinforcement was proposed. The impact strength of a rubber-modified polymer is related to the apparent volume of the rubber phase. This volume consists of the actual volume of the rubber plus the affected portion of the surrounding glassy matrix which, assisted by the segmental motions of the rubber, assumes the same motions.

INTRODUCTION

When the properties of polymers are measured as a function of temperature, changes are noted at specific temperatures which have become associated with transitions between modes of internal motion possible for the macromolecule. Not only homopolymers and copolymers but also multi-

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phase systems such as polymer blends, block and graft copolymers, and composites have been studied. Hopefully, the techniques can be used to study the interfacial layer between the phases or the interaction between phases. An earlier study^{1,2} suggested that the use of nuclear magnetic resonance techniques to measure spin-lattice relaxation times of polymers and polymer blends was promising. For the measurement of relaxation times, the pulsed techniques are used whereby, instead of measuring signals at or near resonance, one observes the decaying signal following a radio-frequency pulse or the free induction decay under resonance conditions. The pertinent references are listed in part I of this series.²

The present study extends the earlier work^{1,2} by including blends, composites, and block polymers, by introduction of $T_{1\rho}$ measurements as well as T_1 data, and by including electron transmission and electron scanning micrography to observe the nature of the composites studied. Attempts were made to interpret the data in terms of the performance of the blends, particularly impact strength.

EXPERIMENTAL

Materials and Preparations

ABS. Cyclocac DH. Marbon Division of Borg-Warner Corp.

ABS-Polycarbonate Blend. A physical blend of 50 wt-% ABS designated Cycloy 800. Marbon Division of Borg-Warner Corp.

Polycarbonate-Glass Fiber Composites. General Electric Lexan 3412-131 with 20% of standard glass fibers. Also LNP Corp. 80 wt-% polymer, 20 wt-% of short glass fibers.

Polycarbonate-Polyethylene Blend. Lexan 140-111 polycarbonate resin filled with 3-4% polyethylene designated DL 666. General Electric Co.

Block Copolymers of Poly(dimethylsiloxane) and Bisphenol A Polycarbonate. General Electric Co. The silicone blocks were 20 dimethylsiloxane units long. The weight per cent of silicone was XD-207 50%, XD-213 55% and XD-201 65%.

Polycarbonate-Poly(dimethylsiloxane) Blend. A physical blend of bisphenol A polycarbonate and poly(dimethylsiloxane). Dried bisphenol A polycarbonate powder, 50 g, was added gradually with vigorous stirring to an excess of poly(dimethylsiloxane) (approximately 100 g) preheated to 210°C. The resulting melt was stirred for another 20 min to ensure homogeneity. The blend was separated from the remaining poly(dimethylsiloxane) liquid, drawn manually from its melt, cooled, and cut into short, thin strips. The material was reduced to small chunks, using an Osterizer blender. The samples were opaque polyblends containing about 10 wt-% silicone.

Polycarbonate-Butyl Rubber Blend. A mechanical blend of Lexan 140-111 bisphenol A polycarbonate with 7 wt-% Polysar Butyl 101 rubber was prepared by the procedure described earlier.¹

Specimens were prepared by molding the powders or pellets into rods 7 mm in diameter and 2 cm long, followed by quenching rapidly. The specimens were annealed for one day at appropriate temperatures to relieve stresses and to remove traces of crystallinity.³

Nuclear Magnetic Resonance Measurements

The equipment and processes are described in part I.² The transitions observed in heterogeneous polyblends were given the designation of the respective component homopolymer. The nonexponential decay of magnetization could be represented as the sum of two exponential components having different relaxation time constants. For T_1 and $T_{1\rho}$ measurements, this is given by⁴

$$M^{I+II}(t) = M_0^{I+II} \{ 1 - x [\exp (-t/T_1^I)] - (1 - x) [\exp (-t/T_1^{II})] \}$$

and

$$M^{I+II}(t) = M_0^{I+II} \{ x [\exp (-t/T_{1\rho}^I)] + (1 - x) [\exp (-t/T_{1\rho}^{II})] \}$$

where M_0^{I+II} is the equilibrium magnetization and x is the percentage of magnetization characterized by the T_1^I or $T_{1\rho}^I$ relaxation time.

Components of the nuclear signal associated with spins of different constituents of the material could be evaluated in terms of the volume or weight percentage of separate phases in the material. The following examples show such calculations.

(i) *Polymer System: Bisphenol A Polycarbonate Reinforced with 20 wt-% Glass Fibers*

Relaxation time $T_{1\rho}$	Magnetization composition (average), %	Remarks	Apparent polycarbonate composition (average), wt-%
Short	20	polymer affected by the filler	20
Long	80	unaffected polymer	80

(ii) *Polymer System: Alternating Block Copolymer of PDMS and BAP 50/50 wt-%*

The magnetization component having shorter $T_{1\rho}$ is assigned to BAP spins, and the one having a longer $T_{1\rho}$ to PDMS spins and to those BAP spins affected by the PDMS.

	Copolymer composition, wt-%	Wt of the repeating unit	No. of protons in repeating unit
PDMS	50	74	6
BAP	50	254	14

The composition of the nuclear signal calculated from the actual wt-% composition of copolymer is

$$\begin{aligned} \frac{14}{254} \times 50 \text{ BAP} + \frac{6}{74} \times 50 \text{ PDMS} &= 2.75 \text{ BAP} + 4.05 \text{ PDMS} \\ &= 40.5\% \text{ BAP} + 59.5\% \text{ PDMS} \end{aligned}$$

The composition of the nuclear signal from the measurements is actually 25% BAP + 75% PDMS.

Relaxation time $T_{1\rho}$	Magnetization composition (average), %	Remarks	Apparent copolymer composition (average), wt-%
Short	25	BAP	30
Long	75	PDMS	70

The increase of 15% represents that part of the nuclear signal which belongs to polycarbonate spins which is affected by the PDMS spins and is equivalent to $(15.5/40) \times 50 \simeq 20$ wt-% of BAP. The apparent amount of the PDMS is therefore equal to the actual amount plus the affected fraction of the BAP: $50 + 20 \simeq 70$ wt-% PDMS.

Electron Microscopy Measurements

Morphological studies of the heterogeneous polyblends were done using electron scanning and transmission microscopy.

A Cambridge Stereoscan electron microscope was used for the electron scanning micrographs. Specimens were prepared by cooling test pieces below the glass transition temperatures of the constituents in the materials, followed by fracture in an Izod impact tester. The fractured surface was rotationally shadowed with aluminium using a Varian VE 10 evaporator. The micrographs were obtained with the microscope stage tilted 25° to 35°.

Specimens for transmission electron microscopy were prepared using ultramicrotomy after hardening with osmium tetroxide. Kato^{5,6} reported that hardening can be effected by soaking the material in 1–2% aqueous osmium tetroxide from at least 48 hr at room temperature. Preferential “staining” of the rubber occurs, so that contrast between rubber and thermoplastic is enhanced.

The procedure was improved by exposing the samples to osmium tetroxide vapors for 2 hr at the top of a hermetically sealed glass container containing 2 g osmium tetroxide on the bottom, the whole at 46°C in an oven. This method produced a 2-mm penetration of the hardener and efficient, selective staining.

Thick sections, 700 to 800 Å, were made with a Reichert ultramicrotome UM-2 using glass knives. Poly(dimethylsiloxane) polycarbonate block copolymers were sectioned by freezing the materials below T_g directly

on an LKB-ultramicrotome. This was done by using an LKB Kryokit attachment. A Phillips EM300 electron microscope was used. The accelerating voltage was 80 kV, and the objective aperture was 30 μ .

Impact Strength

Measured with an Izod impact tester according to ASTM Test Method D-256 (Method A).

Flexural Modulus

Measured on an Instron Universal Testing Instrument following ASTM Procedure D-695.

Infrared Spectra

The composition of polycarbonate blend with poly(dimethylsiloxane) was determined using a Beckman IR-9 spectrophotometer.

RESULTS AND DISCUSSION

The masses of data generated were summarized best by plotting the temperature dependence of the values of T_1 and T_{1p} , rather than by attempting to record individual measurements of T_1 and T_{1p} under all experimental conditions. The temperature range was usually 100°K to 500°K.

