

Network properties: 3. A pulsed n.m.r. study of molecular motions in some AB-crosslinked polymers

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This paper presents the results of a pulsed n.m.r. study of molecular motions in poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) chains in a series of multicomponent network polymers consisting of poly(vinyl trichloroacetate) (PVTCA) crosslinked with PMMA and with PMA, with emphasis on segmental motions. Results of ancilliary broad line n.m.r. and dilatometric studies are included; the latter demonstrate that in PMA containing polymers microphase separation of the components is complete while in PMMA containing polymers a mixed microphase of PVTCA and PMMA and a pure PMMA microphase are formed. α -Methyl group rotations in PMMA chains and segmental motions in both PMMA and PMA chains are modified with respect to those in the corresponding homopolymers. Modifications to the segmental motions in the crosslinking chains are attributed to the fact that their chain ends are attached to PVTCA chains. It is considered that the comparative rigidity of PVTCA chains ($T_g \sim 60^\circ\text{C}$) reduces segmental motions in at least portions of the PMA chains ($T_g \sim 5^\circ\text{C}$) while the comparative mobility of PVTCA enhances segmental motions in PMMA ($T_g \sim 100^\circ\text{C}$). Thus the molecular mobility of chains of one polymer is to some extent transmitted to chains of another polymer to which it is attached.

INTRODUCTION

We use the term AB-crosslinked polymers (ABCPs) to identify polymers in which chains of polymer A are crosslinked by chains of a chemically different polymer B, including materials ranging from simple crosslinked structures to highly crosslinked networks.

Synthetic procedures adopted in preparing ABCPs of known structure have been described in detail¹⁻⁴. In short, synthesis involves the controlled free radical graft polymerization of a monomer (to give B-chains) onto chains of a suitable preformed polymer (the A-component) under conditions such that virtually no B-homopolymer is produced. Knowledge of the relative rates of combination and disproportionation termination of propagating B-chains and control of the reaction kinetics allows random attachment of B-chains to A-chains and permits calculation of the structural parameters of the ABCPs; i.e. crosslink/branch ratios, degrees of polymerization \bar{P}_n of the B-chains and crosslinking indices. We define a relative crosslinking index γ_r as the ratio of the true crosslinking index to that at the gel point; γ_r is the number of crosslinking units per weight average A-chain.

Recently⁵ we reported an electron microscope study of some morphological features of lightly crosslinked ($\gamma_r < 1$) and highly crosslinked ($\gamma_r < 1$) ABCPs; all the polymers exhibited microphase separation. Earlier papers⁶⁻⁸ described the morphologies of highly crosslinked ABCPs as determined by dilatometry and correlated the results with broad line n.m.r. data. It was concluded that in ABCPs containing only crosslinks of the B-component, e.g. poly

(vinyl trichloroacetate) (PVTCA) crosslinked with polystyrene (PS) microphase separation of A- and B-components was essentially complete. ABCPs containing both branches and crosslinks of the B-component, e.g. PVTCA crosslinked with PS and with poly(methyl methacrylate) (PMMA), exhibited only partial microphase separation; the bulk polymers consisted of a microphase of essentially pure B-component and a microphase containing a mixture of A- and B-components. A phenomenological explanation was advanced to account for the preferential incorporation of branches in the mixed phase. N.m.r. studies showed that, with respect to PMMA homopolymer, α -methyl group rotation in PMMA chains was enhanced in the mixed phase and retarded in the pure PMMA phase. Modifications to methyl group rotations were attributed to PMMA chains adopting conformations different to those in the homopolymer.

The present paper extends our investigations into molecular motions in ABCPs and describes the results of pulsed and broad line n.m.r. studies of ABCPs consisting of PVTCA crosslinked with PMMA and with poly(methyl acrylate) (PMA), designated PVTCA/PMMA, PVTCA/PMA, respectively, with particular reference to segmental motions in B-chains.

EXPERIMENTAL

Preparation and characterization of ABCPs

Methyl methacrylate and dimanganese decacarbonyl were purified and PVTCA ($\bar{P}_w \sim 3000$) was prepared as described in previous papers^{1,4,9}. Methyl acrylate (MA) was purified by washing successively with an aqueous solution

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of sodium bicarbonate and with deionized water, followed by drying, distillation, prepolymerization and finally vacuum distillation immediately prior to use. Prepolymerization of MA was performed photochemically at 25°C in the presence of a trace of azobisisobutyronitrile.

ABCPs were prepared by reacting PVTCA in monomer solution using photoinitiation with dimanganese decacarbonyl ($\lambda = 436 \text{ nm}$) at 25°C, as described previously¹. In preparing PVTCA/PMA ABCPs benzene solutions of MA ($[\text{MA}] = 2.19 \text{ mol/l}$ for PVTCA/PMA 1,2 and 5.5 mol/l for PVTCA/PMA 3) were used to prevent occurrence of the Norrish–Tromsdorff effect⁴. Average degrees of polymerization of PMA chains were calculated from known rates of initiation and a value of $k_p/k_t^{1/2} = 0.5 \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ sec}^{-1/2}$; this value of $k_p/k_t^{1/2}$ was determined in the course of the present study and falls between previously reported values⁴. Crosslinking indices were calculated from reaction times and gel times determined in separate experiments. Crosslink/branch ratios were calculated from prior knowledge of the mechanisms of the termination reactions⁴.

