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Dynamic mechanical properties of homopolymers and interpenetrating networks based on diethylene glycol-bis-allyl carbonate

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Homopolymers and interpenetrating networks based on diethylene glycol-bis-allyl carbonate and methyl methacrylate were prepared using free radical initiators and their dynamic mechanical properties were investigated. The changes of glass transition temperature and tan δ_{max} with conversion are reported. This data is used to estimate the changes in the mobility of the system with conversion. The effect of the change in composition in copolymers on tan δ peak width, tan δ_{max} and area under the tan δ curve are used to understand the network distribution, miscibility and damping properties. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: DMA; CR39; MMA)

INTRODUCTION

Polymers cast from diallyl monomers, particularly poly(diethylene glycol-bis-allyl carbonate) (CR39), have found applications in many areas. These vary from optical applications[1] to nuclear track detectors[2]. The properties of the final product were found to depend closely on the polymerisation conditions, and the polymers form densely crosslinked networks that have better thermal and dimensional stability than comparable thermoplastics.

The glass transition (T_g) is one of the most important properties exhibited by a polymer, determining its physical state and influencing other properties such as rheological characteristics, mechanical stiffness and toughness[3]. The glass transition temperature of linear polymers as a function of molecular weight are generally well understood[4]. On the other hand, the T_g region of a thermoset polymer is not so clearly understood in terms of specific molecular factors. The most common approach is to relate the T_g of a crosslinked system to the overall conversion[5], although it is accepted that the variation in T_g is attributed to various molecular parameters such as the molecular weight, the stiffness and the free volume entrapped in the network. It has been observed[6] in epoxy systems, that the increase of the molecular weight by linear polymerisation is the main factor for the increase in T_g before gelation, while after gelation, T_g is effected by a decrease in free volume and/or an increase in the stiffness due to the crosslinking reactions.

Some thermal analytical work has been published on copolymers of diallyl phthalate and glycol-bis-allyl carbonate with various lengths of ethylene glycol units[7]. The relaxation behaviour of poly(diethylene glycol-bis-allyl carbonate) has also been reported[8]. Both of these studies used the fully cured samples. The present study is aimed at interpreting the changes in the dynamic mechanical properties in the glass transition region during homo- and copolymerisation of diallyl monomers. There are several reasons for investigating the properties of the thermosetting systems as a function of cure. For example, there is a need to develop an understanding of the evolution of properties in terms of details of molecular structure and related transitions, since this would facilitate the molecular design of macroscopic properties.

EXPERIMENTAL

Materials and methods

CR39 was obtained from SOLA International Holdings (Adelaide, Australia) and was used without any further treatment. Methyl methacrylate (MMA) was obtained from BASF and was purified by vacuum distillation. Benzoyl peroxide (BPO) was purified by twice recrystallising from methanol. Samples for polymerisation were prepared in 5 mm outside diameter glass tubes, which were degassed through at least three freeze thaw cycles, after which they were sealed under vacuum. The samples were polymerised in a block heater at the required temperatures, and the cure cycles were obtained using FTNIR[9,10]. The reaction was stopped by quenching in liquid nitrogen, after which the samples were kept at liquid nitrogen temperatures until just prior to the testing.

Dynamic mechanical analysis

A Perkin-Elmer DMA7 instrument was used in the parallel plate mode on a sample of approximately 3 mm width and 1.5 mm height or three point bending mode on a sample of approximately 3 mm diameter and 15 mm long. Temperature/time scans or stress/strain scans were carried out at a frequency of 1 Hz. A heating rate of 5 K min^{-1} was used for the temperature/time scans. Normally the T_g value is taken as the point of deflection of the tan δ curve from the base line. However this was difficult in some samples due to the phase separation and appearance of shoulders in the tan δ peak. As such, the temperature at the maximum point of the tan δ peak was taken as the measure of T_g. Since the equations used later require T_g difference values, this was assumed to have no or little error.

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Differential scanning calorimetry

A Perkin-Elmer DSC7 instrument was used to determine the T_g values of the uncrosslinked polymers at a scanning rate of 5 K min^{-1}.

RESULTS AND DISCUSSION

Homopolymerisation of CR39

DMA curves of CR39 samples polymerised to 95% conversion are shown in *Figure 1*. These samples were polymerised at 90°C with 3% BPO using CR39 from two different original suppliers. The GPC curves for the unreacted monomer samples indicate a small difference in oligomers in the two samples. From the DMA curves, there appears to be no difference in the dynamic thermal properties of the resultant products, even though spectacle lens coating properties of the products are reported to be dependent on the oligomer content[11]. The peak at 95°C in the DMA curves presented in *Figure 1* correspond to the similar data provided in previous work[8]. This peak was assigned to glass transition (α process) in the polymer.

The DMA curves also show a broad peak at about -75°C and a shoulder to the α relaxation at about 10°C. Previous[8] work using thermally stimulated depolarization current techniques, identified peaks in the range of -60 to 0°C which have been assigned to β and γ relaxations. It is likely that the peak at -75°C in the present study is due to the combination of β and γ relaxations. The peak at 10°C has been assigned[8] to a non-equilibrium relaxation referred to as α', resulting from the motion of several repeat units of the polymer chain, made possible by increase in free volume and molecular mobility during the cooling through T_g.

Figure 2 shows the loss modulus curve for two CR39 samples cured under two different conditions. The curve shown in *Figure 2a* was for a sample cured at 70°C with 1.5% BPO (slow cure) and the curve shown in *Figure 2b* was for a sample cured at 90°C with 5% BPO (fast cure). In both cases the conversion was 95% and then heated to 110°C to effect complete conversion. As was observed[9] at low conversion, the sample cured at the slower rate showed a broad loss modulus, T_g relaxation curve, compared to the sample cured at the higher rate. This increase in the width of the loss modulus peak for the lower reaction rate may be due to increased breadth of the network chain length distribution. Some cyclisation is known[12] to occur in polymerisation of diallyl monomers, and occurs if sufficient time is allowed for the chain end unit to rearrange during polymerisation. Therefore, it is reasonable to assume that at lower polymerisation rates, there will be a higher chance for the cyclisation to occur. This will result in a broader distribution of chain lengths compared to polymerisation without cyclisation or with reduced cyclisation.

