

# Multiple Transitions in a Dimethacrylate Network

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## Synopsis

Triethylene glycol dimethacrylate, TEGDM, was cured to various dose levels (0.15–2.0 Mrad) by  $\gamma$ -irradiation at 40°C and its dynamic mechanical properties were evaluated. The resultant products had up to four transition phenomena dependent upon dose. The highest temperature transition (IV) was due to the ultimate glass transition. Transition III (ca. 40°C) was due to additional reaction occurring just above the cure temperature. Transition I (ca. -60°C) occurred at low doses and was associated with residual monomer. Transition II (ca. -10°C) is due to association of  $-(\text{CH}_2\text{CH}_2\text{O})-$  units in TEGDM monomer, and the associated regions persist in the crosslinked polymer.

## INTRODUCTION

Ideas about the structure and properties of crosslinked polymers prepared by polymerization of multifunctional monomers have been dominated by Houwink's model of highly crosslinked particles embedded in a matrix that is less crosslinked. Houwink considered networks prepared by condensation polymerization, with special emphasis on phenol-formaldehydes.<sup>1,2</sup> In networks prepared by addition polymerization of monomers with multiple double bonds, evidence for the presence of crosslinked particles has proved to be more elusive.<sup>3-5</sup> Nevertheless, particle formation has been inferred from studies of gelation and spectroturbidimetry. The latter studies also indicate that eventually, at higher degrees of polymerization, the particles are bound indistinguishably into a continuous network.<sup>3,4</sup> On the other hand the persistence of free radicals, evidenced by ESR, in networks prepared by photopolymerization of diacrylates has been interpreted as indicating the persistence of inhomogeneities up to a high degree of polymerization, i.e., 89% conversion of double bonds.<sup>5,6</sup> Furthermore, it has been pointed out that certain physical properties of highly crosslinked polymethacrylates are inconsistent with homogeneous crosslinking but, instead, are more in line with expectations of Houwink's model.<sup>7</sup>

Much work of this kind has been concentrated on networks prepared by polymerization of triethylene glycol dimethacrylate (TEGDM). Infrared spectroscopy showed the expected incomplete conversion of double bonds<sup>8</sup> and also revealed the presence of only the trans-isomer of the group  $-\text{CO}-\text{O}-\text{C}-$ .<sup>9</sup> Spectroturbidimetric analysis indicated that a limited number of particles are formed in the early stages of the reaction, which subsequently increase in size, with increasing conversion.<sup>3</sup> In a related study it was shown that the sol fraction (in acetone) consisted solely of unreacted monomer.<sup>10</sup> This view was sustained

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in subsequent work on polymerization by  $\gamma$ -irradiation, with the additional point made that the particles undergo microsineresis.<sup>11</sup> In other work on the radiation polymerization of TEGDM that may be pertinent, evidence was presented that the rate of conversion of double bonds was influenced by association of monomer units, but only at temperatures below about 60°C.<sup>12</sup>

Heterogeneity in polymeric systems may be inferred from studies of the onset of molecular motion caused by an increase in temperature. Dielectric relaxation was studied in highly crosslinked networks made by stepwise heating (up to 140°C) of TEGDM that contained an initiator.<sup>13</sup> It was stated that three types of dielectrically active intra-chain mobilities were detected at -100, +97, and +167°C at 1 kHz (the figure cited to support this statement indicates values that are greater by 60°C: it is assumed here that the temperature axis is mislabeled). The two lower transitions were assigned to local mobility of ester groups. The highest transition was assigned to a process "linked with movements of the larger fragments of the molecules including the network joints."<sup>13</sup> A study designed specifically to check the applicability of Houwink's model was made using networks prepared by photopolymerization of TEGDM at room temperature, resulting in up to 73% conversion of double bonds. A spin probe (2,2,6,6-tetramethylpiperidine-1-oxyl) was introduced by vapor penetration and judged to reside only in the matrix, not penetrating into grains, i.e., into highly crosslinked particles. Changes in line widths of ESR spectra indicated a range of transitions from -53 to +7°C. These changes were assigned to glass transitions occurring in a "loose, defective interlayer situated between grains".<sup>14</sup> Related conclusions were drawn, independently, from a calorimetric study in the range -196 to +47°C.<sup>15</sup> TEGDM was partially polymerized by exposure to  $\gamma$ -rays at room temperature. Samples were then reirradiated at -196°C to introduce immobilized free radicals. On warming in a calorimeter, a transition was observed in the range -73 to -56°C followed by further polymerization in the range -57 to -37°C. This was assigned to a glass transition occurring in a phase rich in monomer. By more elaborate procedures another transition was detected in the range -43 to -16°C followed by further polymerization in the range -41 to -15°C. This was assigned to a second glass transition occurring in a phase rich in polymer.<sup>15</sup>

Dynamic mechanical studies of TEGDM have been limited to samples prepared using a high dose of  $\gamma$ -rays (20 Mrad). A featureless scan was obtained apart from a glass transition in the range 120-200°C, assigned by reference to changes in storage modulus, with a maximum in internal friction ( $\tan \delta$ ) near 180°C.<sup>16</sup> In respect of sensitivity to DMA such samples would be judged homogeneous, but possibly they correspond to a condition of rehomogenization due to sufficient crosslinking. The purpose of the present work is to investigate evidence for inhomogeneities by DMA studies of samples prepared using low doses of radiation.