ABCPs were isolated by evaporation of volatiles. To remove residual $\text{Mn}_2(\text{CO})_{10}$ and possible paramagnetic impurities derived from the initiator the ABCP networks were swollen in ethyl acetate and collapsed in petroleum spirit; this procedure was repeated three times. Samples were then cast from ethyl acetate and were finally dried under high vacuum for several days, either in thin walled soda glass n.m.r. tubes or in dilatometer bulbs, during which procedure they were heated to 100°C for several hours. N.m.r. samples were sealed under vacuum and, for dilatometry, mercury was used as the containing fluid.

Dilatometric and n.m.r. studies

Dilatometric and broad line n.m.r. studies were performed as described previously^{6,7}. Spin–lattice and spin–spin relaxation times, T_1 , T_2 , respectively, were measured using a Bruker–Physik A.G. pulsed n.m.r. spectrometer (B-KR 322S). Small values of T_2 were obtained from free induction decays and large values ($>500 \mu\text{sec}$) using the Gill–Meiboom modification of the Carr–Purcell spin echo technique¹⁰. Values of T_1 were determined using a 90°–90° pulse sequence. Spectrometer frequencies used in this study were 60 MHz for all broad-line n.m.r. work, for relaxation studies a frequency of 45 MHz was used for PMMA containing materials and 20 MHz for PMA containing polymers and PVTCA homopolymer.

RESULTS AND DISCUSSION

Poly(methyl methacrylate)-containing ABCPs

Structural parameters of PVTCA/PMMA ABCPs are presented in Table 1. Values of γ_r are equal to the ratios of reaction times t_r to times required to produce gelation t_g only under conditions of constant rate of initiation and zero transfer. Actual values of t_r and t_g were corrected for

Table 1 Structural parameters of PVTCA/PMMA ABCPs

PVTCA/PMMA	PVTCA (% w/w)	\bar{P}_n (PMMA crosslinks)	γ_r
1	50	1380	1.57
2	18	4920	1.57
3	17	7280	1.59
4	12	11540	1.60

Table 2 Analysis of dilatometric data from PVTCA/PMMA ABCPs

PVTCA/PMMA	T_{g1} (obs) (°C)	T_{g2} (°C)	a	w	T_{g1} (calc.)* (°C)
2	78	98	0.32	1.7	84
3	77	99	0.50	2.9	88
4	73	99	0.26	2.1	84

* Values of T_{g1} (calc.) were obtained by use of the Kelley–Bueche equation assuming additivity of free volumes and coefficients of expansion and glass transition temperatures reported previously⁶

initiator consumption and transfer to monomer (a minor contribution), using relations quoted previously², to give values t_r^0 and t_g^0 which are proportional to the numbers of crosslinks introduced in times t_r , t_g , respectively. Quoted values of $\gamma_r = t_r^0/t_g^0$ are thus corrected values. In effecting these corrections it was assumed that one radical is produced per primary molecule of $\text{Mn}_2(\text{CO})_{10}$ photolytically decomposed and that one half of the $\text{Mn}_2(\text{CO})_{10}$ decomposed is reconverted to $\text{Mn}_2(\text{CO})_{10}$, i.e. $n = 1/2$ in equation (8) of ref 2. The transfer constant to monomer at 25°C was taken¹¹ to be 10^{-5} . Values of \bar{P}_n for PMMA chains were calculated from kinetic parameters; inclusion of a small correction for initiator consumption would have no influence on the results of this study. Crosslink/branch ratios for PMMA chains are 0.25, assuming 33% combination in the radical termination reaction at 25°C⁴.

Dilatometry. Volume–temperature plots for PVTCA/PMMA 2, 3 and 4 showed two definite glass transitions. The upper transition temperatures T_{g2} corresponded closely to that of PMMA homopolymer. The lower transition temperatures T_{g1} were higher than for PVTCA homopolymer ($T_{g\text{PVTCA}} = 60^\circ\text{C}$, approximately). Observed values of T_{g1} , T_{g2} are quoted in Table 2. The plots were similar to those described previously for other PVTCA/PMMA ABCPs and similar considerations apply to their analysis^{6,7}.

Following our earlier arguments, the elevated observed values of T_{g1} are taken to indicate partial microphase separation in the ABCPs with formation of a mixed phase containing both PVTCA and PMMA; correspondence of T_{g2} with T_g for PMMA indicates the existence of an essentially pure PMMA phase. The original analysis, in Part 1 of this series⁶, approximated the plots to three straight lines in the temperature ranges $T < T_{g1}$, $T_{g1} < T < T_{g2}$, $T > T_{g2}$. From coefficients of expansion of the homopolymers and ABCPs it was possible, assuming a mixed phase of uniform composition (characterized by a single T_g) and a pure PMMA phase, to calculate weight fractions of PMMA incorporated in the mixed phase (values of a in Table 2) and weights of PMMA associated with unit weight of PVTCA in that phase (values of w in Table 2). As pointed out in Part 2 of this series⁷, this simple analysis is not strictly correct. Observed values of T_{g1} do not agree with those calculated from the Kelley–Bueche equation for mixtures of amorphous materials¹² (Table 2). Also, volume–temperature curves are non-linear between T_{g1} and T_{g2} , suggesting that the mixed phase is not of uniform composition, so that values of w represent some average composition for the whole mixed phase; values of T_{g1} indicate the composition of the regions richest in PVTCA. Volume–temperature plots obtained in this work showed little curvature and it is assumed that the simple analysis of the data will suffice for correlation with the n.m.r. data.