Bisphenol A Polycarbonate-20% Glass Fiber Composite

The T_1 data for polycarbonate reinforced with 20% of short glass fibers were similar to those for pure polymer. Figure 1 shows that the T_1 minimum associated with the CH_3 group reorientation (T_δ transition) was

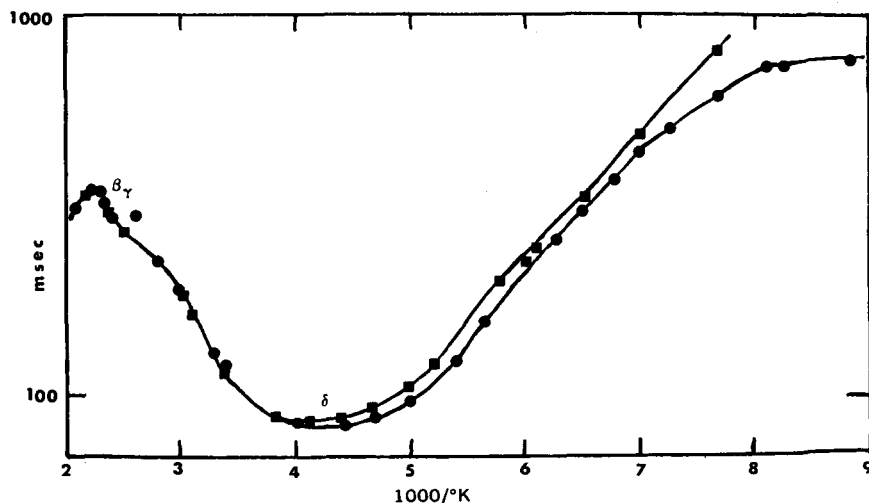


Fig. 1. Temperature dependence of relaxation time T_1 for bisphenol A polycarbonate (■) and bisphenol A polycarbonate-20% short fiber composites (●).

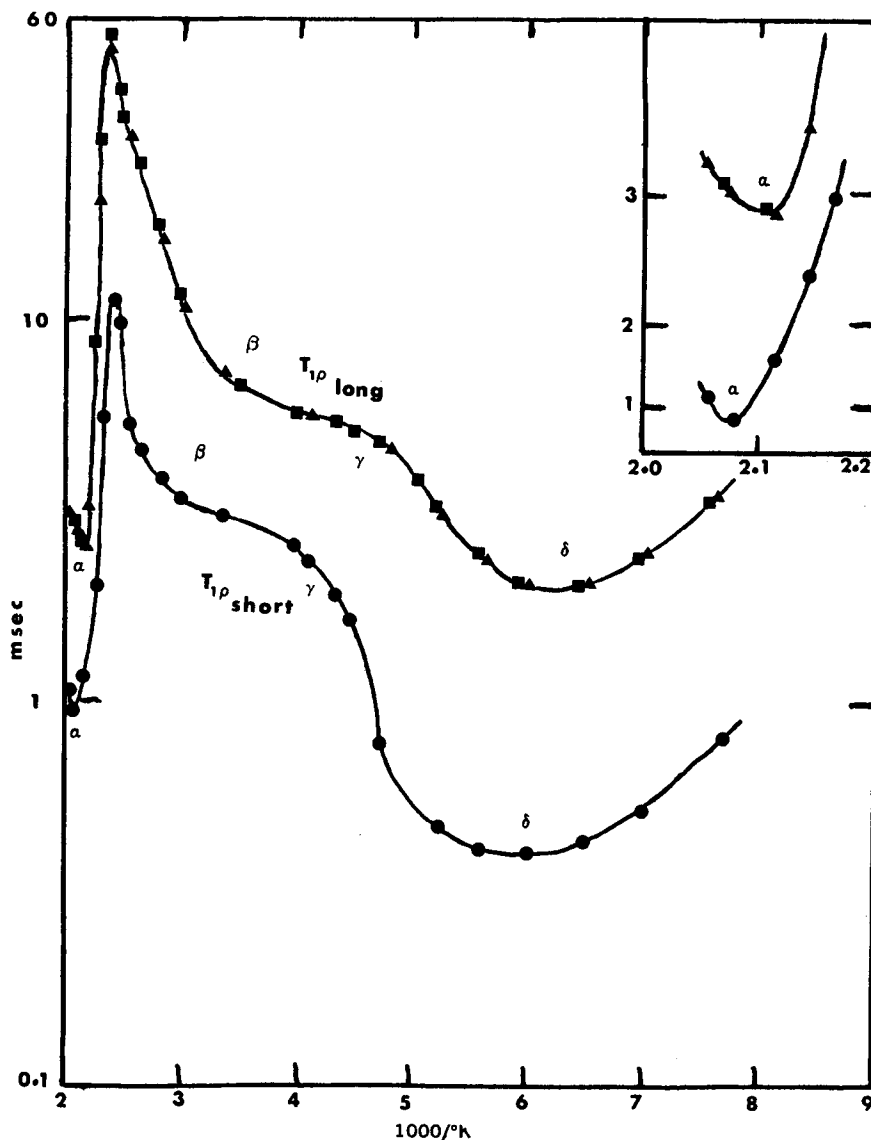


Fig. 2. Temperature dependence of relaxation times $T_{1\rho}$ for bisphenol A polycarbonate (■) and bisphenol A polycarbonate-20% short glass fiber composite (▲ and ●).

broader for a glass-filled sample, indicating a wider distribution of relaxation times for this transition and greater nonequivalence of the side groups of the polycarbonate chain in such a composite.

Unlike the T_1 data which indicated effects of the filler (glass fiber) on overall molecular mobility, the nuclear spin relaxation in rotating frame showed as the most important feature two different relaxation rates over the experimental temperature range which gave evidence of two phases in

TABLE I
Results for NMR Relaxation in Rotating Frame Experiments
for Polycarbonate-20 wt-% Glass Fiber Composite

	Component of the relaxation time	%	$\log \nu_c$	T_α , °K	$T_\beta - T_\gamma$, °K	T_δ , °K
T_{1p} (min)	short	20	5.1	483	~312-238	~164
	long	80	5.1	470	~285-222	~160

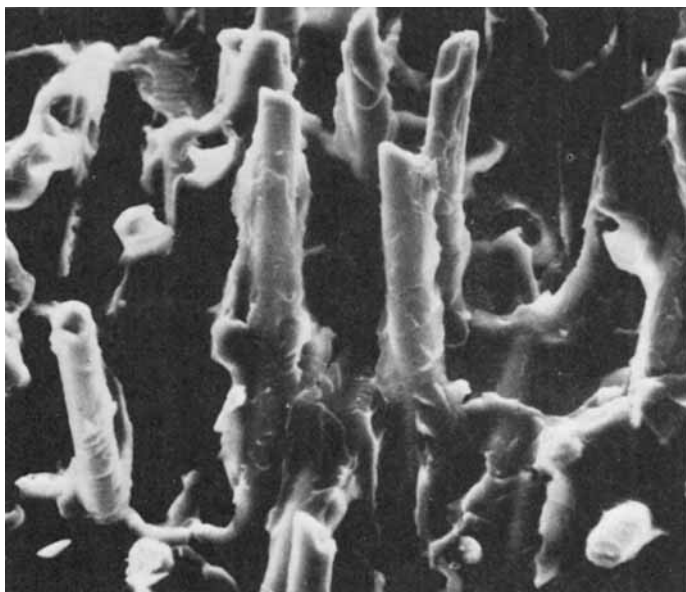


Fig. 3. Scanning electron micrograph of bisphenol A polycarbonate reinforced with 20% standard glass fiber, 1 cm = 20 μ .

the polymer matrix. (Note that glass does not have protons and produces no signal.) The T_{1p} results in Figure 2 showed this phenomenon. The polycarbonate-glass composite was characterized by a nonexponential decay of magnetization. As an approximation, the data were analyzed as the sum of two exponential decays with two T_{1p} constants. One component was about 20% and had a T_{1p} almost five times shorter than the 80% component, the one with the T_{1p} value of the pure polycarbonate (upper curve in Fig. 2). The ratio of the relaxation components was the same (20/80) for all the motions. All the observed minima for the short T_{1p} appeared to be shifted toward higher temperatures (see Table I). The minimum associated with CH_3 group reorientation was the least affected, which indicated little effect from the presence of the glass fiber on this motion. This minimum was also broader and confirmed the T_1 data.