## EXPERIMENTAL

A purified grade of TEGDM [ $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2\text{OCH}_2-$ ]<sub>2</sub> was used as supplied (Esschem, Essington, PA). Films were made by  $\gamma$ -irradiation of TEGDM in vertically located molds made by spacing two microscope slides 0.07 cm apart with a paraffin wax boundary: ambient temperature 40°C; Cs-

137, dose rate = 0.8 Mrad/h (1 rad = 100 erg/g). Samples of about  $6.5 \times 0.4$  cm were cut with a razor blade. In similar experiments using tubes, the gel point was detected by a loss in fluidity. Weighed film samples ( $W_1$ ) were immersed at room temperature, some in acetone and others in methylene chloride (analytical grade reagents). They were periodically removed, mopped, and weighed until reaching an equilibrium weight ( $W_2$ ) after immersion for up to 1 month. Finally, to remove imbibed liquid, the swollen samples were kept in vacuum until reaching constant weight ( $W_3$ ). The soluble fraction was calculated as  $(W_1 - W_3)/W_1$ ; percent swelling as  $100(W_2 - W_3)/W_3$ .

After cooling with liquid nitrogen, samples (ca. 20 mg) were scanned in a differential scanning calorimeter (DuPont 990: DSC Mode), at  $10^\circ\text{C}/\text{min}$  unless specified otherwise.

Samples were clamped at each end, cooled, and then subjected to a sinusoidal tensile strain at intermittent frequencies of 1.1, 11, and 110 Hz during heating at  $2^\circ\text{C}/\text{min}$  [Dynamic Mechanical Analyzer (DMA): Autovibron DDV-IIC, IMASS]. However, as the frequency dependence is small in this range, only data at 11 Hz will be presented. Printouts were made of the temperature dependence of storage modulus ( $E'$ ), loss modulus ( $E''$ ), mechanical loss due to internal friction ( $\tan \delta$ ), and sample length between clamps ( $L$ ). This latter adjunct measurement to DMA takes advantage of a built-in adjustment that, allowing for thermal expansion of the sample, ensures application of a small constant tension.

## RESULTS

TEGDM remained fluid up to a dose of 0.13 Mrad but had gelled after 0.14 Mrad, in the sense that the product was not seen to flow on inversion of its container. There were two indications of inhomogeneity. First, very small flecks of gel were attached to the wall of the container in samples given 0.13 Mrad. Second, film samples given 0.3 Mrad were observed to partially delaminate, at corners and edges, when kept in acetone indicating an inner zone of soluble material. The soluble fraction decreased with increasing dose while the equilibrium swelling of the gel fraction decreased from a high value just after the gel point (850%) to 24% after a dose of 0.3 Mrad. Further irradiation reduced the swelling to 14% (Table I).

DMA scans on specimens with various dose levels are illustrated in Figures 1(A)–5(A). After lower doses, evidence for the occurrence of several transitions is provided by maxima in  $E''$  and, more clearly, in  $\tan \delta$ . On increasing the dose, the lower maxima became almost negligible, as is the case after 2.0 Mrad [Fig. 5(A)]. The assignment of transition temperatures in DMA work is usually made by reference to maximal values of  $\tan \delta$ . This often has the advantage of giving a clearly defined value, although in other cases the maximum appears only as a broad hump. Despite the relatively clear definition sometimes afforded by reference to  $\tan \delta$  (max.), it was found in previous work, on copolymers of TEGDM, that it overestimated values of  $T_g$  relative to a more conventional reference to changes in thermal expansion. In contrast, better agreement with changes in thermal expansion was obtained by noting the temperature at which  $E'$  began a more marked decrease.<sup>16</sup> The onset of this decrease was defined by

TABLE I  
Sol Fraction and Percent Swelling of P(TEGDM) in Acetone

Dose (Mrad)	Sol fraction	Percent swelling
0.15 <sup>a</sup>	0.91	850
0.3	0.12	24
0.4	0.07	20
0.5	0.06	19
0.6	0.04	17
0.8	0.02	16
2.0	N.D. <sup>b</sup>	14

<sup>a</sup> For comparison, using CH<sub>2</sub>Cl<sub>2</sub> as solvent: sol fraction = 0.88: % swelling = 33.

<sup>b</sup> Not detectable.

drawing a tangent as illustrated in Figures 1(A)–5(A). To put these results in perspective, it should be remarked that the  $E'$  method marks the onset temperature of a transition whereas the  $\tan \delta$  (max.) method occurs within a range of temperatures during which the transition is completed.

Plots of sample length versus temperature are generally complex [Fig. 1(B)]. There is a simpler pattern after higher doses [Figs. 2(B)–4(B)], and eventually there is usually a single upturn [Fig. 5(B)]. Upturns, assigned by the method of intersecting tangents, indicate transitions that are accompanied by an increase in the coefficient of thermal expansion. The downturn is attributed to shrinkage accompanying the post-irradiation polymerization of residual double bonds during testing. This is taken as evidence of a transition on the grounds that polymerization occurs when there is an increase in mobility of the reactants. The temperatures at which upturns and downturns of length were detected are illustrated in Figures 1(B)–5(B) and listed for all samples tested in Table II.

DSC runs on TEGDM showed the monomer to have a glass transition temperature of  $T_g = -85^\circ\text{C}$ , using a conventional method of assignment by intersecting tangents. Runs on a sample taken by irradiation (0.15 Mrad) to a conversion just beyond the gel point and then extracted with methylene chloride showed a glass transition in this same region, at  $T_g = -85^\circ\text{C}$  (Fig. 6: run 1). Additionally after vacuum stripping, the extract resembled TEGDM in odor and appearance and consistently had a  $T_g = -85^\circ\text{C}$ . There was further evidence of another transition near  $0^\circ\text{C}$ . The first run was stopped short of  $40^\circ\text{C}$  in order to avoid the onset of polymerization. Then a second run was made at a scan rate of  $2^\circ\text{C}/\text{min}$  for more direct comparison with DMA runs. There was a marked exotherm beginning near  $70^\circ\text{C}$  and peaking at  $140^\circ\text{C}$ . As is usual in DSC work on related systems, this is taken as decisive evidence of polymerization of residual double bonds during the scan. After clearing the exothermal peak, by scanning to  $200^\circ\text{C}$ , a further run (3) was seen to be relatively featureless. There was no indication of any residual monomer. However, the transition near  $0^\circ\text{C}$  persisted. There was no indication of a transition in the range  $100$ – $150^\circ\text{C}$ , but the inability of DSC to detect transitions in highly crosslinked polymers is well known (e.g., Ref. 17).