N.m.r. studies. Since in all samples over 80% of the protons are in PMMA chains, it is assumed that observed

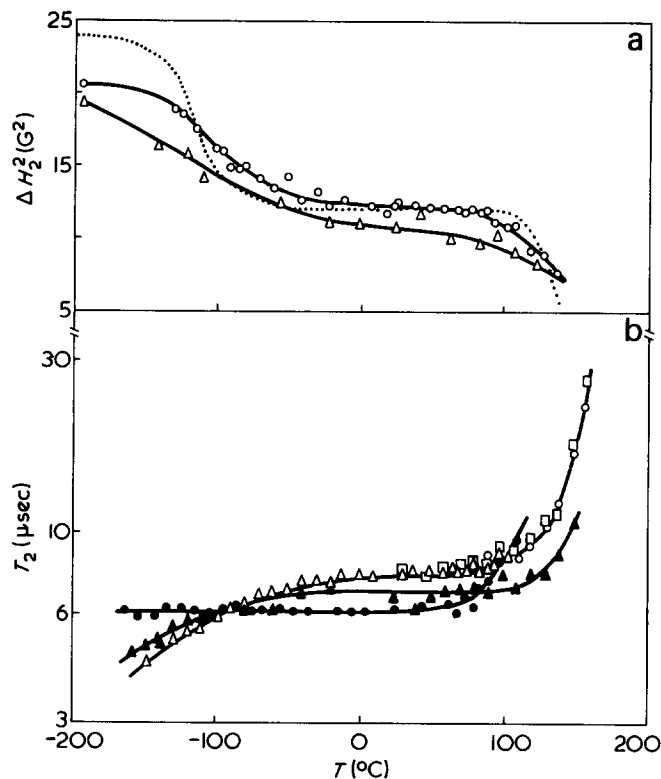


Figure 1 (a) Variation in second moments (ΔH_2^2) of n.m.r. absorption lines with temperature for: PVTCA/ABCPs. Δ , Sample 1; \circ , Sample 4. \cdots , Refers to PMMA (ref 7). (b) Variation in T_2 with temperature for: \blacktriangle , PMMA; \triangle , PVTCA/PMMA 1; \square , PVTCA/PMMA 2; \circ , PVTCA/PMMA 4; \bullet , PVTCA

n.m.r. signals arise from PMMA alone; this assumption was justified in a previous paper⁷.

Broad line n.m.r. data illustrating the variation in second moment (ΔH_2^2) with temperature for ABCPs PVTCA/PMMA 1,4 and PMMA homopolymer are given in Figure 1a; PMMA data are taken from an earlier study⁷. The curves show similar features to those reported for other PVTCA/PMMA ABCPs⁷. Compared with data for PMMA, PVTCA/PMMA 4 shows a relatively gradual development of α -methyl group rotation (the low temperature decrease in ΔH_2^2) with increasing temperature (in PMMA homopolymer all methyl groups may be considered to be rotating above $-80^{\circ}C$ but only at temperatures in excess of $0^{\circ}C$ in the ABCP); correlation of dilatometric and n.m.r. data⁷ suggests that restrictions to α -methyl group rotation arise from PMMA chains in the pure PMMA phase in the ABCPs. In PVTCA/PMMA 1 α -methyl group rotation develops continuously between -196° and $0^{\circ}C$, illustrating both enhanced (decrease in ΔH_2^2 between -196° and $-120^{\circ}C$) and retarded (continued decrease in ΔH_2^2 between -100° and $0^{\circ}C$) α -methyl group rotation compared with that for PMMA homopolymer. Enhanced methyl group rotation has been attributed to PMMA chains in the mixed PVTCA-PMMA phase⁷. The data suggest that in PVTCA/PMMA 1 significant fractions of the PMMA are located in each phase. (Shortage of materials precluded determination of dilatometric data for this sample.) It may be anticipated that if a significant proportion of the PMMA chains are located in the mixed phase their segmental motions will develop at temperatures above T_{g1} but below the normal T_g for PMMA; this may be indicated by the decrease in ΔH_2^2 for this sample at temperatures between 60° and $100^{\circ}C$.

Pulsed n.m.r. Values of the transverse decay time T_2 were estimated from plots of \log (signal intensity) against time, which gave good straight lines except at the lower temperatures. (Strictly, this procedure is only valid for mobile systems with Lorentzian line shapes but was used throughout the temperature range for all samples. Although there may be some error in absolute values of T_2 at low temperatures the data are satisfactory for comparative purposes.) Since, in simple systems, T_2 is inversely related to line width it might be expected that decreases in ΔH_2^2 would correlate with increases in T_2 and this is borne out by comparison of Figures 1a and 1b. T_2 data for PVTCA/PMMA 1 show the slow development of α -methyl group rotation in the ABCP compared with the behaviour in PMMA homopolymer. Lack of correspondence between changes in T_2 for PVTCA and the ABCPs (Figure 1b) support the assumption that observed signals from the ABCPs are attributable to the PMMA chains alone and that deviations from the behaviour of PMMA homopolymer are a consequence of the structure and properties of the ABCPs. Elevated values of T_2 for the ABCPs at the higher temperatures are indicative of enhanced segmental motions of PMMA chains in the ABCPs.