We have also observed[9] a lower rubbery modulus (modulus above glass transition) for a sample which is polymerised at a faster rate. This may be due to the formation of microgels in the early stages of polymerisation, followed by formation of a macrogel via linking of these microgel regions. The concentration of polymer radicals generated in fast cure conditions are higher at one particular time, therefore, microgelation is favoured. This was confirmed in electron spin resonance (e.s.r.) studies[10], where the radical build-up commences at lower conversion when the reaction rate is high. In fast cure systems, microgels may have a higher crosslink density, thus a higher modulus would be expected. However, the modulus of the composite is determined primarily by the modulus of the matrix phase, i.e. the macrophase. The macrophase of the fast cure system has a lower crosslink density, and thus a lower modulus.

The plots of tan δ *versus* temperature for the reaction mixture of 1% BPO/CR39 cured at 80°C to different conversions are given in *Figure 3*. The samples show a gradual increase in the width of the tan δ curve with conversion, particularly after about 66% conversion. At this conversion, radical concentration begins to increase and the e.s.r. signal changes from a sharp to a broad signal[9,10]. A gradual broadening of the tan δ curve with increasing crosslinking density has been reported previously[13]. This

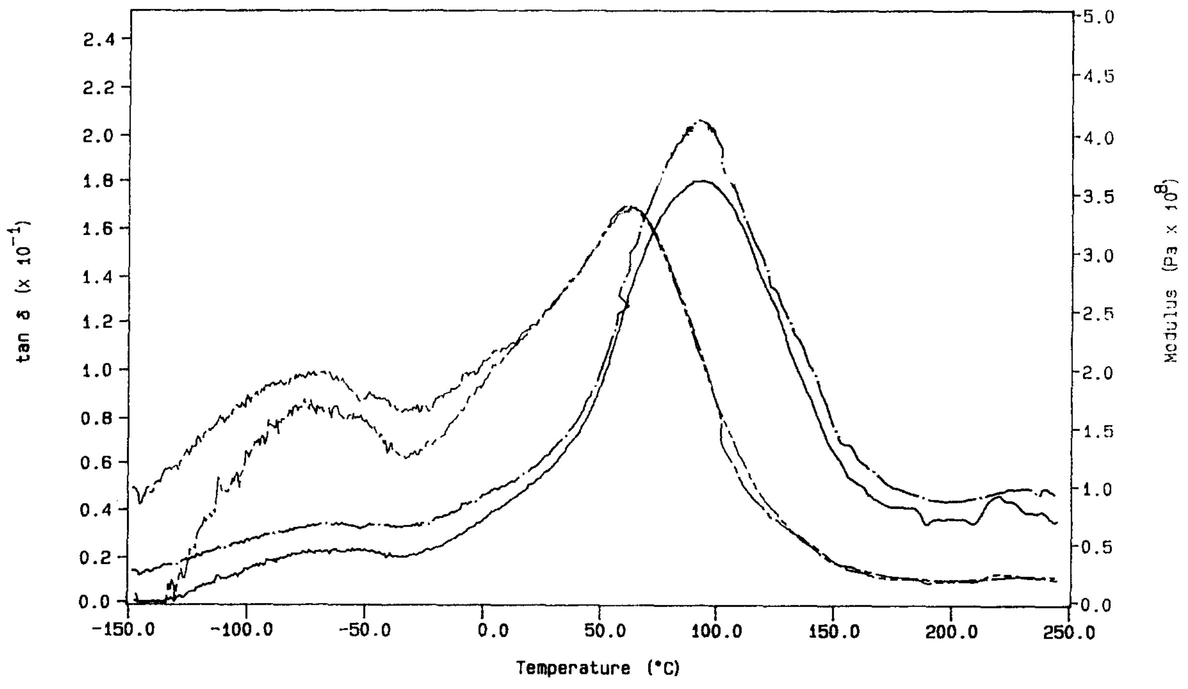


Figure 1 Tan δ *versus* temperature curves for two 95% polymerised CR39 samples. The two CR39 resins were obtained from different suppliers

broadening has been explained as being due to the increased width of the network chain distribution. Since the average chain length between crosslinks in the system investigated here depends on the amount of cyclisation formed during polymerisation, the increased width of the tan δ curve indicates a change in the percentage of cyclisation over the polymerisation range. However, estimates of the percentage of cyclisation using kinetic parameters[9] and shear modulus indicate that the percentage cyclisation remains at approximately 20–25% during the whole range of polymerisation at 90°C and with 5% BPO. Therefore, the broadening of the tan δ curve should be due to heterogeneity introduced in the system. Beyond 66% conversion, the crosslinking seems to be heterogeneous. In other words, the crosslink density is not the same in all sections of the network, and thus the radicals in these sections may become trapped in these highly crosslinked regions. This may result in non-uniform formation of cyclisation and crosslinking, which will increase the network chain distribution. This is clearly observed in *Figure 4*, which shows the variation in the loss modulus for samples cured to different extents. Up to about 70% conversion, the loss modulus indicate a single curve.