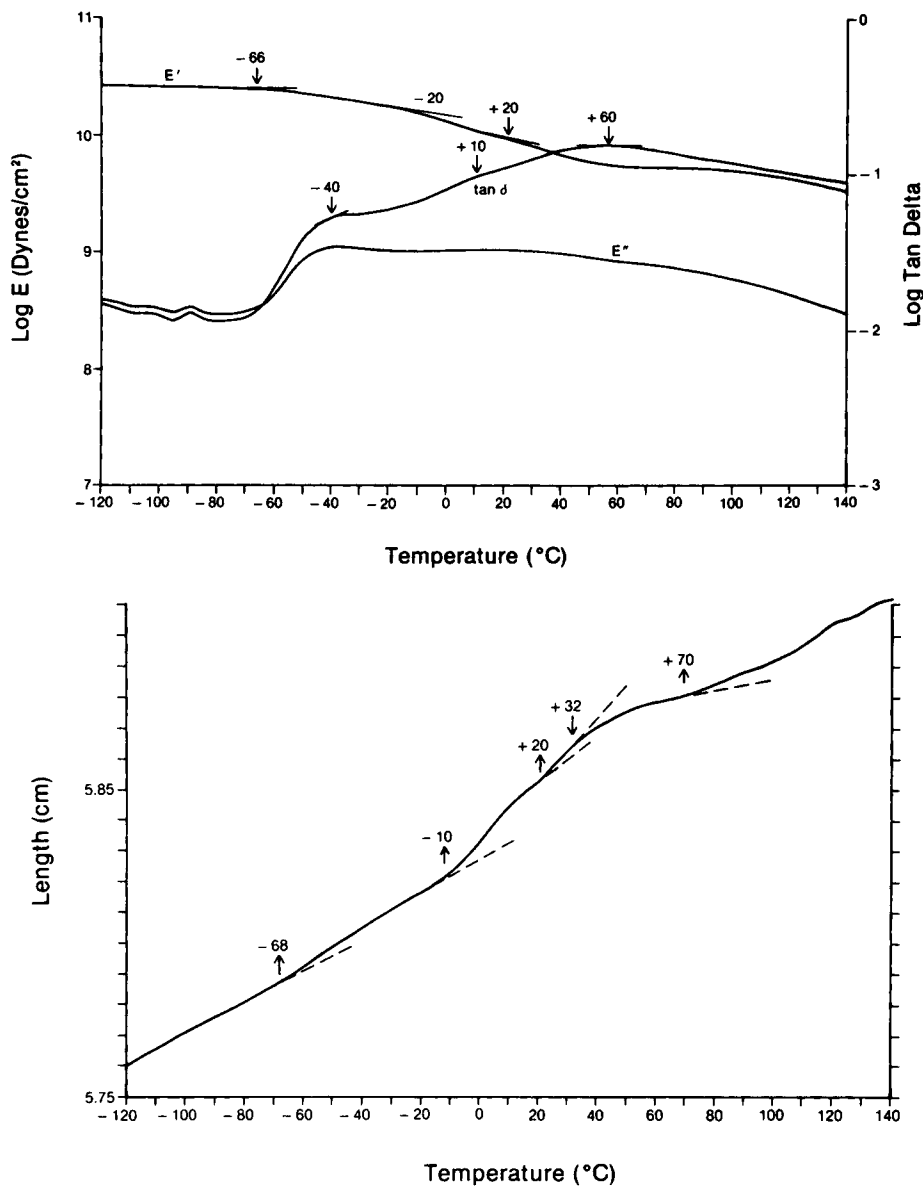


Fig. 1. Dose 0.3 Mrad. (A) DMA scan; (B) sample length.

## DISCUSSION

From its DSC value of  $T_g = -85^{\circ}\text{C}$  the sol fraction is presumed to be TEGDM monomer, in agreement with previous reports of chemical analysis.<sup>10</sup> DSC also allows characterization of samples after low doses and, from its value of  $T_g = -85^{\circ}\text{C}$ , shows that TEGDM is present as a microphase.

The results in Table II indicate that varying from sample to sample, one, two, or three transition temperatures are detected by DMA. An overall pattern