Figure 2 presents T_1 data for PVTCA/PMMA 1 and for PMMA over the temperature range -140° to $+110^{\circ}C$; both curves show features similar to T_1 data for PMMA reported by Slichter¹³. With increasing temperature, slight increases in T_1 at the lowest temperatures arise from the high temperature side of the T_1 minima for ester-methyl rotation. The T_1 minima in the central region are ascribed to the development of α -methyl group rotation and decreases in T_1 at the highest temperatures are associated with the onset of segmental motions of the PMMA chains¹³.

From the limited data available, there is no evidence that rotation of ester-methyl groups is modified in the ABCPs. Some differences in shape of the T_1 minima associated with α -methyl group rotation are apparent from Figure 2, indicating that the distributions of correlation times for their motions in the ABCP and in PMMA homopolymer are different. These differences are consistent with broad line and T_2 data which also indicate variations in the development of this motion between the ABCP and

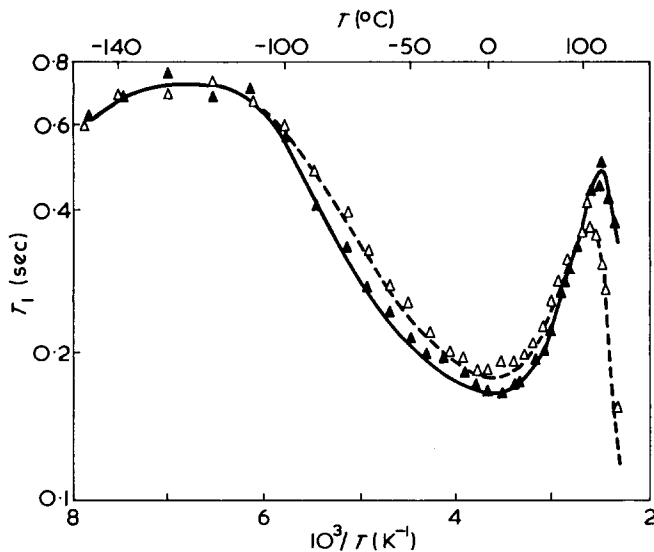


Figure 2 Spin-lattice relaxation times T_1 as a function of temperature for: \blacktriangle , PMMA; \triangle , PVTCA/PMMA 1

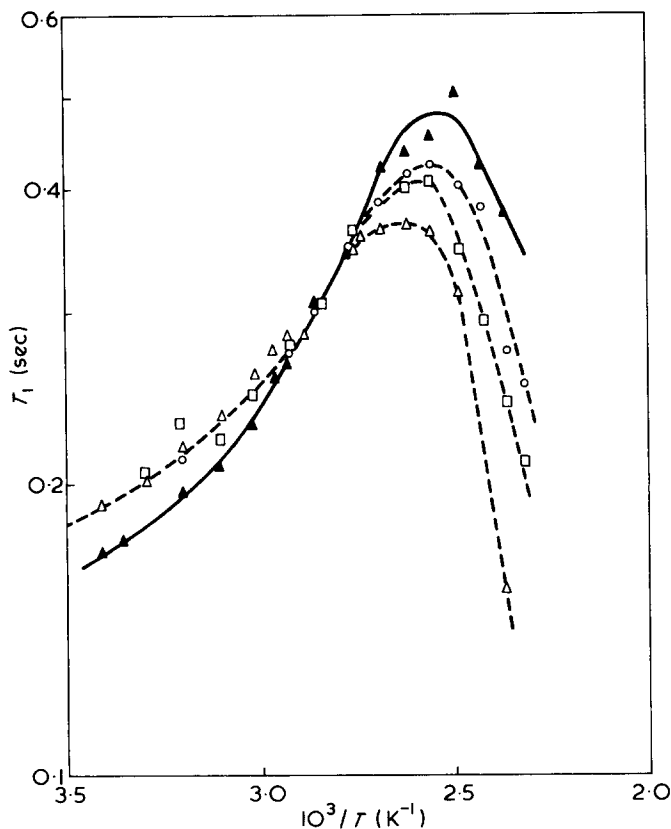


Figure 3 Temperature dependence of T_1 for: \blacktriangle , PMMA; \triangle , PVTCA/PMMA 1; \square , PVTCA/PMMA 2; \circ , PVTCA/PMMA 4

PMMA. The higher absolute value of T_1 for the ABCP at the central minimum suggests that, overall, relaxation through α -methyl rotation in the ABCP is less efficient than in PMMA while the slight shift of the minimum to lower temperatures indicates that more of the α -methyl groups in the ABCP have their rotations enhanced than retarded; qualitatively this behaviour appears to be in agreement with the temperature variation of ΔH_2^2 shown in Figure 1. At present it is not possible to provide a more detailed interpretation of the shapes of the T_1 minima or to correlate them with polymer morphology.

The temperature variation of T_1 in the vicinity of T_g for PMMA is shown in greater detail in Figure 3, along with additional data for other ABCPs. Experimental limitations prevented the acquisition of data at higher temperatures. The development of segmental motions is seen first as a reduction in the rate of increase of T_1 with temperature and then as a rapid decrease in T_1 at the higher temperatures. It is difficult to identify exact temperatures at which segmental motions first become apparent, but, for comparative purposes, we may take the temperatures corresponding to the maximum slopes of the curves in Figure 3. On this basis it appears that segmental motions in the ABCPs commence at slightly lower temperatures than in PMMA. What is more apparent is the different rates at which the segmental motions develop with increasing temperature, the order being PVTCA/PMMA 1 > PVTCA/PMMA 2 > PVTCA/PMMA 4 > PMMA.

