(butene-1 sulfone) was shown to be due to a reduction in *G* values for SO_2 and butene-1 production. This is the result of the reversibility of the polymerization reaction. Radiation-induced copolymerization of butene-1 and SO_2 in the gas phase, with the concurrent formation of sulfinic acids, has been investigated in detail.[18]

Permanent chain fracture was only slightly temperature dependent. This could be explained by radicals trapped during irradiation at low temperatures reacting on warming. However, the *G*(fracture) values are much higher than the yield of trapped radicals, *G*(radicals) = 3 ± 1, and it is probable that the fracture reaction occurs during irradiation.

The present investigation was restricted to two poly(olefin sulfones) for which similar results were obtained. It can be predicted that high *G*(fracture) values will be obtained for all poly(olefin sulfones). However, as the size of the olefin increases, the importance of cross-linking reactions, which are characteristic of long-chain alkanes and of polyalkanes, will increase. Depropagation to the two comonomers would also be expected to increase with irradiation temperature and to show a correlation with the ceiling temperature.

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Radiation-Cross-Linked Poly(vinyl chloride). Phase Studies

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ABSTACT: The presence of multiple phases in a mixture of poly(vinyl chloride) and tetraethylene glycol dimethacrylate was investigated by electron microscopy, calorimetry, and dynamic viscoelasticity studies. The glass-transition temperatures of these phases increased with increasing doses of electron irradiation until finally only a single transition was observed at a dose of about 1 Mrad. The relationship between the extent of radiation-induced polymerization reaction and the viscoelastic and calorimetric properties of the system was elucidated.

In another paper,[1] the mechanism of radiation cross-linking of poly(vinyl chloride) (PVC) with tetraethylene glycol dimethacrylate (TEGDMA) was investigated. Rapid polymerization took place to form a three-dimensional network onto which PVC was grafted. The rate of disappearance of the double bond in the monomer and the rate of gel formation were measured as a function of radiation dosage. In the present investigation morphological, calorimetric, and dynamic-mechanical studies have been undertaken in order to elucidate the interrelation between the extent of chemical reaction and the physical properties of the system.

Experimental Section

(1) Materials. Tetraethylene glycol dimethacrylate from Ware Chemical Corp. and PVC (Opalon 660) from Monsanto Co. were used. All the mixtures investigated contained 33% by weight of monomer. The monomer was added slowly to PVC in a high-speed blender at 80°; from these powders, sheets were compression molded at 140° for 3 min. Irradiation was carried out at 80° under nitrogen using 1-MeV electrons from a van de Graaff generator. The dose rate was 0.01 Mrad/sec. Unsaturation was determined by infrared absorption. Gel content was measured by extraction; in addition, the gel was analyzed for chloride content to determine the extent of PVC grafting.

(2) Calorimetry. The glass transitions and changes in specific heat, ΔC_P, of the samples were studied by a differential scanning calorimeter, Perkin-Elmer DSC-1. All measurements were made at a heating rate of 40°/min in a manner which has been reported in detail elsewhere.[2]

(3) Dynamic Modulus. Measurement of dynamic viscoelasticity was made by the use of a direct-reading dynamic viscoelastometer from the Toyo Measuring Instrument Co., Vibron DDV-II, at a frequency of 110 Hz.

(4) Electron Microscopy. The state of mixing of TEGDMA in PVC before irradiation was studied under the electron microscope. The technique used here was based on Kato's method of staining double bonds with osmium tetraoxide (OsO_4).[3] However, an additional step was introduced for obtaining thin sections of soft materials. In the two-step sectioning method,[4] slices as thick as 10 μ were first cut with a hand microtome at liquid nitrogen temperature, stained with OsO_4 vapor, and then embedded in an epoxy resin. Ultrathin sections of about 800 Å in thickness were obtained by the use of Reichert ultramicrotome, and electron micrographs were taken by direct observation of the ultrathin sections.

(5) Absorption–Desorption Studies. Compression-molded PVC sheets were immersed in TEGDMA at various temperatures for at least 3 days. Each specimen was pat dried quickly at the temperature of the experiment and the weight gain determined. Desorption experiments were carried out by allowing the swollen specimens to cool, in the presence of the monomer, to lower temperatures for at least 5 days.

Results

(1) Recapitulation of Previous Results. The disappearance of the double bond and the formation of insoluble gel as a function of radiation dosage are shown in Figure 1. The gelation dose was reached at 0.05 Mrad. During this period, 45% of the unsaturation was consumed. In the

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[1] W. A. Salmon and L. D. Loan, to be published.

[2] H. E. Bair in "Analytical Calorimetry," Vol. 2, R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N. Y., 1970, p 51.

[3] K. Kato, *Polym. Eng. Sci.*, 7, 38 (1967).

[4] M. Matsuo, T. K. Kwei, D. Klempner, and H. L. Frisch, *ibid.*, 10 (6), 327 (1970).

region 0.05–0.10 Mrad, gel formed rapidly until the gel content reached 45%. The level of unsaturation decreased from 55 to 45% during this stage. The gel was found to contain approximately a constant amount, 29%, of PVC during this period of rapid cross-linking.