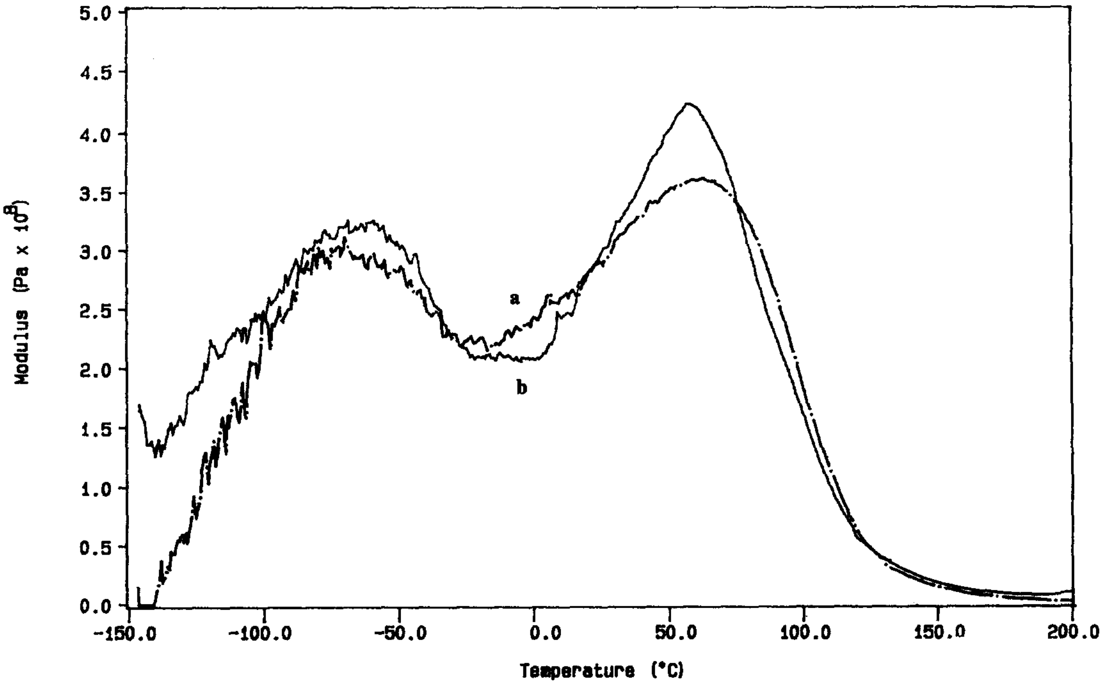


Figure 2 Loss modulus curves of the poly CR39 cured at (a) 70°C with 1.5% BPO and (b) 90°C with 5% BPO

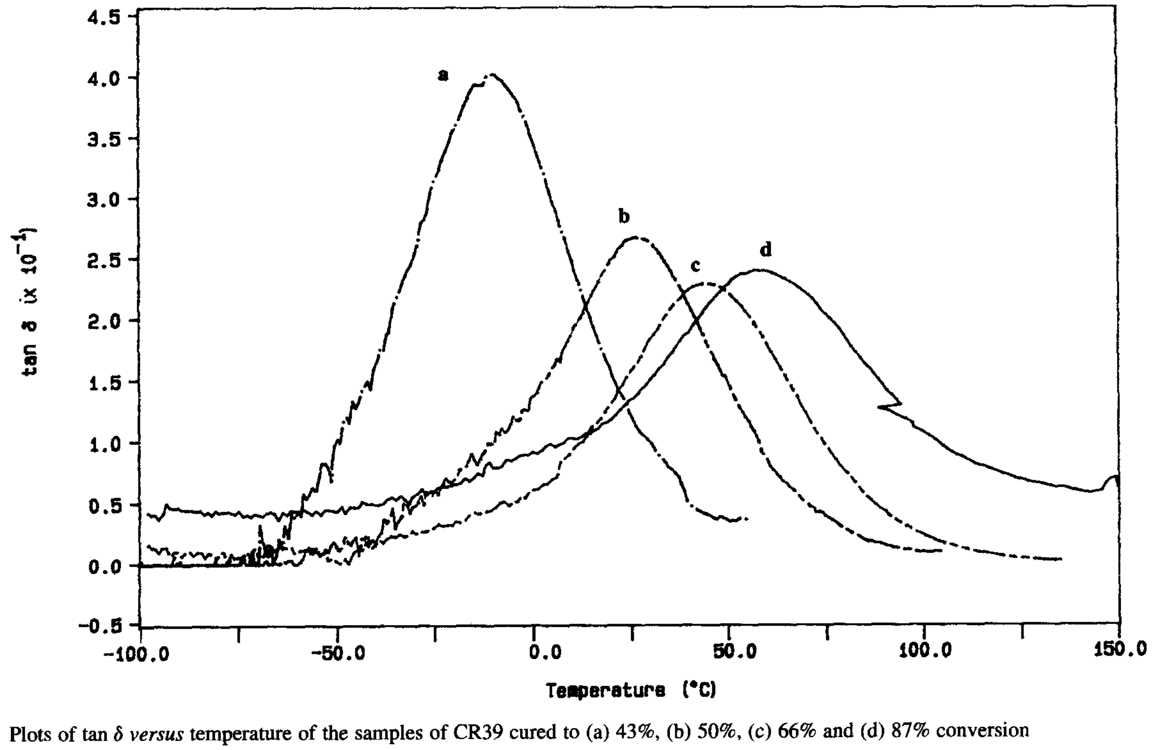
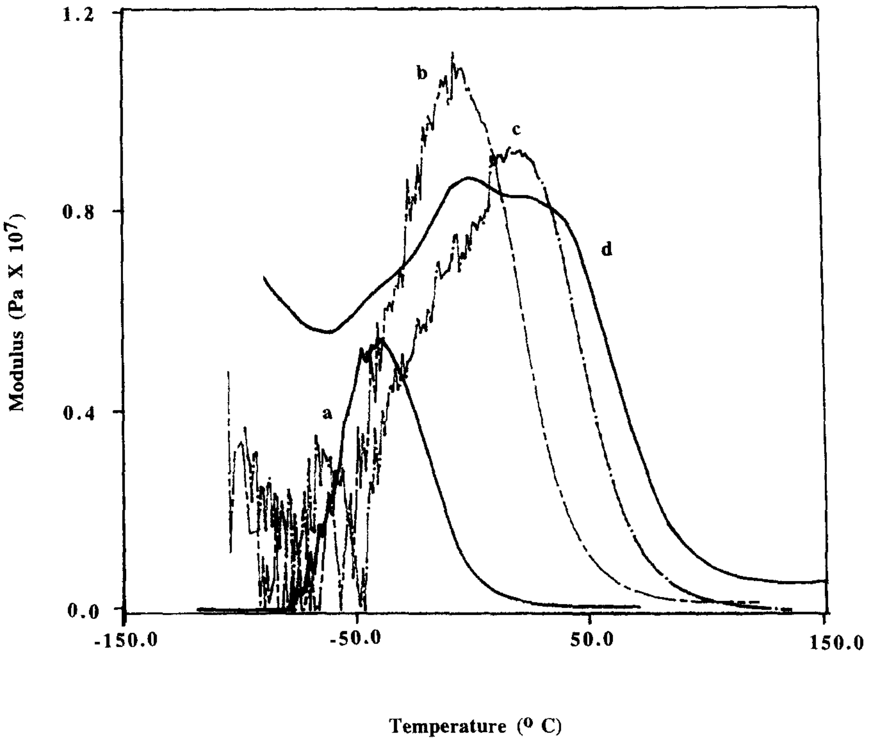