We may attempt to correlate the more rapid rate of development of segmental motions with temperature in the ABCPs than in PMMA with broad line n.m.r. and dilatometric data. These motions develop most rapidly in PVTCA/

PMMA 1 which, according to broad line data, displays a marked enhancement of α -methyl group rotation at low temperatures (<100°C). Following our previous arguments, the latter observation indicates that a large proportion of the PMMA is located in a mixed PVTCA/PMMA phase associated with a glass transition temperature lower than that of PMMA and, hence, in a relatively mobile phase. Samples PVTCA/PMMA 2,4 exhibit similar variations in T_1 with temperature. According to the dilatometric data (Table 2), the proportions of PMMA chains in the mixed phases and the compositions of those phases are similar. PVTCA/PMMA 2 has a slightly larger proportion of PMMA in the mixed phase and appears to show a slightly more rapid development of segmental motions than PVTCA/PMMA 4 at the lower temperatures. Although it is possible to correlate the more facile development of segmental motions in the ABCPs with the existence of a mixed phase (with $T_g < T_{g,PMMA}$) and the composition of that phase, it is not necessary, as we shall see later, to ascribe all the enhancement of the segmental motions to PMMA chains in the mixed phase. We believe that at least part of the effect is associated with PMMA chains in the pure PMMA phase and arises from the attachment of those PMMA chains to PVTCA chains.

Poly(methyl acrylate)-containing ABCPs

In calculating the structural parameters of PVTCA/PMA ABCPs (Table 3) similar procedures were adopted as described earlier for PVTCA/PMMA ABCPs, assuming rates of initiation are monomer independent⁴. Gel and reaction times were corrected for initiator consumption but, in the absence of relevant data, corrections for transfer (probably negligible) were not applied. Values of γ_r were calculated from the corrected times. According to previous studies⁴ the propagating PMA radicals probably terminate exclusively by combination at 25°C so that PVTCA/PMA ABCPs contain no PMA branches.

Dilatometry. Volume-temperature plots for PVTCA/PMA ABCPs showed two well defined glass transitions at temperatures corresponding closely to those of the component homopolymers (PMA, $T_g = 5^\circ\text{C}$; PVTCA, $T_g = 60^\circ\text{C}$; PVTCA/PMA 1, $T_{g1} = 10^\circ\text{C}$, $T_{g2} = 60^\circ\text{C}$). In the temperature regions $T < T_{g1}$, $T_{g1} < T < T_{g2}$, $T_{g2} < T$ the plots were straight lines and coefficients of expansion were as expected for each component exhibiting its own glass transition independent of the presence of the other component. Such behaviour indicates essentially complete microphase separation without formation of a mixed phase; the slight shift in T_g for PMA in the ABCP may suggest the existence of a small amount of PVTCA in the PMA phase. Similar data have been reported for PVTCA/polystyrene ABCPs which contain no polystyrene branches⁶ and the present data reinforce the idea expressed previously that formation of a mixed phase depends largely on the presence of branches of the crosslinking polymer.

N.m.r. studies. Since the bulk of the protons are located in PMA chains we again assume that n.m.r. signals obtained

Table 3 Structural parameters of PVTCA/PMA ABCPs

PVTCA/ PMA	PVTCA (% w/w)	\bar{P}_n (PMA crosslinks)	γ_r
1	27	2800	4.75
2	12	2800	9.4
3	20	24 000	1.81

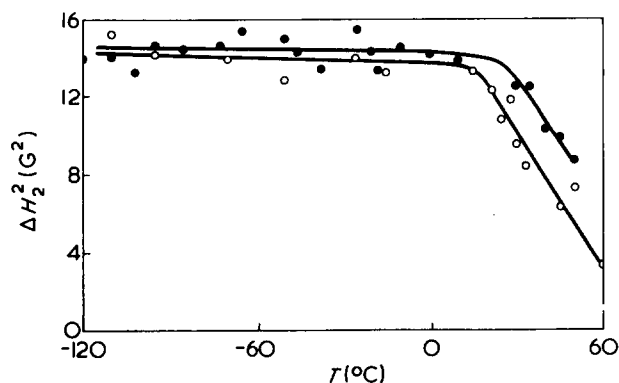


Figure 4 Variation in second moments of n.m.r. absorption lines with temperature for: ○, PMA; ●, PVTCA/PMA 1