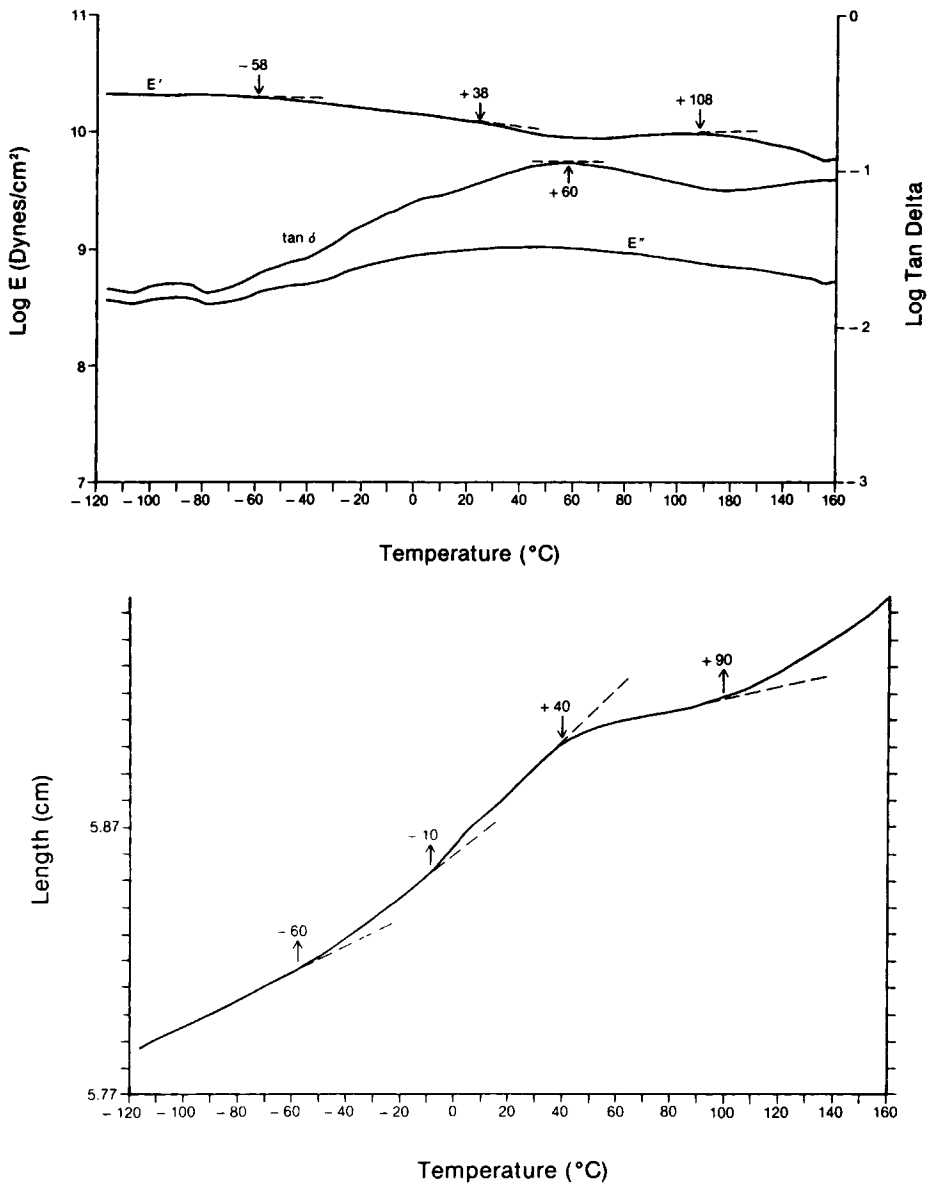


Fig. 2. Dose 0.4 Mrad. (A) DMA scan; (B) sample length.

is discerned more clearly when plots are made of transition temperatures versus dose (Fig. 7). A similar overview is obtained when transition temperatures are assigned by reference to changes in length but, in addition, there is another transition in the range  $-10$  to  $-20^{\circ}\text{C}$  (Fig. 8). Transition I, occurring in the range  $-70$  to  $-50^{\circ}\text{C}$  is judged to be related to the presence of residual TEGDM because it is detected only after low doses (cf. Table I and Figs. 7 and 8). It is tentatively assigned to a glass transition. In order to account for the rather small change in the coefficient of thermal expansion that accompanies this

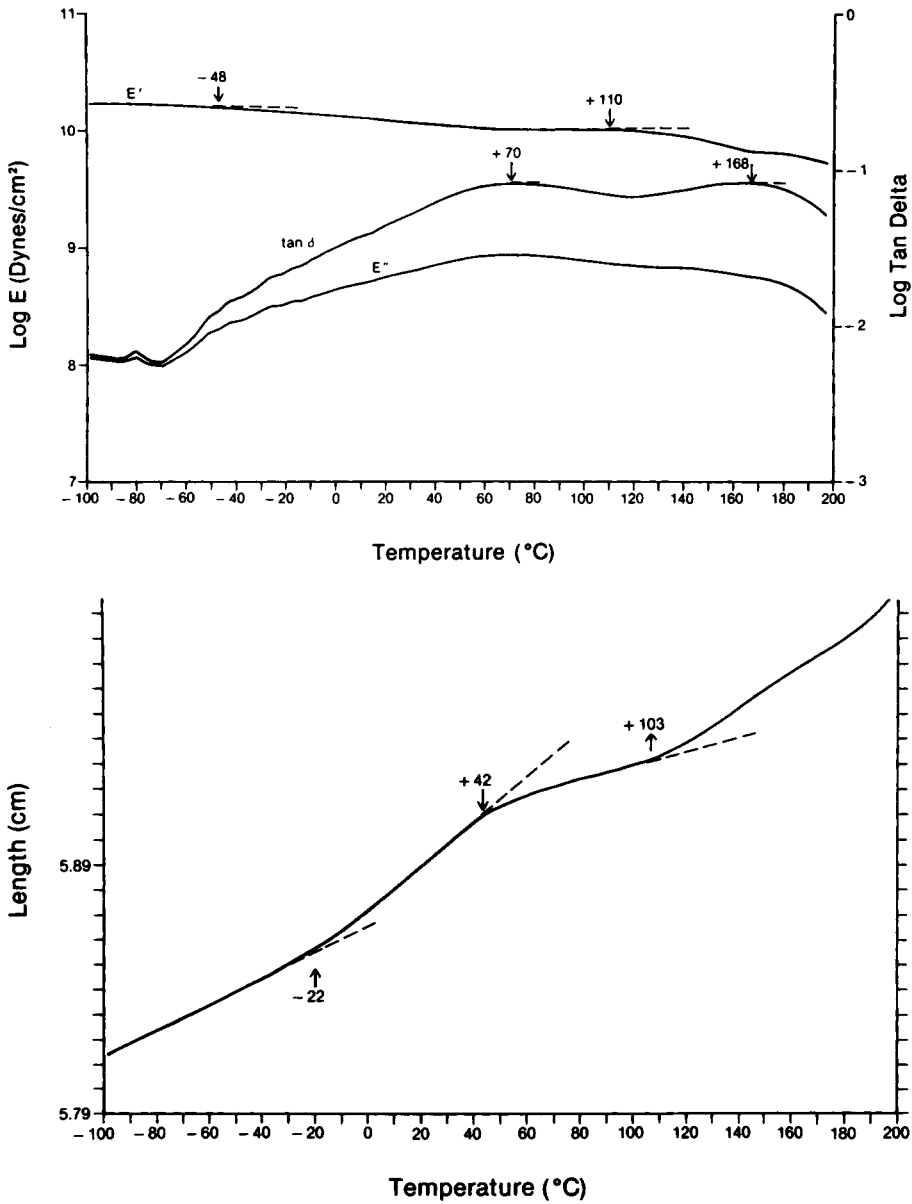


Fig. 3. Dose 0.6 Mrad. (A) DMA scan; (B) sample length.