Figure 3 Plots of tan δ *versus* temperature of the samples of CR39 cured to (a) 43%, (b) 50%, (c) 66% and (d) 87% conversion



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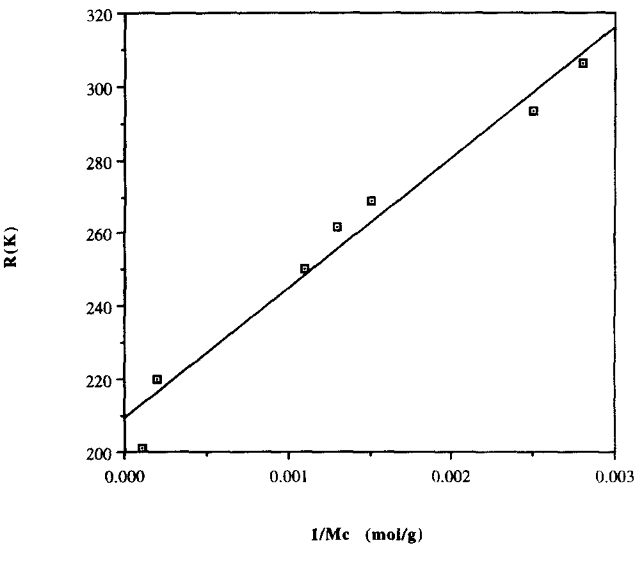

Figure 5 *R versus* $1/M_c$ (refer to Eq. (3)) for the polymerisation of CR39 resin

This curve becomes broader including several shoulders, in samples cured to higher extents.

Figure 3 also shows an increase in T_g with conversion for homopolymerisation of CR39. This increase may be caused by several factors; consumption of monomer, an increase in the molecular weight, and an increase in crosslink density which causes a reduction in the mobility of the polymer chains. But the molecular weight of allylic polymers are controlled by chain transfer to the monomer during the free radical polymerisation reaction, and a number average molecular weight of 55 is obtained for CR39 polymer before gelation[9]. No significant change in the molecular weight is observed in the free radical polymerisation in the pregel period. A Trommsdorf effect is not present in the homopolymerisation of CR39[14], as such there could not be any contribution from molecular weight changes to the change in T_g during the cause of the free radical polymerisation of these allylic monomers. Thus, the increase in T_g for the homopolymerisation of CR39 can only be due to monomer consumption and crosslinking.

Fox and Loshaek[15] derived an expression relating the T_g of a network to the crosslink density by assuming the specific volume of the polymer at the glass transition to be a linear function of T_g;

$$T_{gP} = T_{gL} + K_n/M_c \qquad (1)$$

where T_{gL} is the T_g of an uncrosslinked polymer and K_n is a material constant. In addition, the theory of Kelly and Beuche[16] relates the T_g of a polymer/monomer mixture, to the composition of the mixture;

$$T_g = (\alpha_P\phi_P T_{gP} + \alpha_M(1-\phi_P)T_{gM})/(\alpha_P\phi_P + \alpha_M(1-\phi_P)) \qquad (2)$$

where α_M and α_P are the volume expansion coefficients of the monomer and polymer, and ϕ_P is the mole fraction of polymer. Then substituting equation (1) into equation (2) gives an equation relating the T_g of the polymerising mixture to the crosslink density and fraction of monomer polymerised. The value of K_n can be calculated by fitting equation (3) to the experimental data points, as shown in *Figure 5*. A K_n value of 3.6×10^4 was calculated for homopolymerisation of CR39, which may be compared to the value of 1.3×10^4 reported[17] for a trifunctional network of polystyrene and of 2.5×10^4 for a crosslinked polyethylene glycol[18].

$$R = T_{gL} + K_n/M_c = (\alpha_P\phi_P T_g + \alpha_M(1-\phi_P)(T_g - T_{gM}))/\alpha_P\phi_P \qquad (3)$$

DiBendetto[19] derived an equation relating the shift in the glass transition temperature to the degree of conversion. The

DiBendetto equation is:

$$T_g - T_{gL} = T_{gL}\{[(E_x/E_m - F_x/F_m)c]/[1 - (1 - F_x/F_m)x]\} \quad (4)$$

where E_x/E_m is the ratio of the lattice energies for crosslinked (x) and uncrosslinked (m) polymers, F_x/F_m is the ratio of the segmental mobilities for the same two polymers, and c is the degree of conversion. The ratio E_x/E_m can be approximated by;

$$E_x/E_m = (d_m/d_x)[(M_0)_x/(M_0)_m](\delta_x/\delta_m)^2 \quad (5)$$

where d_m and $(M_0)_m$ are the density and molecular weight of the monomer units in uncrosslinked polymer, d_x and $(M_0)_x$ are the density and molecular weight of monomer unit in crosslinked polymer, and δ_M and δ_P are the solubility parameters for the monomer (M) and polymer (P). DiBendetto has estimated that $E_x/E_m = 1.2$ for a styrene–divinyl benzene system, and a similar value should hold for many other crosslinking systems. Therefore equation (4) should approximate to

$$F_x/F_m = [1.2T_{gLx} + (T_g - T_{gL})_x - (T_g - T_{gL})]/[(T_g - T_{gL}) + T_{gLx}] \quad (6)$$

A plot of F_x/F_m *versus* double bond conversion for the homopolymerisation of CR39 is shown in *Figure 6*. The data indicate that the segmental mobility of the crosslink polymer is similar to the uncrosslinked polymer up to about 60% double bond conversion for the homopolymerisation in CR39. After that the ratio F_x/F_m decreases. The conversion at which segmental mobility starts to drop (60%) is just prior to the conversion (66%) at which radicals start to build-up as observed from the e.s.r. experiments and increase in the peak width of the tan δ curve as mentioned before. The rate constant for the propagation reaction (k_p) also commences to drop at this conversion, due to the drop in the segmental mobility in the system[10].