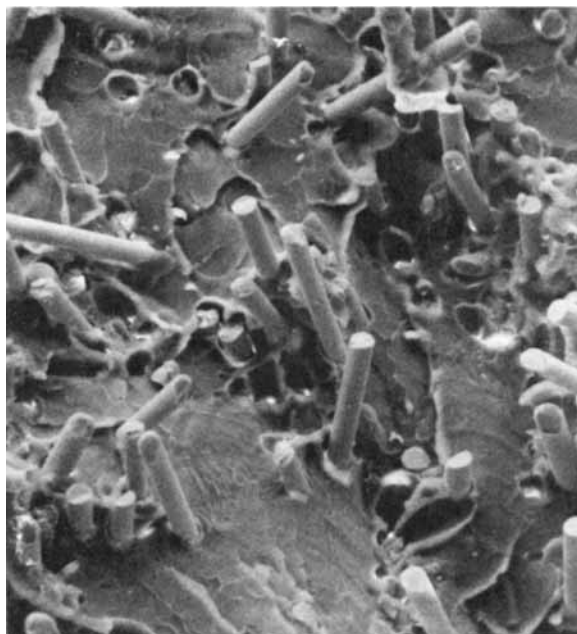


Fig. 4. Scanning electron micrograph of bisphenol A polycarbonate reinforced with 20% short glass fiber, 1 cm = 40 μ .

The explanation of the behavior of the composite is based on a two-phase model. One phase is the polycarbonate near the filler interface which imposes motional restraints on the polymer chains. The other phase is further away from the filler, and its motions are the same as these of pure polycarbonate. The amount of polymer affected by interaction with filler approximately equals the amount of filler in the composite (the sample contains 20 wt-% of glass). One would expect that this would depend also on the surface area of the filler. Previously reported effects of the filler concentration on the glass transition temperature of a polymer^{7,8} and the shift in dynamic mechanical transitions⁹ are in good agreement with these results.

The morphology of the composite used in the measurements is shown in Figure 3. The scanning electron micrograph of polycarbonate reinforced with 20% of short glass fibers is presented in comparison with a standard composite of the same composition (Fig. 4). The short glass fiber composite showed random orientation of the fibers (~ 1 mm long, 10 μ in diam.) and generally 10% to 20% higher bulk mechanical properties¹⁰ than conventional composites.

Bisphenol A Polycarbonate-Polyethylene Blend

The relaxation data for a mixture of polycarbonate and 3 to 4 wt-% polyethylene and for pure polycarbonate are summarized in Figure 5. Both

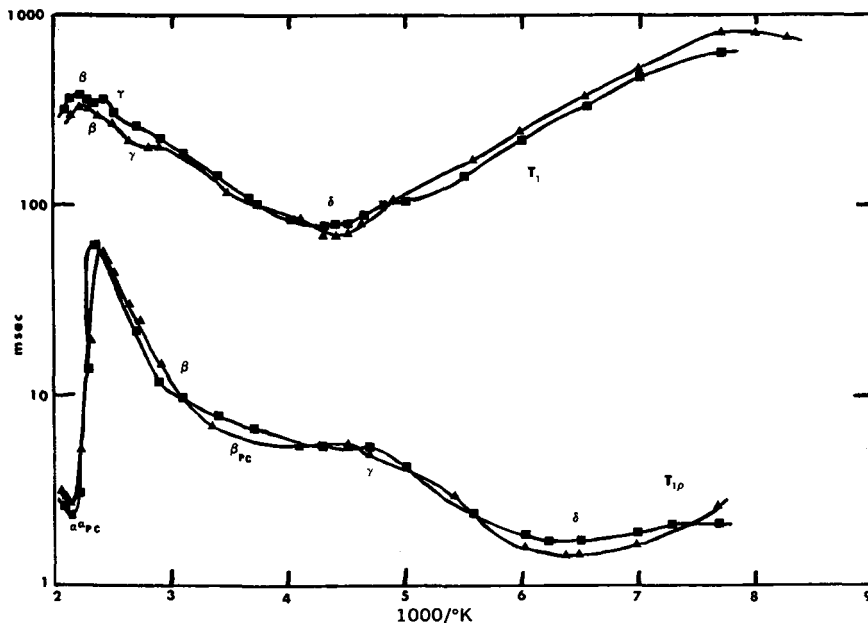


Fig. 5. Temperature dependence of NMR relaxation times for bisphenol A polycarbonate (\blacktriangle) and polycarbonate filled with 3 wt-% polyethylene (\blacksquare).

T_1 and T_{1p} data showed some effect of the polyethylene on the overall molecular mobility of the polycarbonate matrix, but no evidence of multiple phases was observed. This suggests that low percentages of polyethylene in a polyblend behaved as a filler which may affect the mobility of the surrounding matrix polymer, but the total volume affected was too small to be observed by NMR.

The morphology of this system is shown in Figures 6 and 7. The transmission electron micrograph (Fig. 6) revealed the spherical shape and uniform size (about $350 \text{ m}\mu$ in diameter) of the dispersed polyethylene phase. Scanning electron micrographs of the fractured surface of the same material (Fig. 7) also indicated incompatibility of the constituent polymers which was reflected in the poor adhesion of the polyethylene particles to the polycarbonate matrix. As a result the affected zone of the matrix polymer near the polyethylene interface is relatively small, which is in agreement with the observations made from NMR relaxation measurements.

Table II summarizes the relaxation data for this polyblend. All the observed motional minima appear affected in comparison to those of unmodified polycarbonate. The glass transition was lowered. T_β was shifted toward higher temperatures, and this motion appeared more effective (more pronounced, sharper minimum) in the blend. The T_γ transition was less affected and higher from the T_1 data although it appeared unshifted in the T_{1p} results. The T_δ minimum was unshifted in both T_1 and T_{1p} measurements, but it was broader and indicated that this motion

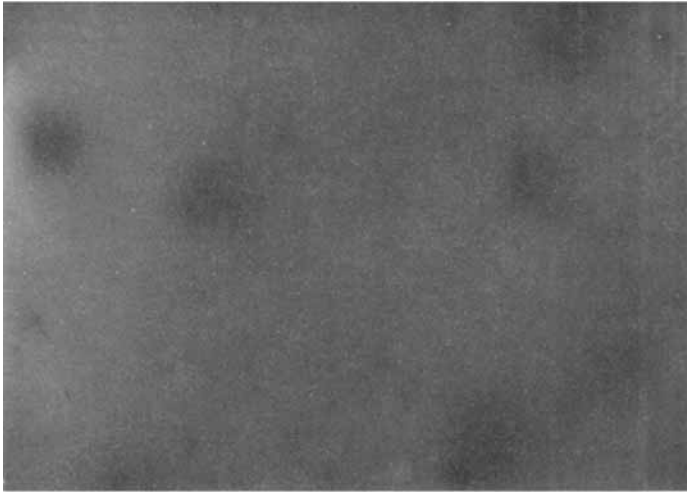


Fig. 6. Transmission electron micrographs of 97 wt-% polycarbonate-3 wt-% polyethylene blend, 1 cm = 0.5 μ .

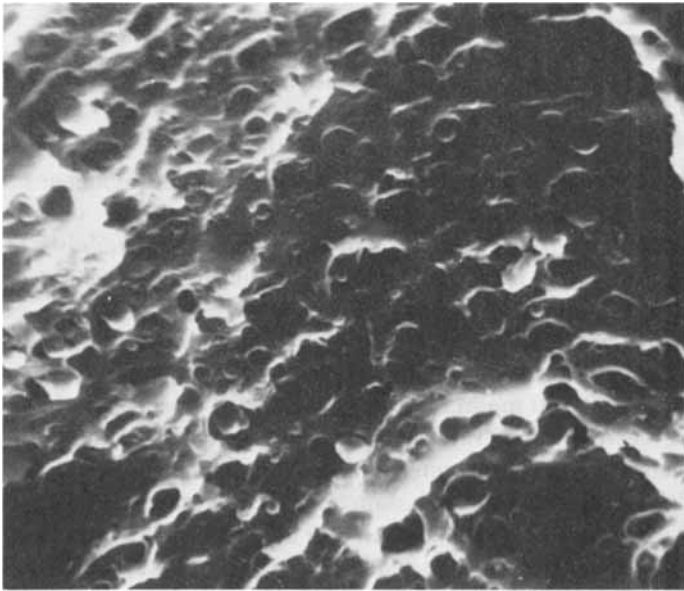


Fig. 7. Scanning electron micrograph of 97 wt-% polycarbonate-3% polyethylene blend.