change [cf. Figs. 1(B) and 2(B)], this transition is supposed to occur in a minor microphase.

Transition II occurring in the range -10 to -20°C, by reference to changes in length (Fig. 8), is tentatively supposed to be due to the same molecular motions detected by DSC near 0°C (Fig. 6). This transition is unusual in that it occurred in the unreacted monomer (Fig. 9, curves 1, 2, and 3) and in the "fully reacted" polymer (Fig. 6, curve 3). There are no apparent changes in modulus or damping that could be attributed to this transition. A possible

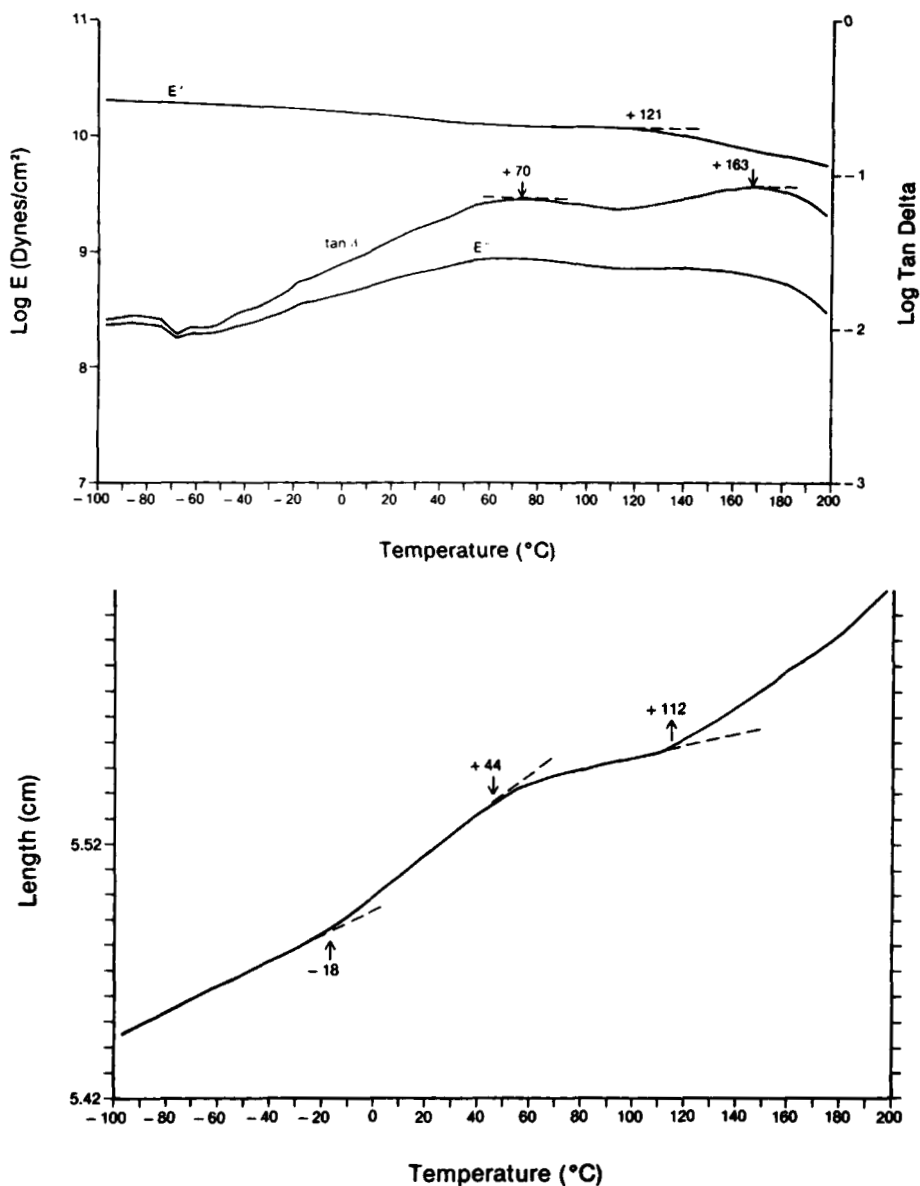


Fig. 4. Dose 0.8 Mrad. (A) DMA scan; (B) sample length.

explanation of the transition is that it arises from a crystallization and melting or from devitrification of small, ordered regions in the system associated with aligned  $-(\text{CH}_2\text{CH}_2\text{O})-$  units.

TEGDM,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{CO}(\text{CH}_3)\text{C}=\text{CH}_2$ , is generally a mixture where  $n$  has an average value of 3, but it can vary.<sup>18</sup> The bridge between the methacrylate units is triethylene glycol when  $n = 3$  and tetraethylene glycol when  $n = 4$ . The tri- and tetraethylene glycols have  $T_m = -5^\circ\text{C}$  and  $-6^\circ\text{C}$ , respectively, which is in close proximity to transition II.