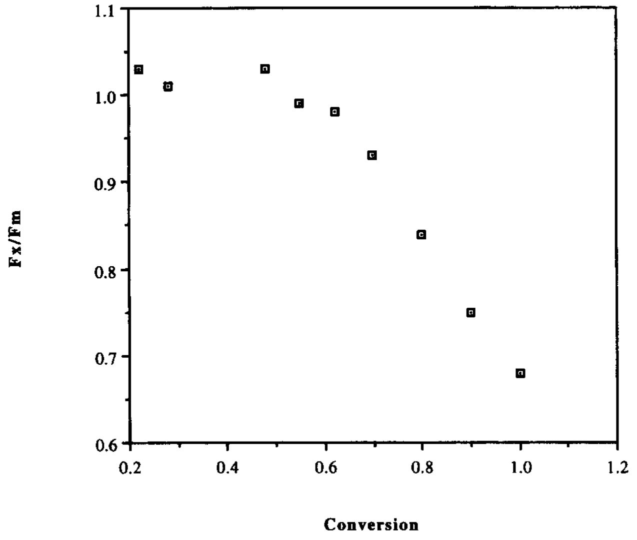

Figure 6 F_x/F_m *versus* conversion for CR39 polymerisation

Unlike other linear polymers such as polymethyl methacrylate, uncrosslinked CR39 contains long side chains. These side chains contribute to the segmental mobility in poly CR39. Even though in CR39 the first crosslinked network (gel) begins to form[20] at about 22–23% double bond conversion, most of the long side chains remain free up to about 50% conversion, contributing to high segmental mobility in the polymer. It is only after most of the CR39 molecules are bound to the polymer and most have formed crosslinks that the segmental mobility starts to drop in this system.

The intensity of the tan δ peak at the glass transition temperature reflects the extent of mobility of the macromolecular chain segments at that temperature[21]. Since crosslinks restrict main chain mobility in the polymer, one would expect that the area under the loss modulus curves *versus* temperature to increase with a decrease in crosslink density. This trend will be reflected in the intensity of the tan δ peak. *Figure 7* shows the tan δ_{max} *versus* $1/M_c$ for homopolymerised CR39. An increase in the crosslink density reduces the tan δ_{max} as expected. Two linear regions can be observed in *Figure 7*. An initial region characterised by a small slope and a second region where the slope is much greater, with the intersection between these two

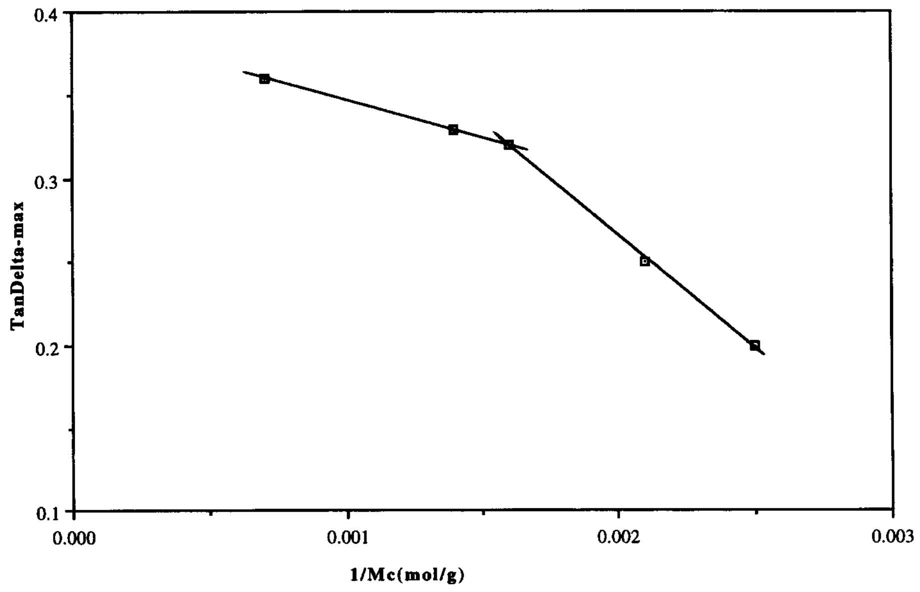

Figure 7 Tan δ_{max} *versus* $1/M_c$ for CR39 polymerisation

regions at about 1.7 × 10^{-3} mol g^{-1}. Similar effects have been observed[19] in other crosslinking systems, for example, in polypropylene glycol networks a decrease in tan δ_{max} was observed at high crosslink densities, whereas at low crosslink densities, there was virtually no effect on tan δ_{max}. In polypropylene glycol the change in tan δ_{max} occurred between 8×10^{-4} and 2×10^{-2} mol g^{-1} average molecular weight between crosslinks and below the value 8×10^{-4} mol g^{-1} there was no change in tan δ_{max}.

The tan δ_{max} values of polyCR39 samples cured to 25 and 40% under different polymerisation conditions are given in *Table 1*. The values indicate that tan δ_{max} continues to increase at low crosslinking densities so that the plateau region observed in polypropylene glycol is not observed in polyCR39. Further, the data given in the table show that the tan δ_{max} is always higher for a polymer cured at a faster rate. This indicates that the crosslinking density is lower in the samples cured at the higher rates, confirming the observation made from the modulus data.