(CH₃ group rotation) in the blend was somewhat less affected (lower relaxation rates at T_1 and T_{1p} minima). On the low temperature side of the T_1 minimum for this transition, a broad experimental shoulder was observed below 200°K. This was interpreted as an impurity effect of unknown origin. A similar effect was observed previously¹ and was characterized as a paramagnetic impurity. The motion of a side methyl group also showed

TABLE II
NMR Relaxation Results for Polycarbonate Modified with 3% Polyethylene

	$\log \nu_c$	T_α , °K	T_β , °K	T_γ , °K	T_δ , °K
T_1 (min)	7.6	—	~430	~390	~230
$T_{1\rho}$ (min)	5.1	465	~328	~220	~156

a wider distribution of relaxation times in polyethylene-modified polycarbonate.

Block Copolymers of Poly(dimethylsiloxane) and Bisphenol A Polycarbonate

Figure 8 shows the NMR relaxation data for three copolymers. They vary in weight per cent of silicone: curves 1, 2, and 3, 50%; curves 4, 5, and 6, 55%; and curves 7, 8, and 9, 65%. The relaxation data for bisphenol A polycarbonate, poly(dimethylsiloxane), and their 50/50 wt-% block copolymer are summarized in Figures 9 and 10.

The temperature dependence of T_1 and $T_{1\rho}$ for poly(dimethylsiloxane) exhibited three different motions between 110° and 500°K. The T_1 minimum observed at 200°K was associated with the glass transition of the polymer. The corresponding $T_{1\rho}$ minimum was observed at 170°K. Both minima correlate with dielectric data on the transition map.¹¹ The activation energy deduced from the temperature dependence of the correla-

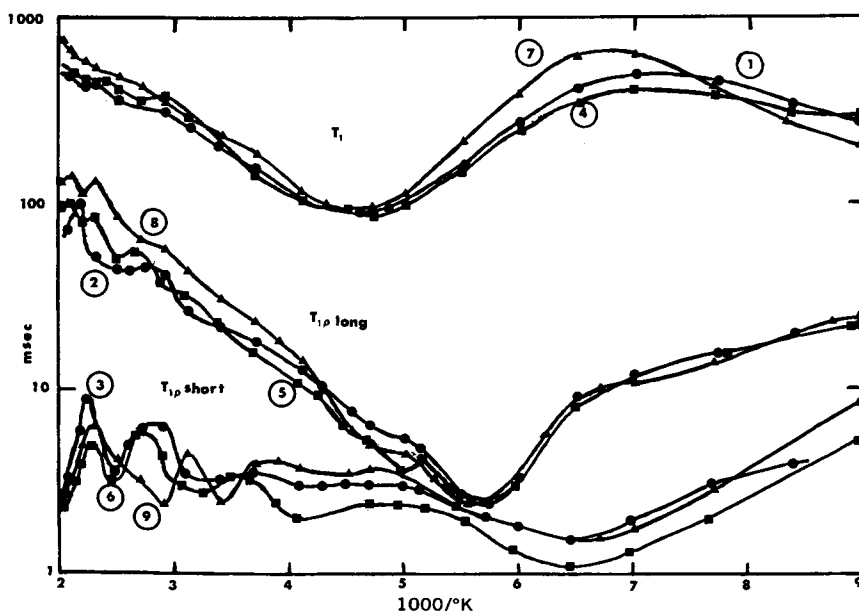


Fig. 8. Temperature dependence on NMR relaxation times for three different block copolymers of poly(dimethylsiloxane) and bisphenol A polycarbonate: (\blacktriangle) 65 wt-% silicone; (\blacksquare) 55 wt-% silicone; (\bullet) 50 wt-% silicone.

TABLE III
NMR Relaxation Data for Poly(dimethylsiloxane) (PDMS)

	$\log \nu_c$	T_α , °K	T_{L1} , °K	T_{L2} , °K
T_1 (min)	7.6	~200	~360	~400
T_{1p} (min)	5.1	~170	—	~320

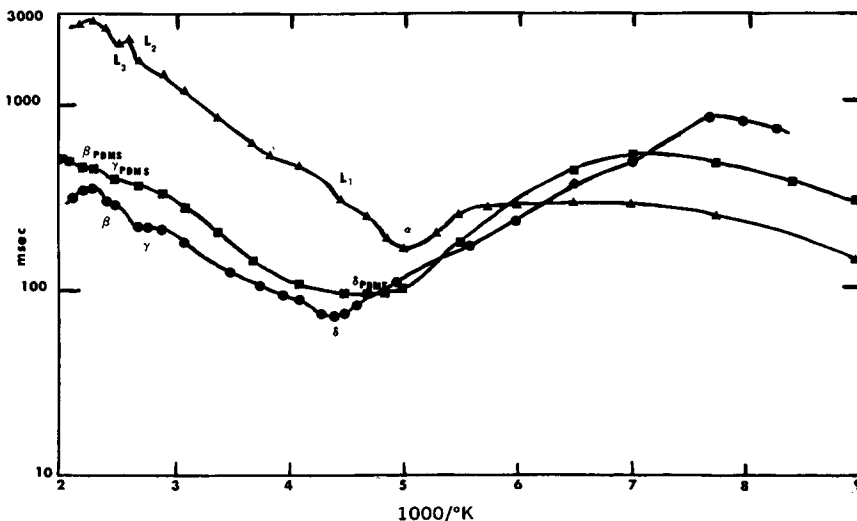


Fig. 9. Temperature dependence of relaxation time T_1 for bisphenol A polycarbonate (\blacktriangle), poly(dimethylsiloxane) (\blacksquare), and block copolymer of poly(dimethylsiloxane) and bisphenol A polycarbonate (containing 50 wt-% silicone) (\bullet).

tion frequency at low ν_c 's was more than 50 kcal/mole. The other two minima observed at temperatures $T > T_g$ were associated with liquid transitions and designated T_{L1} and T_{L2} . The observed transitions are listed in Table III.

The T_1 plot for the block copolymer of poly(dimethylsiloxane) and polycarbonate reflects the overall motional behavior of the material. The observed minima can be interpreted as a combination of the transitions present in the constituent homopolymers.

The T_{1p} data indicated the heterogeneity of the system. Nonexponential decay of magnetization was observed over almost the entire temperature range of the experiment. It was analyzed into two components, one of about 25% having a shorter T_{1p} (curve 4) and the other of about 75% with a longer T_{1p} value (curve 3, Fig. 10).

The observed motional minima on curve 3 coincided with those observed for poly(dimethylsiloxane) homopolymer (curve 2). The relaxation time values were one order of magnitude shorter, except for the low temperatures between 110° and 165°K where this difference becomes smaller. In addition, curve 3 showed one weak minimum at ~208°K. These observations

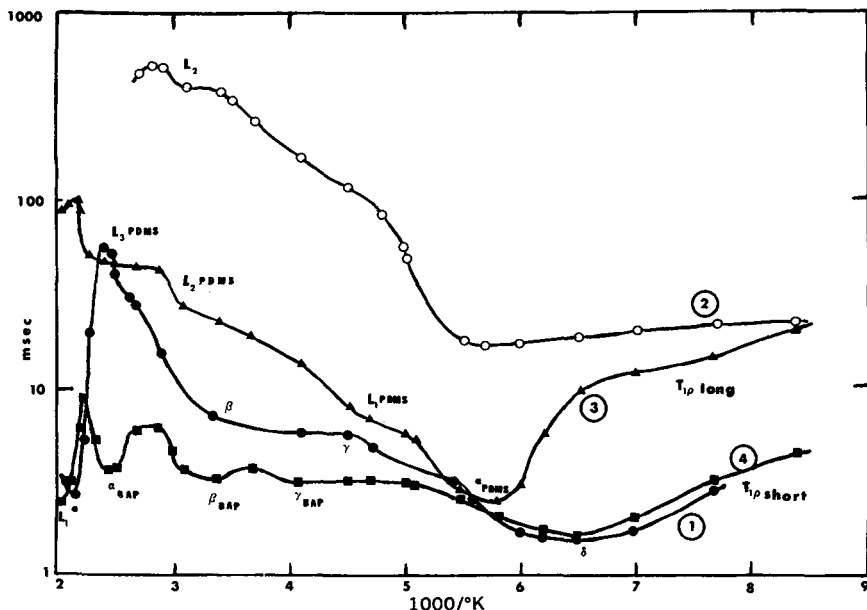


Fig. 10. Temperature dependence of relaxation time T_{1p} for bisphenol A polycarbonate (●), poly(dimethylsiloxane) (○), and block copolymer of poly(dimethylsiloxane) and bisphenol A polycarbonate (containing 50 wt-% silicone) (PDMS ▲, BAP ■).

indicated that the longer T_{1p} component represents the poly(dimethylsiloxane) phase in a block copolymer.