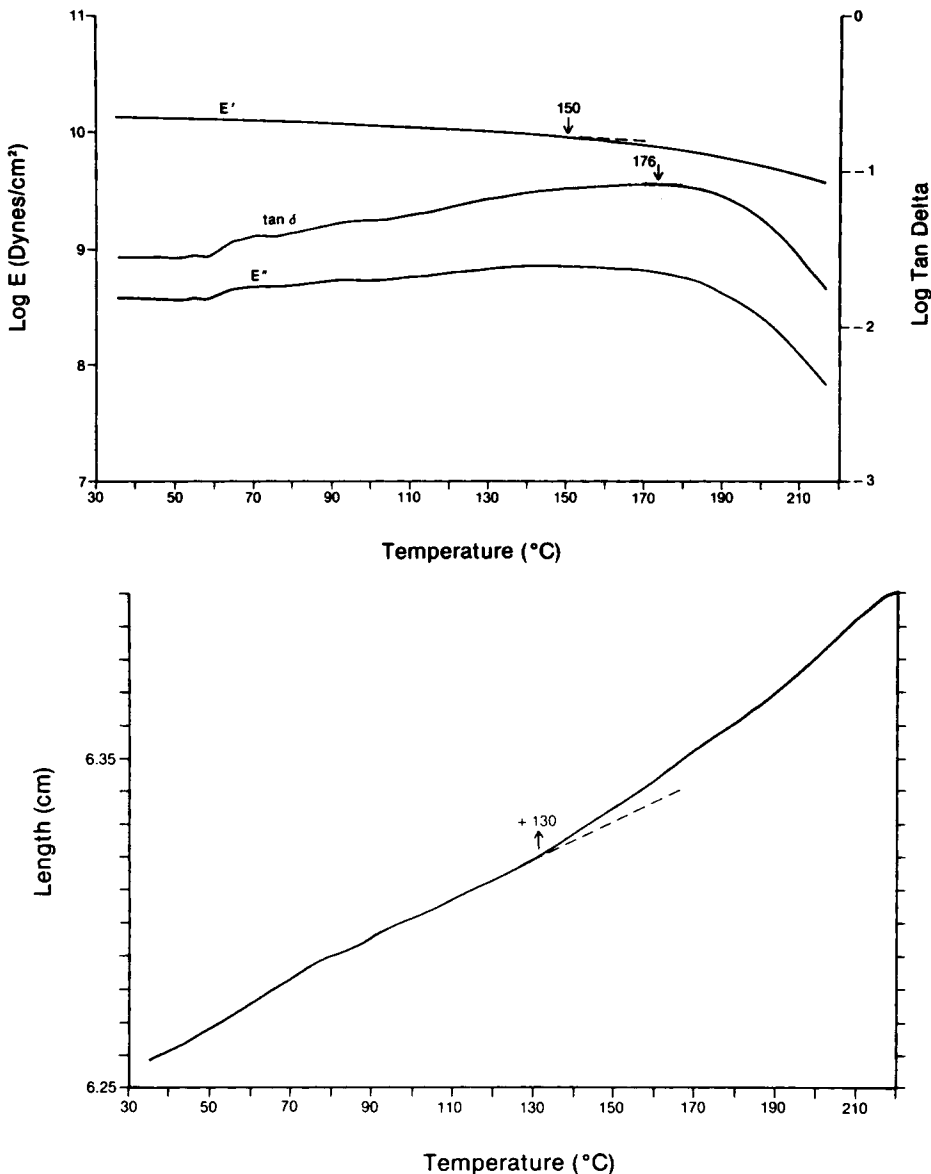


Fig. 5. Dose 2.0 Mrad. (A) DMA scan; (B) sample length.

The first three DSC curves in Fig. 9 show TEGDM monomer cooled to varying degrees. In curve 1, the sample was cooled to  $-45^{\circ}\text{C}$  and upon heating displayed a peak at  $-2^{\circ}\text{C}$ . In the second curve, the sample was cooled to  $-65^{\circ}\text{C}$ , and the peak shifted to  $+2^{\circ}\text{C}$ . In curve 3, the monomer was cooled to  $-130^{\circ}\text{C}$  and displayed a glass transition at  $-85^{\circ}\text{C}$  and a peak at  $+5^{\circ}\text{C}$  followed by a small endotherm. This behavior was reversible in the sense that if the sample was cooled to  $-45^{\circ}\text{C}$  again, then the transition would return to  $-2^{\circ}\text{C}$ . Evidently the extent of cooling affected the transition temperature and behavior. The lower temperatures permitted more time for association of the  $-(\text{CH}_2\text{CH}_2\text{O})-$

TABLE II  
Transition Temperatures ( $^{\circ}\text{C}$ ) Determined by DMA and by Changes in Length

Dose (Mrad)	Sample no.	$E'$	$L$ (upturn)	$L$ (downturn)
0.3	1	-66, -20, +20	-68, -10, +22, +70	+32
	2	-58	-50, -10	
	3	-62, +21	-10, +80	+42
0.4	4	-58, +38, +108	-60, -10, +90	+40
	5	-50, +98	-54, -12, +100	+40
	6	-55, +30, +118	-58, -12, +90	+40
	7	-38, +75	-14, +112	
0.5	8	-52, +38, +120	-15, +103	+42
	9	-51, +112		
0.6	10	-48, +110	-22, +103	+40
	11	+52	-18	
0.8	12	+121	-18, +112	+44
1.0	13	+30, +120	-13, +102	+50
1.5	14	+139	-19, +98	+40
	15	+130	+135	
2.0	16	+150	+130	+45
	17	+125	-20, +110	
	18	+148	+130	
	19	+132	+130	

groups, and this increased the transition temperature slightly. The same phenomenon was observed in tetraethylene glycol dimethacrylate with similar results under comparable conditions ( $T_g = -81^{\circ}\text{C}$ , other transition temperatures  $\pm 1^{\circ}$ ).