Copolymerisation of CR39 and MMA

The tan δ and loss modulus curves for a MMA/CR39, 50/50, sample cured to complete conversion using a temperature profile of 80–175°C is shown in *Figure 8*. The data obtained with three point bending mode, indicate that this copolymer has two glass transition regions: 60–80 and 75–125°C. The broad shoulder at 60–80°C proved to be irreversible, by repeating the DMA heating cycle for the same sample. Therefore, this shoulder is not due to the α' transition discussed for the homopolymer CR39. The two glass transition regions could be due to phase separation into a MMA rich region and a CR39 rich region.

The tan δ curves for MMA/CR39 50/50 mixtures at different conversions at 60°C with 1% BPO are shown in *Figure 9*. There is no change in the width of the tan δ curves with conversion, over the total conversion range of 44–80%. According to the reaction mechanism proposed[22] for this system, the polymerisation could be divided broadly into two regions. Region I, from 0–45% total conversion, predominantly MMA polymerises with a very small amount of CR39. Beyond this total conversion, i.e. 45%, region II, remaining MMA polymerises with the bulk of CR39. The absence of change in tan δ curve width during region II indicates that there is no change in the network chain distribution during this region of polymerisation. However, according to the reaction mechanism discussed before, one would expect a change in the network chain distribution in this region. As the MMA is consumed, there will be an increase in the unreacted CR39 proportion of the mixture. This will lead to an increase in CR39 in the instantaneous polymer composition as the reaction proceeds. The incorporation of CR39 molecule will result in the introduction of a crosslink site. Thus there will be a change in the crosslink chain length as the polymerisation proceeds, and an increase in the width of the crosslink chain distribution. However, the absence of any change in the width of the tan δ curve implies the formation of a interpenetrating network where the polymers are (1) PMMA rich or (2) CR39 rich. Since the crosslink density of the CR39 rich polymer is greater, that crosslink density becomes more effective. However, a certain portion of the PMMA rich region is phase separated as indicated by the two glass transition regions in *Figure 8*.

The curves in *Figure 9* also indicate an increase in the T_g with conversion for a CR39/MMA 50/50 mixture. This increase in T_g is due to monomer consumption and an increase in the crosslink density. As has been observed[22], for this sample composition, the Trommsdorf effect was

Table 1 Tan δ_{max} values of polyCR39 samples of low conversions

Initiator conc. (%) (BPO)	Temperature of polymerisation (°C)	Conversion (%)	Tan δ_{max}
5	90	40	0.55
1.5	70	40	0.4
5	90	25	1.15
1.5	70	25	0.75

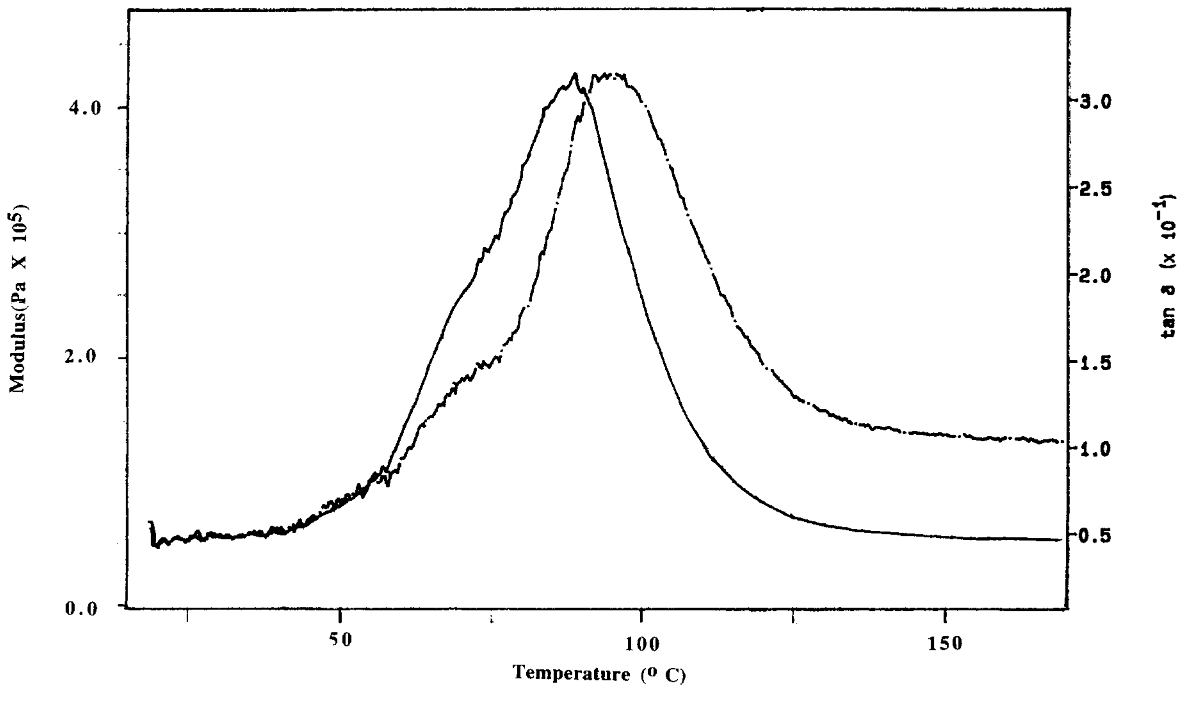

Figure 8 Tan δ and loss modulus curves for the fully polymerised copolymer of CR39 and MMA obtained with three point bending mode

greatly reduced compared to homopolymerisation of MMA. Thus any contribution from molecular weight may be ignored. Up to 50% total conversion the change in T_g is mainly due to monomer consumption, as there is no significant change in the crosslink density. At low degrees of crosslinking, the shift in the T_g is very small, but at higher degrees of crosslinking the shift becomes very large and is sensitive to relatively small changes in M_c, the average molecular weight between crosslinks.