The results for the short T_{1p} component (curve 4) were less obvious. Four to five motional minima were indicated. The low-temperature transition at $\sim 156^\circ\text{K}$ coincided with T_g observed for polycarbonate. The other minima were at $\sim 240^\circ\text{K}$ (T_γ), $\sim 300^\circ\text{K}$ (T_β), and 410°K (T_α). There was an indication of another high-temperature transition above 500°K . These data were interpreted as motions of the polycarbonate phase in the block copolymer.

The glass transition temperature (T_g) of the polycarbonate phase was lower due to the short length of the polycarbonate block. For the alternating block copolymer with 50 wt-% siloxane, the average length of the polycarbonate block includes six monomer units if siloxane blocks are 20 units long.¹² The β - and γ -transition temperatures remained unchanged, but the motions appeared to be more effective in the short blocks. The motions above 500°K were probably associated with the liquid transition involving the entire copolymer chain.

With these findings, it is possible to compare the copolymers with the same siloxane block length but higher siloxane content and therefore shorter polycarbonate blocks. The relaxation times are given in Figure 8. Results were obtained for copolymers with 55 wt-% siloxane copolymer ($\overline{DP}_{\text{BAP}} = 5$) and 65 wt-% siloxane ($\overline{DP}_{\text{BAP}} = 3.3$) in addition to 50 wt-% siloxane copolymer ($\overline{DP}_{\text{BAP}} = 6$). All three copolymers exhibited similar

behavior. The 65 wt-% siloxane copolymer showed the largest difference in T_1 (curve 7) as well as for both components of T_{1p} (curves 8 and 9). The results for the short T_{1p} component representing the polycarbonate blocks are interesting. The minimum ascribed to the α -transition was at a lower temperature in the case of 65 wt-% silicone copolymer (345°K) than the corresponding minima for the 50 and 55 wt-% siloxane copolymers (T_α 400°K). T_β was also shifted to a lower temperature, while T_γ and T_δ remained at approximately the same temperatures for all three block copolymers. The decrease in polycarbonate block length from six to three monomer units resulted in a decrease of the α - and β -transition temperatures (both transitions are associated with segmental motions of the chain) but did not affect the temperatures for restricted rotations of the main chain (T_γ) and side group motions (T_δ).

Since the average length of the poly(dimethylsiloxane) blocks is the same in all three copolymers (20 units) the apparent differences in T_{1p} data (curves 2, 5, and 8 in Fig. 8) can be interpreted as intermolecular and intramolecular effects from the polycarbonate blocks on the liquid transitions ($T > T_g$) of the poly(dimethylsiloxane) blocks. This depends on the morphology of the particular copolymer. The observed motions for bisphenol A polycarbonate (BAP), poly(dimethylsiloxane) (PDMS), and their block copolymers are given in Table IV.

It appears that, despite the reduced precision caused by the separation of the nonexponential decay into linear components, the data were sufficiently reliable to obtain values of relaxation times and temperatures for the observed motions. From Table IV one also observed that the amount of the shorter T_{1p} component ascribed to the polycarbonate blocks equals, on the average, one half of its concentration in the copolymer.

The transmission electron micrograph of the 55 wt-% silicone copolymer (Fig. 11) revealed some morphological characteristics of these systems. The heterogeneity of the system exists on a very small scale from 50 to 100 Å. The micrograph showed that polycarbonate blocks were aggregated in discrete domains (darker regions) separated by predominantly poly(dimethylsiloxane) phase. The alternating block copolymers were unique in their morphology because of the short length of the blocks. The physical blend prepared from bisphenol A polycarbonate and poly(dimethylsiloxane) of approximately the same chain length as the silicone blocks in the copolymer showed drastically different morphology (Fig. 12).

The extensive studies of these systems done recently^{13,14,15} confirmed the microdomain structure over the entire range of compositions, molecular weights, and block lengths. It was also proposed¹⁴ that discrete particles of associated polycarbonate blocks existed in the silicone matrix at low polycarbonate contents. Both continua exist at intermediate concentrations, and silicone particles in a polycarbonate matrix exist at the high concentrations of the polycarbonate. A model proposed by LeGrand^{15,16} implied that polycarbonate blocks were associated to form domains irrespective of the composition of the copolymer. A distribution of the poly-

TABLE IV
NMR Relaxation Data for BPA, PDMS, and Their Alternating Block Copolymers

wt-% PDMS	Block copolymer \overline{DP} BAP	Correlation frequency $\log \nu_c$	% (Average) component of signal	T_{α} , °K	T_{β} , °K	T_{γ} , °K	T_{δ} , °K	T_{L1} , °K	T_{L2} , °K	T_{L3} , °K	Remark
0	—	120	—	—	~417	~370	~230	—	—	—	BAP
50	20	6	—	470	~285	~220	~156	—	—	—	overall PDMS
			75	~170	~455	~400	~213	~210	~322	~400	
			25	~410	~300	~240	~155	~500	—	—	BAP
55	20	5	—	—	~455	~380	~213	—	~400	~455	overall PDMS
			78	~175	~300	~230	~155	~500	—	—	
			22	~410	~300	~230	~155	~500	—	—	BAP
65	20	3.3	—	—	475	435	217	~210	~400	~455	overall PDMS
			82	~175	—	—	—	~500	—	—	
			18	~345	~290	~240	~155	~500	~363	~400	BAP
100	20	—	—	~200	—	—	—	~200	~322	(>370)	PDMS
			—	~170	—	—	—	—	—	—	



Fig. 11. Transmission electron micrograph of poly(dimethylsiloxane)-polycarbonate block copolymer (55 wt-% of silicone), 1 cm = 0.2 μ .

carbonate blocks in the rubbery siloxane phase was postulated in order to explain certain mechanical and optical properties. The exact nature of the domain is still unknown, but it was suggested that instead of the thermodynamic phase boundary at the surface of the domain, phase boundaries exist within the system.¹⁷

In order to examine the role which domains play in the physical properties of these systems, several investigators had found evidence of multiple transitions by using DTA, dielectric, and mechanical spectroscopy methods.^{12,15} In some cases, transitions observed have been correlated with the T_g 's of the constituent homopolymers. The NMR relaxation experiments gave evidence of multiple phases. Supported by the available physical and morphological information, these observations can be rationalized in the following manner.

Polycarbonate blocks are partly associated in domains which show motional and therefore physical characteristics of the homopolymer with short chain length. In between such regions, the nature of the material is dominated by poly(dimethylsiloxane) blocks. As a result of such dynamic interaction, the polycarbonate blocks in "boundary layers" (or those extended between associated regions) assume the motional frequencies of poly(dimethylsiloxane), thus reducing the apparent volume content of polycarbonate blocks by one half of the actual content of copolymer. The results mechanical properties of these copolymers depend not only on the transitions of the domains (rigid polycarbonate) but also on those of the volumes in between, which, for the copolymer compositions examined, were very similar to those of pure poly(dimethylsiloxane).