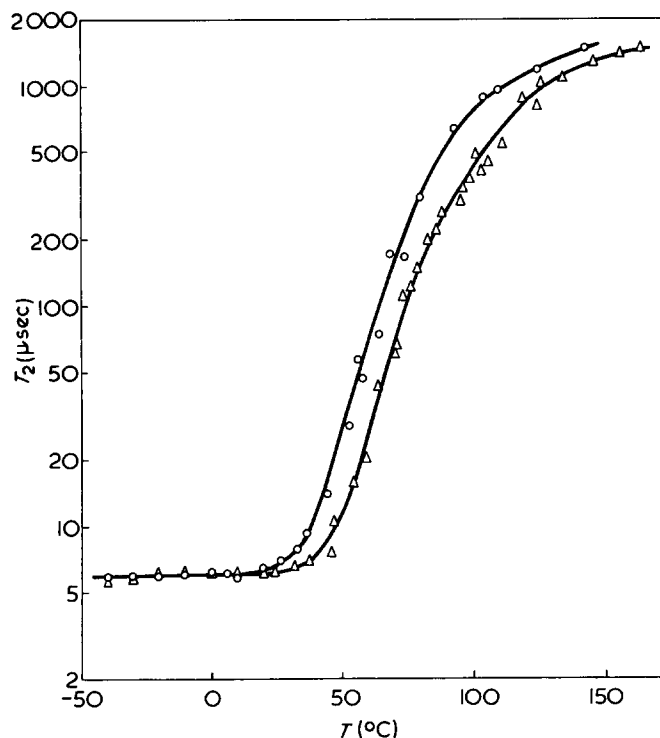


Figure 5 Variation in T_2 with temperature for: ○, PMA; △, PVTCA/PMA 3

from the ABCPs arise from PMA chains alone. For comparative purposes a sample of PMA was prepared by polymerizing MA using $Mn_2(CO)_{10}$ plus ethyl trichloroacetate as the photoinitiating system under conditions comparable to those used in preparing ABCPs.

Broad line n.m.r. Data illustrating the variation in ΔH_2^2 with temperature for PVTCA/PMA 1 and for PMA homopolymer are presented in Figure 4. The only major feature of these curves is the decrease in ΔH_2^2 accompanying the development of segmental motions in PMA above the glass transition temperature of that polymer. Comparison of the curves reveals that the onset of such motions of the PMA chains in the ABCP is retarded slightly with respect to that in the homopolymer. Since dilatometry indicates complete microphase separation it is concluded that modifications to segmental motions occur in the 'pure' PMA phase, with little or no contribution from a mixed phase.

Pulsed n.m.r. T_2 data for PMA and for PVTCA/PMA 3, over the temperature range -50° to $+150^\circ C$, are presented

in Figure 5. Data for PMA and PVTCA/PMA 1,2, over the range 0° to $150^\circ C$, are given in Figure 6; at lower temperatures the data for the ABCPs are similar to those in Figure 5. The data show that segmental motions in the ABCPs are retarded compared with those in the homopolymer, in accordance with broad line data. Materials containing the largest proportion of PVTCA show the greatest effect. Although there are considerable differences between absolute values of T_2 for PMA and the ABCPs at a given temperature, it is seen from Figures 5 and 6 that the major effect (in the range 25° to $125^\circ C$) is a shift in the T_2 -temperature curves for the polymers relative to each other while their shapes remain similar.

Values of T_1 for PMA over the temperature range -40° to $+150^\circ C$, at an experimental frequency of 20 MHz, are shown in Figure 7. At lower temperatures T_1 decreases towards a minimum associated with ester-methyl group rotation while the minimum in Figure 7 is ascribed to segmental motions. These data are very similar to those reported previously¹⁴ for a frequency of 18.6 MHz. At an experimental frequency of 45 MHz we obtained a minimum value for T_1 of 0.8 sec at a temperature of $130^\circ C$ (i.e. the temperature at which contributions of segmental motions to relaxation are maximal).

From the variations in T_1 with temperature for PMA and PVTCA/PMA 3 below $50^\circ C$ (Figure 7) it is seen that

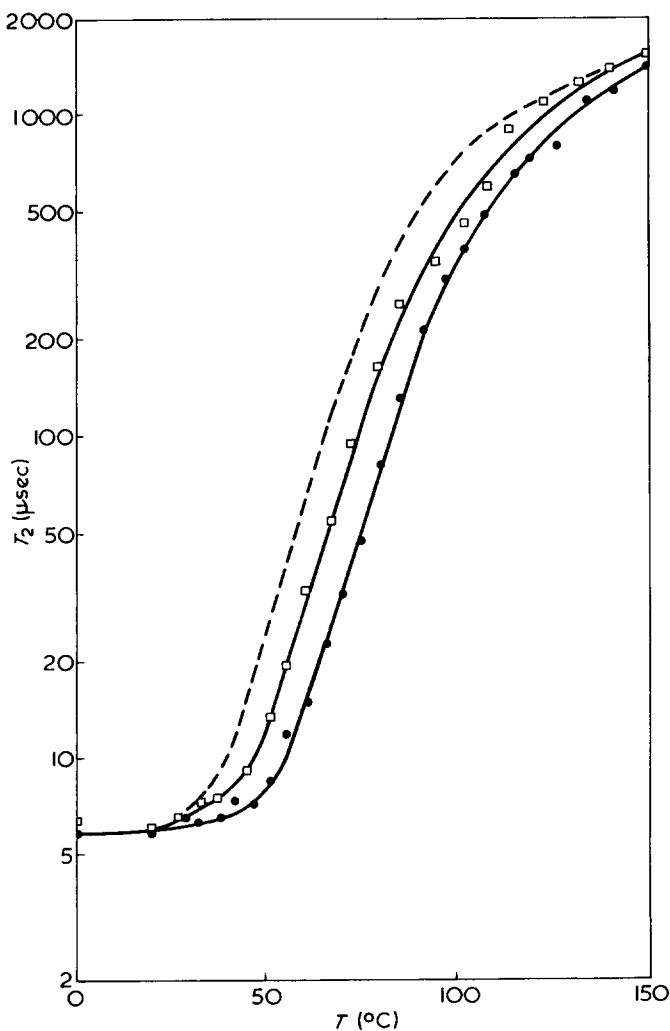


Figure 6 Variation in T_2 with temperature for: ●, PVTCA/PMA 1; □, PVTCA/PMA 2. ---, Refers to PMA data from Figure 5