The effect of different compositions on T_g of uncrosslinked polymers is shown in *Table 2*. These samples were prepared by using different feed compositions and the samples were isolated after about 80% MMA have reacted. This is just prior to the formation of the gel. With increased CR39 in the feed, copolymers with increased CR39 are obtained. Increased CR39 in the polymer molecule reduces the T_g.

The tan δ curves for polymers prepared from different proportions of MMA/CR39, polymerised to complete conversion using a temperature profile between 60–85°C with 1% BPO are shown in *Figure 10*. These curves were obtained with the parallel plate mode, thus the two glass

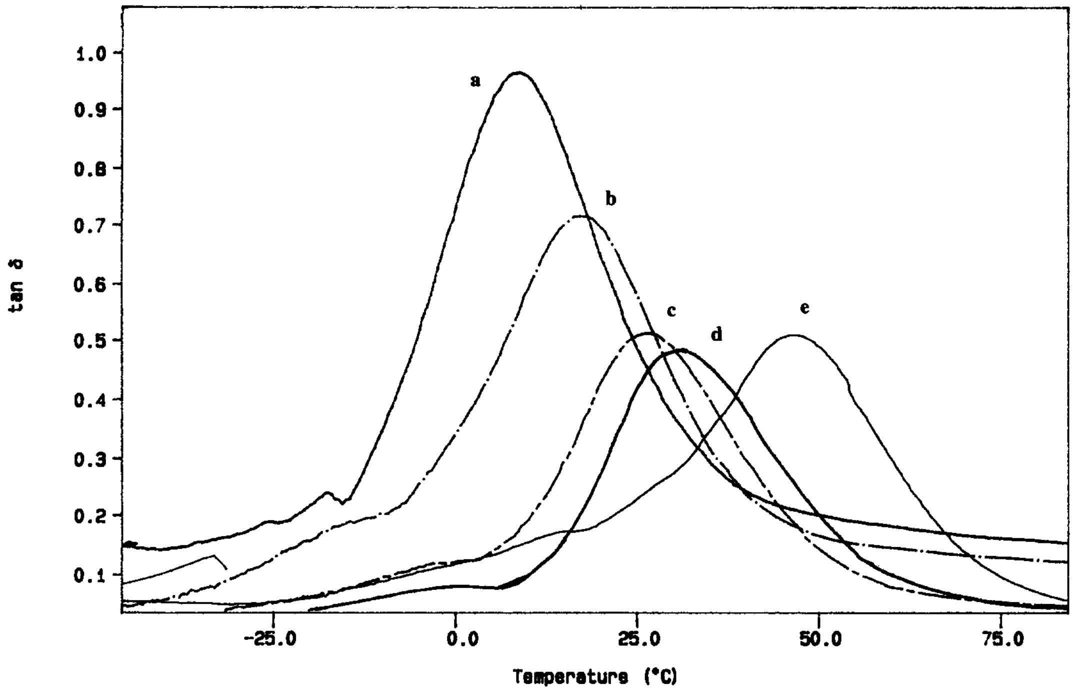

Figure 9 Tan δ *versus* temperature for the samples of copolymer MMA/CR39 (50/50 mixture), cured to (a) 44%, (b) 57%, (c) 72%, (d) 75% and (e) 80% conversion obtained with parallel plate mode

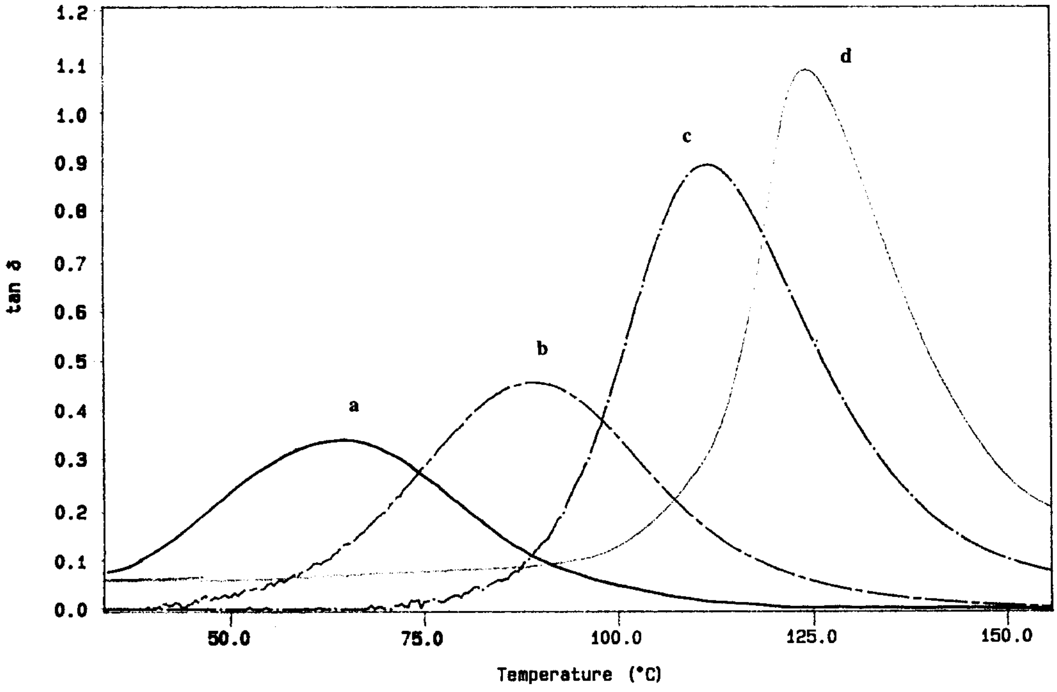

Figure 10 Tan δ *versus* temperature curves for copolymers of (a) polymethyl methacrylate and (b) 75/25, (c) 50/50 and (d) 25/75 copolymers of MMA and CR39 feeds obtained with parallel plate mode