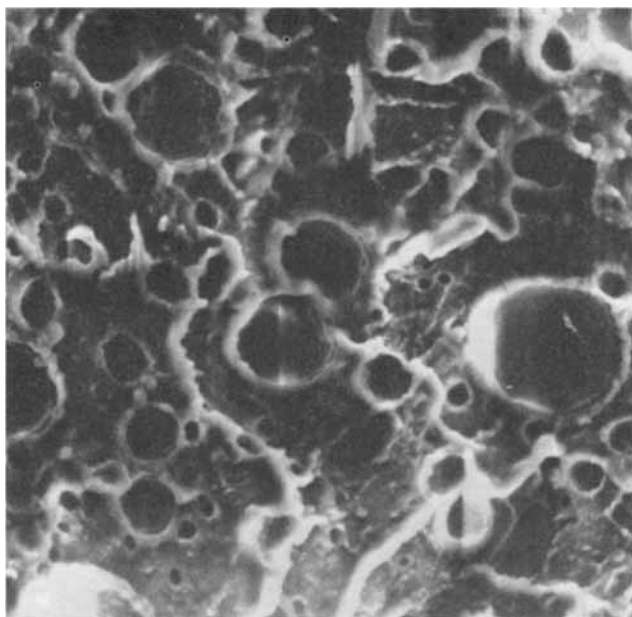


Fig. 12. Scanning electron micrograph of physical blend of poly(dimethylsiloxane) and polycarbonate (10 wt-% silicone).

Bisphenol A Polycarbonate-ABS (Acrylonitrile-butadiene-Styrene) Polyblend

A physical blend of polycarbonate and ABS is a three-component system consisting of polycarbonate phase and polybutadiene particles (rubber phase) in a continuous matrix of styrene-acrylonitrile polymer (SAN phase). The electron micrographs of 50/50 polycarbonate-ABS polyblend showed a more complex morphology of this system. Figure 13 indicated that the three phases were not separated completely. The polycarbonate phase (light areas on the transmission electron micrographs) was discontinuous consisting of irregularly shaped discrete particles about 3 to 7 μ long and about 1 to 2 μ wide. This phase contained occlusions of polybutadiene and SAN. Polybutadiene was present in the form of discrete spherical particles of about 50 to 350 $m\mu$ in diameter (dark areas). The cellular structure of rubber particles indicated the presence of the rigid (SAN) component, which is typical for grafted copolymers.⁶

Figures 14 and 15 show the scanning electron micrograph in comparison with the transmission electron micrograph of the fractured surface and indicate good adhesion between the phases. Figure 16 shows details of the fracture surface of the same material taken from the area of high stress concentration which had developed during the fracture impact. The micrograph showed stress-induced orientation of the polycarbonate phase in the material in comparison with unoriented portion of the surface (Fig. 17).

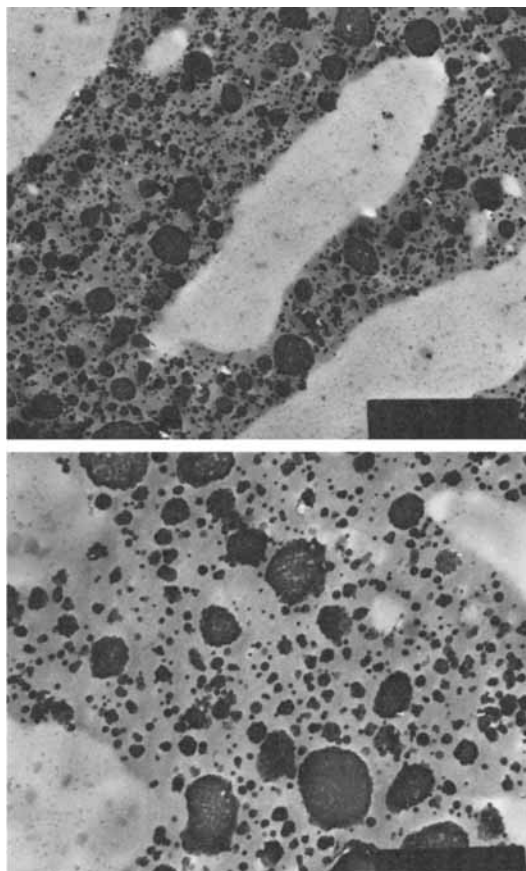


Fig. 13. Transmission electron micrographs of 50 wt-% polycarbonate-50 wt-% ABS blend at different magnifications, upper 1 cm = 0.6μ ; lower 1 cm = 0.3μ .

The NMR results for polycarbonate-ABS blend are presented in Figure 18 together with those for polycarbonate homopolymer. A nonexponential decay of magnetization was observed for both T_1 and $T_{1\rho}$ relaxation times over most temperatures between 110° and 500°K . The data were approximated by the sum of the two exponential decays representing the fractions of the total nuclear signal.

The T_1 data (curves 3 and 4) from Figure 18 showed that the longer of the times (curve 3) was about 75% of the nuclear signal, except for the temperatures between 210° and 280°K where T_1 (long) was about 50%. The 25% of the signal with shorter T_1 is plotted as curve 4. Curve 1 is for pure polycarbonate.

The $T_{1\rho}$ data (curves 5 and 6) from Figure 18 for long and short relaxation times agreed well with the T_1 data. Exponential decay of magnetization was observed between 250° and 350°K . Between 150° and 170°K , the fractions for both components were almost equal (50/50); and for the rest of the temperatures, the components were 25% for shorter and 75% for longer relaxation times.

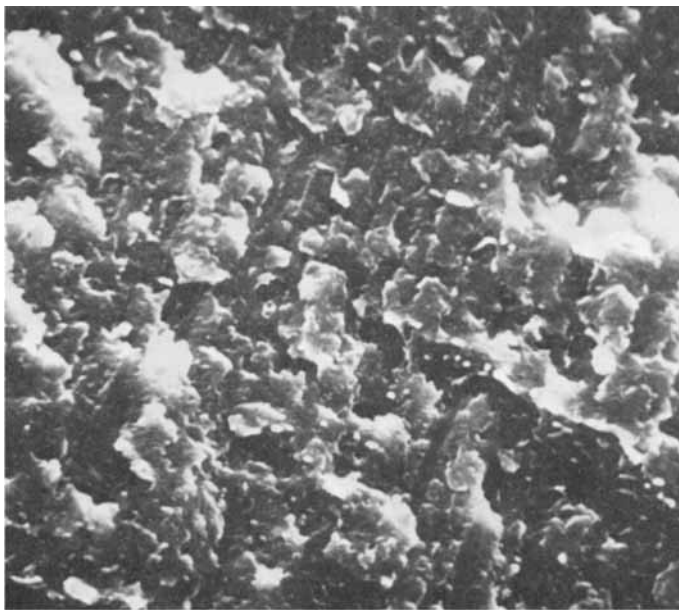


Fig. 14. Scanning electron micrograph of polycarbonate-ABS blend, 1 cm = 10 μ .

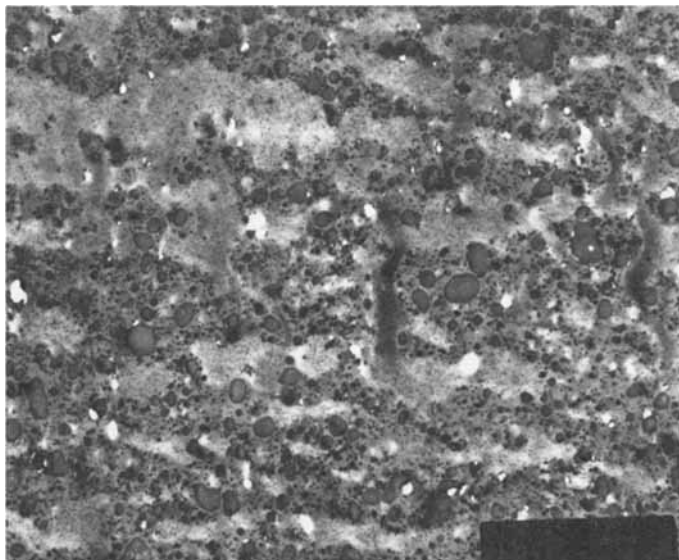


Fig. 15. Transmission electron micrograph of polycarbonate-ABS blend, 1 cm = 2 μ .