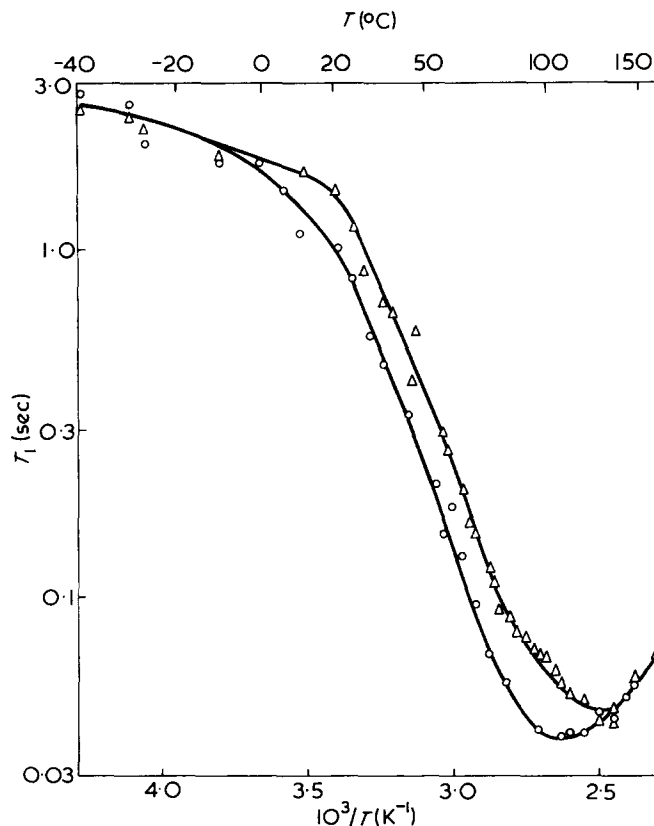


Figure 7 Spin-lattice relaxation times as a function of temperature for: \circ , PMA; \triangle , PMA/PVTCA 3

the onset of segmental motions in the ABCP is retarded relative to PMA. The dependencies of T_1 on temperature for PMA and for various ABCPs, over the temperature range including the T_1 minima, are illustrated in Figures 7 and 8. From these data it is immediately apparent that the T_1 minima for the ABCPs are located at higher temperatures than the minimum for PMA homopolymer. Apparent activation energies E_a for relaxation were estimated from the low temperature side of the T_1 minima, using data between 40° and 100°C; values of E_a are tabulated in Table 4 along with values of T_1 at the minima ($T_{1\min}$) and the temperature at which the minima occur. Lower values of E_a coupled with higher values of $T_{1\min}$ for the ABCPs are indicative of a broader distribution of correlation times in the ABCPs than in PMA homopolymer.

We note that differences exist between the shapes of the T_1 -temperature curves and locations of the T_1 minima for the various ABCPs. In samples PVTCA/PMA 1, 2 degrees of polymerization of PMA chains are identical (Table 3) and values of E_a (Table 4) are very similar. The major difference in T_1 data between these samples is the greater shift in the minimum to higher temperatures for PVTCA/PMA 1, i.e. the sample with the greater PVTCA content. At temperatures higher than those corresponding to the minima values of T_1 for the ABCPs appear to become coincident. PVTCA/PMA 3, which has long PMA chains shows a higher value of E_a and at the highest temperatures values of T_1 appear to become coincident with those for PMA homopolymer, possibly because a relatively small proportion of the PMA chains is affected by attachment to PVTCA chains.

As in the case of PVTCA/PMMA ABCPs, discussed earlier, n.m.r. data for PVTCA/PMA ABCPs do not result from a simple superposition of data for the component homopolymers. Thus, restrictions to segmental motions and

modifications to relaxation processes observed for PMA chains must arise as a consequence of the morphologies of the polymers and the attachment of PMA chains to PVTCA chains.

Comparison of data for PVTCA/PMMA and PVTCA/PMA ABCPs

In preceding sections we described dilatometric and n.m.r. data for the two types of ABCP. With both types of material modifications to molecular motions in the crosslinking chains, compared with the behaviours of the corresponding homopolymers, have been observed and are a direct consequence of the structures and morphologies of the polymers. Restricting this comparison to segmental motions, we pointed out that at least some enhancement of chain mobility in PMMA chains may arise from PMMA chains located in the PVTCA-PMMA mixed phase with T_g lower than for PMMA homopolymer. While formation of a mixed phase of PVTCA and PMA would place some PMA