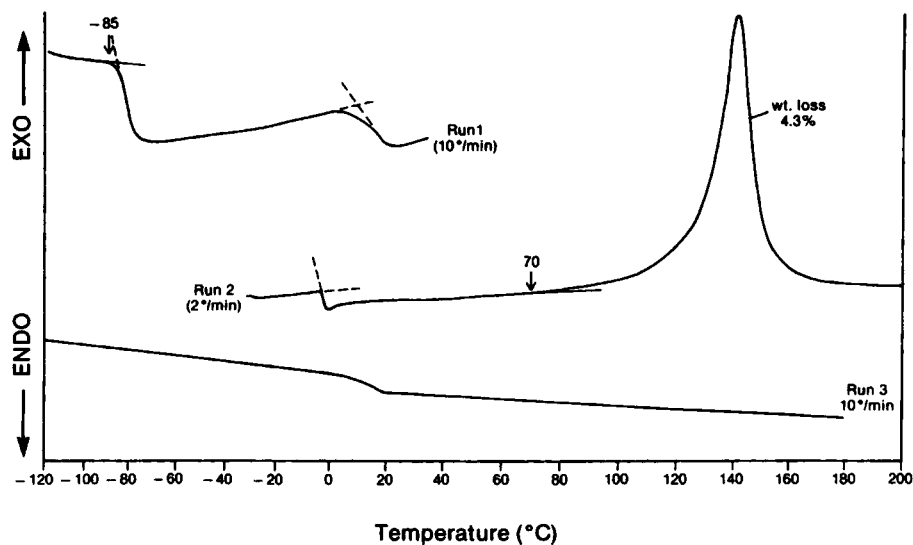


Fig. 6. DSC of TEGDM gel, dose 0.15 Mrad, extracted with  $\text{MeCl}_2$ , weight loss of 4.3% after run 2.

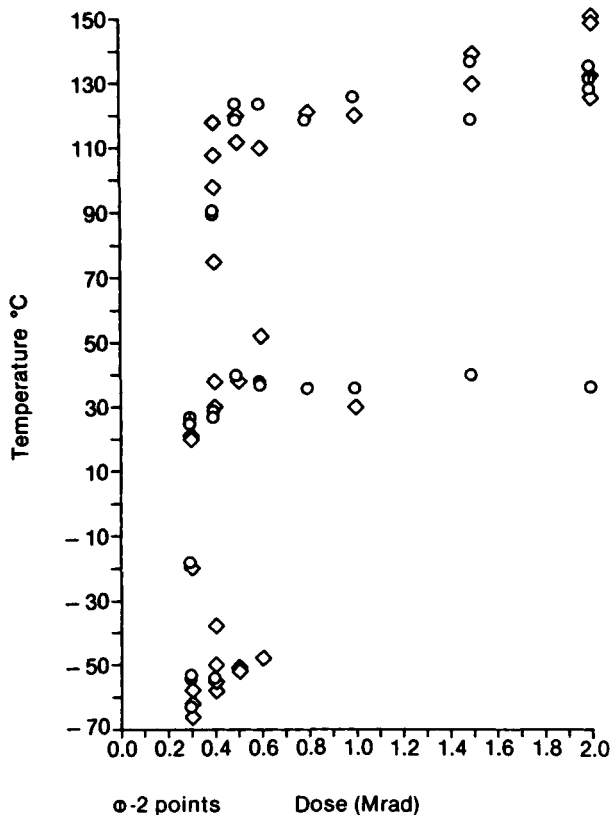


Fig. 7. Transition temperatures detected by DMA (from  $E'$  spectra).

To show that this transition is due to association of the ethylene oxide groups, a suitable model compound, 1,10-decane diol dimethacrylate, was tested. This model compound would provide a bridge between the methacrylate groups of similar length to three or four ethylene oxide units. A melting endotherm commencing at  $-20^{\circ}\text{C}$  was detected by DSC (Fig. 9, curve 4). There was no peak and no apparent glass transition.

From the DSC results on the different dimethacrylates, the transition ca.  $0^{\circ}\text{C}$  seems to be dependent on the association of  $-(\text{CH}_2\text{CH}_2\text{O})-$  units. It should be noted that TEGDM monomer is a transparent liquid at temperatures greater than  $-85^{\circ}\text{C}$ ; therefore, the associated regions are very small, i.e., less than the wavelength of visible light.

Transition III is assigned to the onset of further conversion of double bonds primarily because it is accompanied by sample contraction (Fig. 8). The onset of molecular mobility, which makes this reaction possible, is also detected at a similar temperature (ca.  $40^{\circ}\text{C}$ ) by DMA (Fig. 7). The occurrence of transition III just above the temperature at which samples were polymerized (by  $\gamma$ -irradiation) suggests that it is another glass transition. As an example of this type of reasoning, in the free-radical polymerization of methyl methacrylate a similar correspondence was recognized by DSC and interpreted to mean that polymerization came to a halt due to vitrification at the temperature of polymer-