The procedure used to resolve the nonexponential decay signals into linear components reduced the reliability of the data in this case. The necessary approximation of analyzing the signal as the sum of two linear components despite the fact that the system itself consists of at least three phases is particularly significant. Fortunately, polybutadiene exhibits only one motional minimum over the temperature range of the experiment,¹⁸ which makes such approximations more acceptable. In spite of

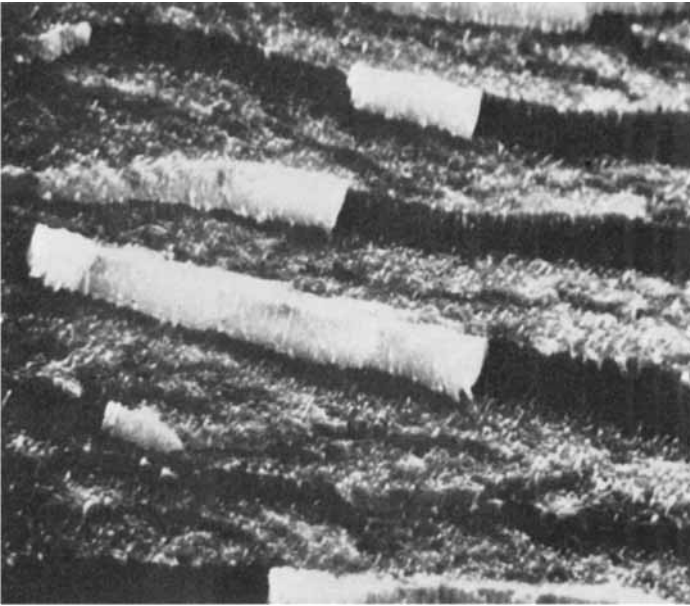


Fig. 16. Scanning electron micrograph of polycarbonate-ABS blend showing stress orientation of the polycarbonate phase, 1 cm = 10 μ .

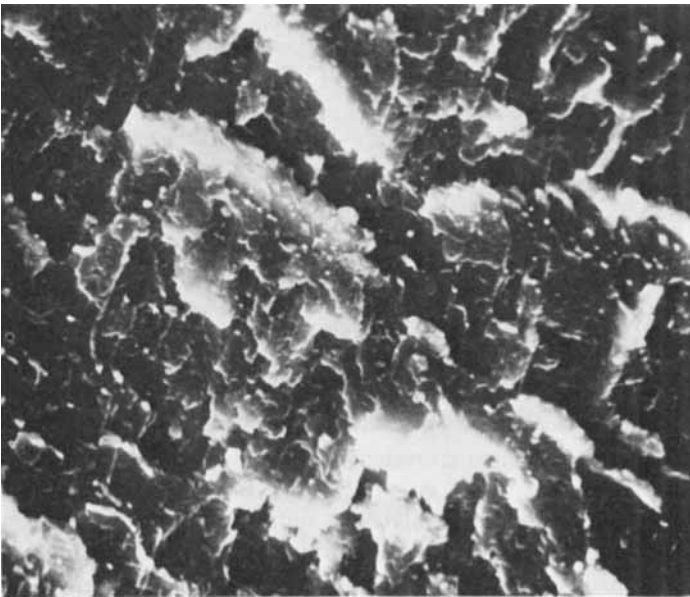


Fig. 17. Scanning electron micrograph of polycarbonate-ABS blend in which stress orientation is absent, 1 cm = 10 μ .

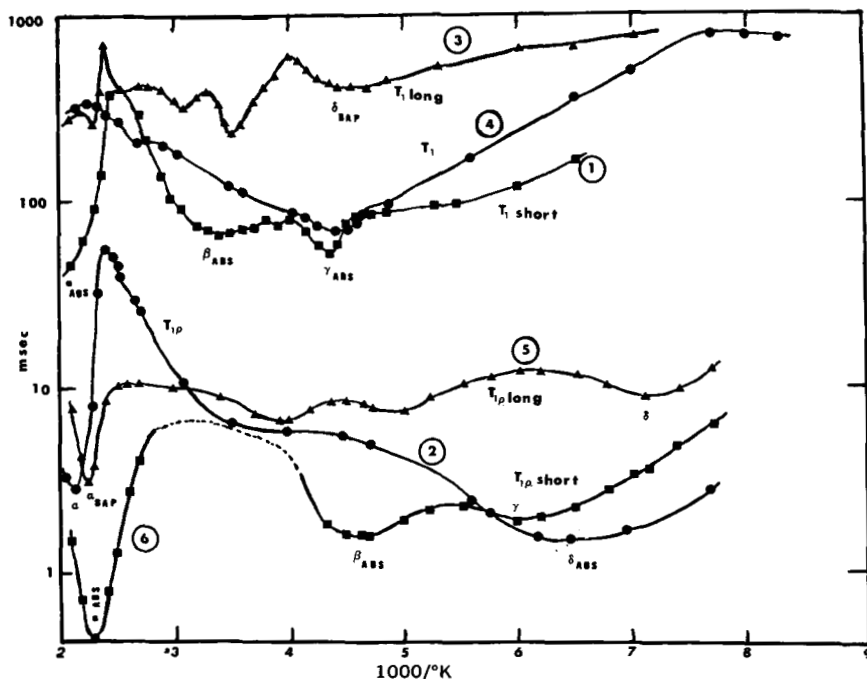


Fig. 18. Temperature dependence of NMR relaxation times for bisphenol A polycarbonate (●) and bisphenol A polycarbonate-ABS blend (■, ▲).

these limitations, the discussion is based only on the main features of the relaxation plots in Figure 18.

The NMR relaxation data for polystyrene and polybutadiene taken from the literature together with dielectric data for polyacrylonitrile are given in Table V. Based on a comparison of the data in Table V and the data for polycarbonate (curves 1 and 2) with the temperatures and relaxation time values for the minima observed in the polyblend, the longer relaxation times (curves 3 and 5) were ascribed to the polycarbonate phase and the shorter ones (curves 4 and 6), to the ABS phase. The relaxation between the phase composition of the polyblend and the fractions of the short and long components of the relaxation times were as follows:

	Content, wt-%	C_1	C_2^*	
SAN Copolymer	42	25	25	50
Polybutadiene	8			
Polycarbonate	50	75		50

where C_1 = nuclear signal composition at the temperatures where the polybutadiene motion is not effective; C_2 = nuclear signal composition at the temperatures where the polybutadiene motion is effective; and * = deduced values (see below).

TABLE V
Published NMR (and Dielectric) Relaxation Data
for Constituent Homopolymers of ABS

Polymer	wt-% in ABS	log ν_c		T_1 or T_{1p}	T_g , °K	Ref.
				value, msec		
Polystyrene	62	T_1 (min)	7.6	50	365	(19)
		T_{1p} (min)	4.8	0.5	420	(19)
Polybutadiene	16	T_1 (min)	7.6	50	243	(20)
Polyacrylonitrile	22	(dielec)	4.8	—	420	(10)

The above findings can be rationalized in the following way. Each phase comprising the blend exhibited distinctive motional properties which could be characterized as motions of homogeneous polymers (namely, polycarbonate, polybutadiene, and SAN copolymer) modified by the occlusions present in the phase. At the temperatures where the main chain motions of the elastomer phase were not effective (motions associated with T_g of polybutadiene), the motions of the material immediately surrounding the polycarbonate particles were affected by the polycarbonate phase. The affected portion of the material assisted by the motions of the polycarbonate phase exhibited the same characteristics as the polycarbonate phase itself. Since NMR measures the motions of the discrete phase and affected surrounding zone as the same, this transforms these motions into the apparent volume content of polycarbonate, which is 75%.

Near the temperatures where motions of the polybutadiene chains were effective, the rubber phase was the one affecting the dynamics of the surrounding SAN material in a similar way, except that the interaction in this case was more effective. The affected portion of the material surrounding the rubber particles was about twice its actual volume. The resulting apparent volume of the polybutadiene was about 25%. The increased interaction of the rubber particles with the surrounding material could be interpreted in terms of a different morphology (smaller size, spherical shape) and different dynamics (increased flexibility) of the rubber.