Table 2 Glass transition temperatures of copolymers of CR39 and MMA (samples recovered after 80% of MMA reacted)

Monomer feed (MMA/CR39)	T_g (°C)
100	124
75/25	111
50/50	97
25/75	84

Table 3 Analysis of DMA data

	T (°C)	Half width of tan δ curve (°)	Normalised area of tan δ curve	Normalised activation energy
CR39	30	80		
CR39/MMA = 75/25	15.6	39	0.79	3.8
CR39/MMA = 50/50	17.7	36	0.79	2.8
CR39/MMA = 25/75	13.1	24	1.12	1.1
MMA	10.7	22.6	1	1

transition regions mentioned in *Figure 8* were not observed here. Some samples were brittle, and therefore, sufficiently long pieces to run three point bending mode could not be recovered. *Figure 10* shows a decrease in T_g of the fully polymerised product with increasing CR39 content. This corresponds to the difference in the T_g values of the two homopolymers (T_g of PMMA is 120°C and that of polyCR39 is 90°C).

The half width, normalised area of the tan δ curve, and the difference between tan δ_{max} and loss modulus $_{max}(T)$ for the fully polymerised homo- and copolymers of CR39 are given in *Table 3*. The half width of the tan δ curve for poly CR39 is about 80°, and T is about 30°. In many low crosslinked single phase systems, including rubber networks, the value of T is much lower. For example, in polybutadiene networks[23] the value is only 3–6°. The crosslink density in such systems are much less than poly CR39. However, the width of the tan δ curve is much higher in polydimethacrylates compared to poly CR39[24]. Both half widths of the tan δ curve and T is less in copolymers of CR39–MMA and they increase as the CR39 content is increased. The increase in the tan δ curve width with increased CR39 content could be due to the difference in the change in the chain length distribution during curing in these systems as explained before or due to phase separation.

Using the reactivity ratios reported[22], the instantaneous polymer composition (f) at 0 and at 80% conversion could be calculated for each feed composition.

$$f = [F(r_1F + 1)]/(F + r_2) \qquad (7)$$

where F is the feed MMA/CR39, f the instantaneous polymer MMA/CR39, r_1 the reactivity ratio of MMA = 32, and r_2 the reactivity ratio of CR39 = 0.03.

The values are given in *Table 4*. The calculations show that the ratio of f at 0% and at 80% is 20–25% in all three compositions. This indicates that the crosslink chain length change during polymerisation is similar in all three compositions. Therefore the change in tan δ peak widths (higher width in higher CR39 feeds) could not be due to crosslink chain length distribution difference.

Table 4 Change in instantaneous polymer composition with conversion in different feed compositions

	MMA/CR39		
	25/75	50/50	75/25
F	0.46	1.38	4.16
f at 0% = $f0$	19	56	167
f at 80% = $f80$	5	12	34
% of ($f0$/$f80$)	25	21	20

At the time of near depletion of MMA in the cure mixture, the system is a lightly crosslinked network (polymethyl methacrylate crosslinked through few CR39 molecules) swollen in CR39 monomer. The amount of monomer CR39 inside the network, depends on the swelling index of this crosslinked polymer in the solvent CR39. The swelling index, in turn, depends on solubility of the polymer in the solvent and the crosslink density. Therefore it is likely that in the mixtures with greater CR39 contents (50%, 75%), the amount of CR39 outside the network will be higher. More CR39 in the feed means more crosslinks in the network and more free CR39 acting as the solvent. This will result in phase separation during the final curing stages. This phase separation is therefore the cause of the higher peak width of the tan δ curves in mixtures with higher CR39 contents. This system is therefore expected to contain two regions: a PMMA rich region which is an interpenetrating network (IPN) of PMMA-co-CR39 with CR39, and a CR39 rich region which is CR39-co-MMA (a very small percentage of MMA).

The area under the tan δ curve has been shown to be related to the activation energy of the backbone motion in magnitude[25]. For example, the average activation energy of transition for IPN materials can be calculated from the dynamic mechanical data as proposed before[26], using the equation

$$t_A = (\ln E_G - \ln E_R)(R/E_A)(\pi/2)(T_g)^2 \qquad (8)$$

where t_A is the area under the tan δ curve, E_G and E_R are the storage modulus at glassy phase and rubbery phase respectively, and E_A is the activation energy. The calculated values are also given in *Table 3*. The activation energies are the normalised values since the peak areas could not be calculated directly, but had to be calculated by the cutting and weighting method. The data given in the table indicate an initial increase and then a drop in tan δ peak area, and an increase in activation energy with increasing CR39 content. Increased crosslinker concentration reduces the backbone motion due to more network interlock. This confirms the interpenetrating network behaviour with CR39 polymer contributing to effective crosslinks in the system.

In the MMA/CR39 50/50 mixture, the value of tan δ_{max} does not change during the region where polymerisation of MMA predominates but begins to drop after 44% total conversion up to 72% conversion. As observed for the homopolymerisation of CR39, there is no change in tan δ_{max} beyond 70% conversion. The higher the CR39 content, the lower is tan δ_{max} at complete conversion, as shown in *Figure 10*. This is due to an increase in the crosslink density.

CONCLUSIONS

Different network transition regions for fully polymerised homopolymer CR39 and its copolymer with methyl methacrylate were identified by DMA data. Controlled, slow curing of CR39 was shown to give networks which are homogeneous with higher crosslink densities in the macro phase than observed for rapid cure. During the homopolymerisation of CR39, the segmental mobility of the polymer remains unchanged until 60% of the double bonds are converted, but beyond this conversion the segmental mobility commences to drop again significantly. This conversion corresponds to the data obtained by e.s.r.

In the MMA/CR39 system, a phase separation is indicated by two T_g, regions particularly in systems with higher CR39 contents. The system consists of two regions: one with a CR39 rich polymer which is densely crosslinked but with a small amount of MMA molecules; the second region consists of a copolymer of MMA (predominantly) and CR39 (few), which is then locked in by a CR39 network.

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