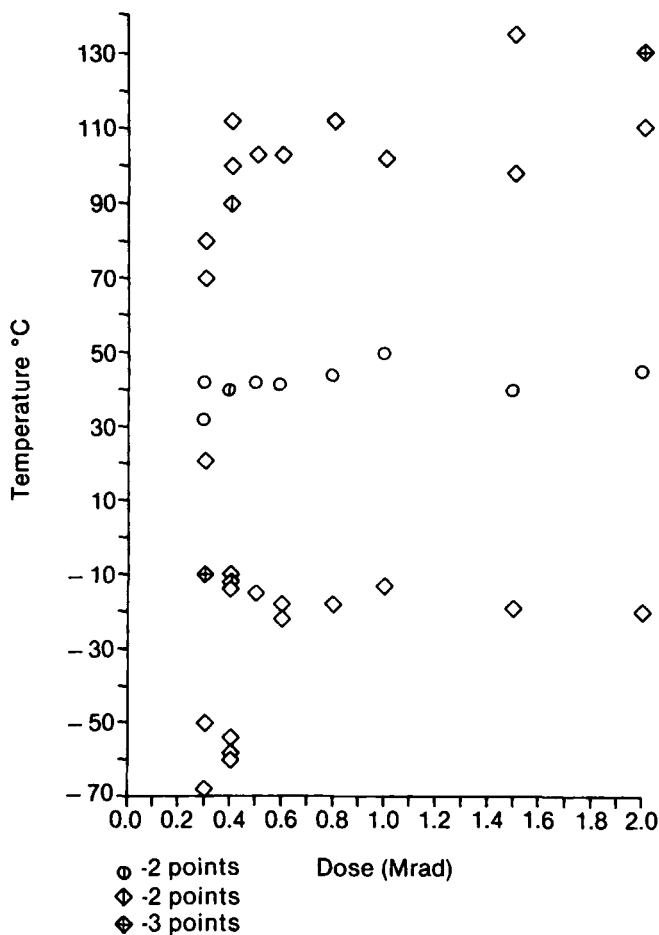


Fig. 8. Transition temperatures detected by changes in sample length.

ization.<sup>19</sup> In respect of the present work it seems surprising that free radicals should be available at a temperature as low as 40°C to initiate polymerization. It is more difficult to pinpoint the onset of polymerization in DSC runs, but it would seem to occur at a higher temperature, probably due to the extraction step (ca. 70°C: Fig. 6). Investigation for immobilized free radicals would be desirable.

The highest transition (IV) is assigned to a glass transition primarily from DMA data but also from changes in thermal expansion. Transition IV is not detected by DSC, but it is well known that this technique is insensitive to glass transitions in highly crosslinked networks. Transition IV does not provide simple information about samples prepared by irradiation in those cases where further polymerization occurs, during testing, because of heating. It can only be said that transition IV in this study is a measure of a high value of  $T_g$  as crosslinking approaches a limiting value, whether due to prolonged irradiation or to heating. Apparently, in a previous investigation at high doses (20 Mrad), transition IV would correspond to the limiting value of  $T_g$  due only to irradiation.<sup>16</sup>

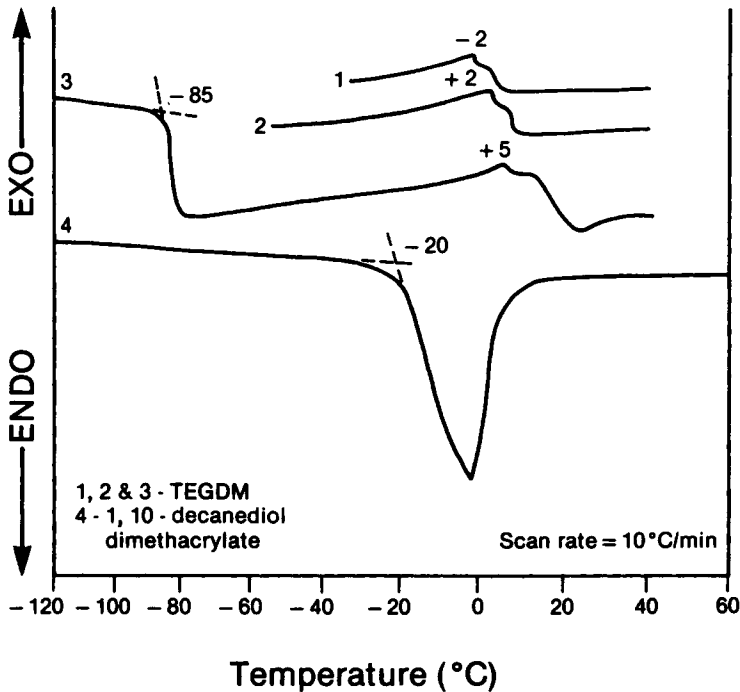


Fig. 9. DSC of TEGDM monomer (curves 1, 2, and 3) and 1,10-decane diol dimethacrylate (curve 4).

The preceding interpretation of DMA data as due to several glass transitions in a heterogeneous system is unconventional in ignoring sub- $T_g$  transitions ( $\beta$ ,  $\gamma$ , etc).<sup>20</sup> Such transitions, involving more localized modes of molecular motion than occur at  $T_g$ , are detected in polymers by DMA and by other relaxation techniques. In fact such transitions have been detected in highly crosslinked poly(TEGDM) by the method of dielectric relaxation,<sup>13</sup> which is inherently more sensitive than dynamic mechanical techniques to small domains within a network.<sup>21</sup> In contrast, no sub- $T_g$  transitions were detected by DMA in poly(TEGDM) that had been highly crosslinked by irradiation [cf. Fig. 3 of Ref. 16 (20 Mrad)] and less decisively after the lower dose of 2.0 Mrad [Fig. 5(A)].

Assignments made in the present work can be brought to mind more clearly by reference to a model involving highly crosslinked particles. A schematic structure of a single particle indicating crosslinks and pendant double bonds has been depicted by Dusek.<sup>22</sup> The highly crosslinked core (transition IV) is inaccessible to other such cores and largely inaccessible to liquid penetrants such as TEGDM. Judging from the work of Roschupkin et al., its diameter might grow into the micrometer range as polymerization proceeds.<sup>3</sup> The less highly crosslinked peripheral regions to the core are more accessible to penetrants, i.e., the TEGDM monomer that is present at low doses (transition I). Transition III is largely an artifact of the cure temperature in that the network vitrified and immobilized the free radicals. Transition II is an unusual phe-

nomenon since it appears that small, ordered regions exist in a liquid monomer and persists even after conversion into a highly crosslinked polymeric network.

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