General Discussion and Summary

Based on the transitions of bisphenol A polycarbonate, molecular motions in different types of heterogeneous polymer systems based on bisphenol A polycarbonate were studied over a wide temperature range. Using high ($\sim 10^8$ Hz) and medium ($\sim 10^5$ Hz) experimental frequencies, characteristic changes in all of the examined materials were observed. The interpretation of these effects is qualitative and given in terms of the component materials of the system. For the heterogeneous blends, morphological information obtained by electron microscopy provides supporting information for the interpretation of the relaxation results.

The various heterogeneous polymer systems observed in the experiments included alternating block copolymers in which heterogeneity existed on a small scale (~ 100 Å) in the form of microdomains, physical mixtures with two or even three distinct phases present, and a composite with an

inert rigid filler. They differ in their morphology, nature, quantity, and number of constituents present.

Nuclear magnetic relaxation studies of these systems showed evidence of multiple phases or complex heterogeneity. In all of the materials investigated, it was found that one phase affects the motions of the surrounding material in such a manner that the affected zone (layer, volume) exhibits motional properties which are similar to those of the discrete phase itself. The affected volume could be defined as an *interaction zone* the size of which depended on morphological (supramolecular) and dynamic (motional) characteristics which were governed by the thermodynamics of the system.

If the relaxation time values were different enough, NMR will detect the motions of each phase as a separate linear component of the nuclear signal, thus transforming the motions of the phase into the *apparent volume* content of that phase. A difference between apparent and actual volume content in the material is the interaction zone. The NMR relaxation results for the heterogeneous polymer systems can be interpreted in terms of the concepts introduced.

Polycarbonate modified with 20 wt-% short glass fibers showed that about 20 wt-% of the matrix was affected by the presence of the inert filler. The interaction zone around the filler (where the motions of the matrix was restricted in respect to the material further from the filler) was about equal to the volume of the filler present. Similar effects of the morphological changes on the polymer induced by the filler using the NMR relaxation methods have been observed by several investigators.^{21,22,23}

In block copolymers of poly(dimethylsiloxane) and polycarbonate, the motions of the polycarbonate blocks between the associated regions were assisted by the motions of flexible (liquid-like) poly(dimethylsiloxane) blocks. This reduced the apparent volume of polycarbonate by 50% in respect to the actual volume for all three copolymers studied.

In a polycarbonate-ABS polyblend, polycarbonate particles affected the motions of the surrounding material at temperatures where motions from the polybutadiene phase were not active. The apparent volume of the polycarbonate increased by 50% in respect to its actual content. Near the glass transition temperature for polybutadiene, the rubber phase became dominant in affecting the motions of surrounding material. Since the elastomer was more effectively dispersed and more flexible than polycarbonate, the interaction zone was about twice its actual volume. The latter result is in agreement with T_1 data for rubber-modified polycarbonate obtained from the previous measurements.¹

Scanning electron micrographs (Figs. 19 and 20) indicated the morphology of the polyblend. In addition to the discrete spherical particles of about 0.3 μ in diameter, the "rope-like" morphology of the rubber phase was observed. This particular morphology, together with the structural similarities between the phases (both polymers have two methyl groups attached to a carbon atom of the main chain), ensured good dynamic compatibility which resulted in particularly efficient phase interaction in this material.



Fig. 19. Scanning electron micrograph of polycarbonate and 7 wt-% butyl rubber blend at high magnification, 1 cm = 0.2 μ .

In order to relate these results to the mechanical properties of heterogeneous materials, the relation of molecular motions to the impact strength of rubber-modified thermoplastics must be considered. Various explanations proposed in connection with the mechanism of rubber reinforcement do not provide a definite answer. The following explanation of this phenomenon is based on the conclusions made from NMR relaxation data for heterogeneous polymer systems.

The presence of a small percentage (5 to 7 wt-%) of the rubber in a rigid matrix introduces a low-temperature transition in the system. This transition, usually called "beta transition," can be identified as a glass transition of the rubber, and the motions associated with it are thus general main-chain motions.

A portion of the matrix material near the rubber interface, assisted by the motions of that phase, assumes similar motions. The amount of affected material defines the interaction zone and depends on dynamic compatibility between the phases in the system. In rubber-reinforced materials in this zone may be two to three times the volume of the rubber. As a result, the apparent volume of the rubber is three to four times its actual volume. The apparent volume (rubber plus the volume of affected matrix) is related to the impact strength of the material.

In a polycarbonate modified with 7 wt-% butyl rubber, for example, the apparent volume of the butyl (as measured by the NMR) was found to be four times the actual volume.¹ The impact strength of this material in 58 ft-lb/in. of notch or almost four times the value for pure polycarbonate (15.2 ft-lb/in. of notch). Since it was estimated²⁴ that rubber by itself accounts for only up to 25% of the total impact energy absorbed, the above results are in excellent agreement with the proposed mechanism. The

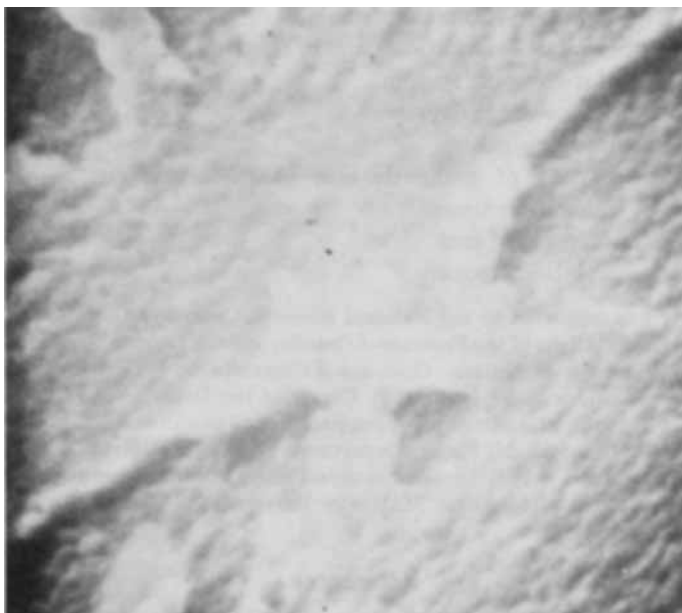


Fig. 20. Scanning electron micrograph of polycarbonate and 7 wt-% butyl rubber blend at lower magnification, 1 cm = 0.5 μ .

impact strength results for rubber-modified polystyrenes^{24,25} can be interpreted in the same manner.

List of Symbols

\AA	angstrom
ABS	acrylonitrile-butadiene-styrene copolymer
BAP	bisphenol A polycarbonate
\overline{DP}	average degree of polymerization
DTA	differential thermal analysis
ΔE	activation energy
Hz	unit of frequency, cycles per second
K	Kelvin
kV	kilovolt
M_0^{I+II}	equilibrium magnetization
M^{I+II}	magnetization, sum of two exponential components having different relaxation times
MHz	megahertz
m μ	millimicron
NMR	nuclear magnetic resonance
PDMS	poly(dimethylsiloxane)
SAN	styrene-acrylonitrile copolymer
T	temperature
T_g or T_α	glass transition temperature
$T_\beta, T_\gamma, T_\delta$	secondary transition temperatures ($T < T_g$)
T_{L1}, T_{L2}	transition temperatures for which $T > T_g$

T_1	spin-lattice relaxation time
$T_{1\rho}$	spin-lattice relaxation time in rotating frame
T_1^I	T_1 for complex system
$T_{1\rho}^I$	$T_{1\rho}$ for complex system
t	time
x	per cent of magnetization characterized by T_1^I and $T_{1\rho}$ relaxation times
μ	micron (10^{-4} cm)
ν_c	correlation frequency

This study was supported by the National Research Council of Canada, the Department of University Affairs of the Province of Ontario, and the Defence Research Board of Canada. The receipt of Ontario Graduate Fellowships is acknowledged. Fruitful discussions were held with Professor J. P. Carver of the Department of Cell Biology, University of Toronto, who offered many suggestions and permitted the use of the NMR instrument. Professor M. M. Pintar, Department of Physics, University of Waterloo, supplied facilities used in initial experiments and made helpful suggestions. Mr. Tom Bistricki, Department of Medicine, McMaster University, assisted in the preparation of the electron micrographs.

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Received September 17, 1973