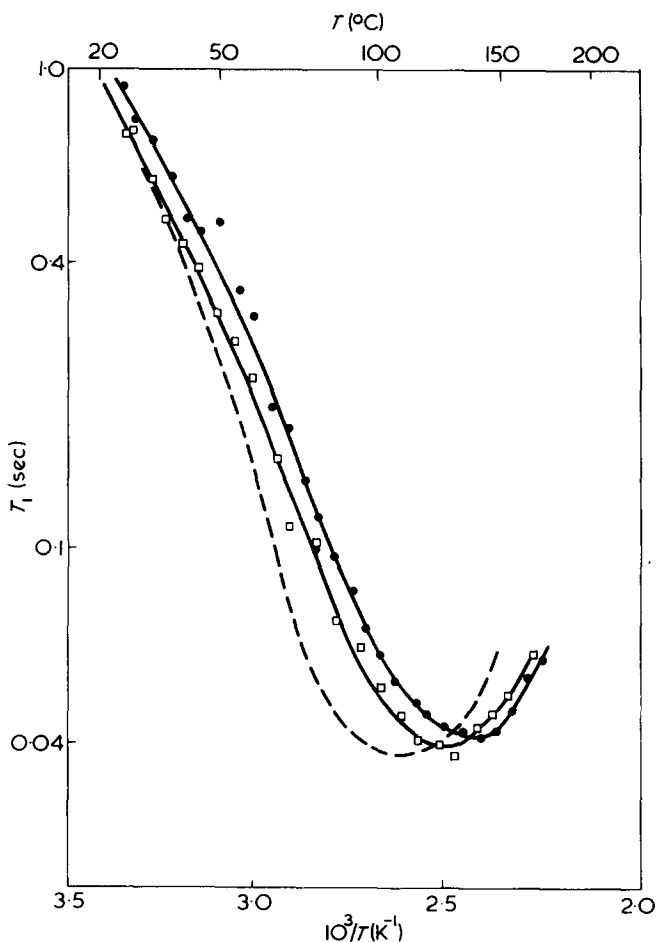


Figure 8 Spin-lattice relaxation times as a function of temperature for: \bullet , PVTCA/PMA 1; \square , PVTCA/PMA 2. ---, Refers to PMA data from Figure 7

Table 4 Analysis of T_1 data for PVTCA/PMA ABCPs

Sample	E_a (kJ/mol)	$T_{1\min}$ (msec)	Temperature for $T_{1\min}$ (°C)
PMA	50.2	37	108
PVTCA/PMA 1	40.5	42	142
PVTCA/PMA 2	41.0	40	127
PVTCA/PMA 3	43.9	44	131

chains in regions with T_g higher than for PMA, thereby reducing segmental motions in some PMA chains (as observed), no evidence for such a mixed phase in these polymers was obtained. We therefore conclude that restrictions to PMA chain mobility arise in the pure PMA phase and believe that a least some enhancement of mobility of PMMA chains in PVTCA/PMMA ABCPs arises in the pure PMMA phase.

In the course of an n.m.r. study of styrene-butadiene diblock copolymers, Anderson and Liu¹⁵ observed that for materials containing more than 50% styrene the T_1 minima for polybutadiene chains were modified, corresponding to a restriction of segmental motions in the polybutadiene blocks. They suggested that the polybutadiene chains were encapsulated in a polystyrene matrix as a result of microphase separation so that expansion of the polybutadiene domains and development of segmental motions were restricted by the lower coefficient of expansion of the polystyrene matrix. Such an explanation is not valid for the ABCPs under discussion since, on the basis of composition, it is expected that the PMA chains of PVTCA/PMA ABCPs would form the matrix, consistent with the rubbery texture of the polymers at room temperature, so that PMA chains would not be under such constraints. Similarly, PMMA chains are expected to form the matrix of most of the PVTCA/PMMA ABCPs.

It might be anticipated intuitively that the presence of crosslinking points on a polymer chain will modify molecular motions in that chain, probably hindering the motions (as observed in ABCPs containing PMA) due to lack of translational freedom of the junction points. In fact, the opposite effect is observed in ABCPs containing PMMA chains. For samples PVTCA/PMA 1,2 the modification of segmental motions actually decreases as the crosslinking index increases. From the data in this paper it appears to be the samples with the highest PVTCA content which show the greatest effects. Unlike a conventional crosslinked homopolymer, as the crosslinking index increases in ABCPs the number of junction points per B-chain (PMA and PMMA) does not increase but the distance between junction points on the A-chains and, thus, the effective length of A-chain (PVTCA) associated with each B-chain decreases.

We note that the glass transition temperature of PVTCA ($\sim 60^\circ\text{C}$) is between those of PMA ($\sim 5^\circ\text{C}$) and PMMA ($\sim 100^\circ\text{C}$) and that both ends of all PMA chains, and at least one end of each PMMA chain, are attached to PVTCA chains. Thus, at temperatures above T_g of PMA, the ends of PMA chains are attached to relatively rigid material and, in consequence, the mobilities of the chain ends will be

greatly diminished in the ABCPs. Similarly, at temperatures above T_g of PMMA, ends of PMMA chains are attached to PVTCA chains well above their T_g and more mobile than normal PMMA chains, thus enhancing the mobilities of chain ends in PMMA. We therefore, believe that modifications to segmental motions in PMA and PMMA arise as a direct consequence of the attachment of those chains to PVTCA chains and that modifications to the mobilities of chain ends are transmitted to, at least, sections of the chains close to the junction points. As a result of the cooperative nature of segmental motions in polymer chains, molecular motions in other sections of chains close to the interface between the microphases may also be affected. Molecular motions in portions of the chains well removed from the interface may be less affected, in accord with T_1 data for PVTCA/PMMA ABCPs for which effects on segmental motions decrease with increasing length of the PMMA chains, at similar crosslinking indices.

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