At a dose of 0.1 Mrad, virtually all the monomer and 20% of the PVC had cross-linked. Further irradiation resulted in the continued but slower grafting of PVC.

(2) Absorption–Desorption Characteristics. The results of absorption–desorption experiments are shown in Figure 2, where the solid line represents the absorption curve and the dotted lines represent the desorption curves. The equilibrium absorption was 7% by weight at room temperature. It increased rapidly as the temperature increased and reached 60% by weight at 90°. At first thought, a naïve notion may be entertained that the TEGDMA absorbed at a higher temperature ought to redistribute itself, at room temperature, in two macroscopic phases: the pure TEGDMA phase and a phase containing 7% TEGDMA. However, as seen in Figure 2, actual desorption of TEGDMA by lowering the temperature was insignificant. This implies that once the equilibrium is reached at a higher temperature, the swollen PVC retains nearly all the absorbed TEGDMA when cooled to room temperature.

(3) Electron Microscopy. Although macroscopic phase separation was not observed, there was evidence which tended to suggest that some PVC–plasticizer mixtures were far from homogeneous on a microscopic scale. In the electron microscope examination of PVC–diallyl phthalate mixtures, Hattori, *et al.*,[5] clearly observed areas rich in diallyl phthalate separated from areas rich in PVC. For this reason, we have also undertaken an electron microscope study of the PVC–TEGDMA mixture. The monomer contains double bonds which can be stained by osmium tetraoxide and shows as dark spots in the micrograph.

The electron micrograph of the ultrathin section for the unirradiated sample (33% TEGDMA) is exhibited in Figure 3. It is apparent that relatively bright domains of the order of 1 μ in size are separated by relatively dark interdomain phases. Closer examination of the micrograph reveals that in both phases there are dark spots, rich in monomer, interspersed with bright areas, rich in PVC. They are shown more clearly in the insert of Figure 3. The sizes of these finer structures are about 100 Å. The domain structure of the order of 1 μ in size undoubtedly comes from the particle structure[5,6] of the original PVC powder, which was not destroyed by the relatively mild processing conditions used in our study.

(4) Calorimetry. TEGDMA monomer showed a glass-transition temperature of −82° (Figure 4). The polymer of TEGDMA undergoes a small transition at about 92°; the temperature range of this glass transition is twice as broad as is usually observed for other polymers. The value of T_g for the TEGDMA polymer is to be compared with the glass temperature of two similar polymers: 130° for poly(ethylene glycol dimethacrylate) and 82° for poly(decamethylene glycol dimethacrylate).[7] The T_g of PVC is 84°.

In Figure 4, plots of changes in specific heat as a function of temperature are constructed for seven TEGDMA–PVC samples with the following radiation doses: 0, 0.04, 0.05, 0.06, 0.08, 0.15, and approximately 1 Mrad. For the purpose of comparison, all the ΔC_P measurements for each sample were superimposed on the C_P curve of the 0.15-Mrad sample. The specific heats of the latter sample in the temperature range −38 to 122° are listed in Table I.

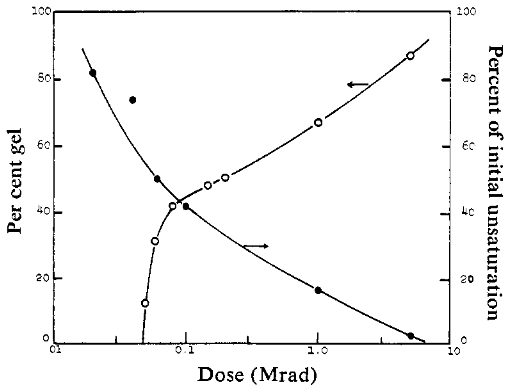

Figure 1. Rate of polymerization and gel formation.

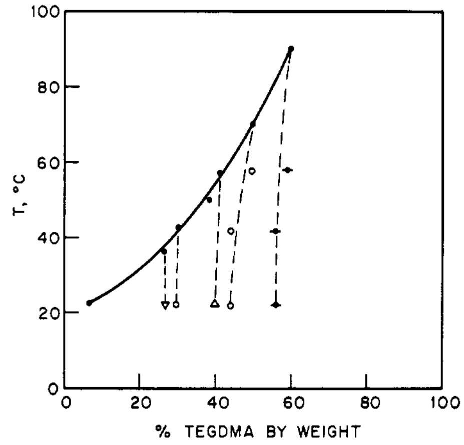

Figure 2. Absorption–desorption of TEGDMA by PVC.

TABLE I
SPECIFIC HEAT OF TEGDMA–PVC MIXTURE
IRRADIATED AT 0.15 MRAD

Temp, °C	C_P, cal °C^{-1} g^{-1}
−38	0.205
−18	0.220
38	0.249
44	0.257
52	0.265
58	0.281
81	0.294
91	0.338
101	0.354
112	0.375
122	0.387

The unirradiated sample has three transitions at −64, −33, and 40°, respectively. The transition at −33° seems to be the major one because it is accompanied by a large increase in C_P. Irradiation up to 0.04 Mrad shifted each of the three transitions to higher temperatures, namely, −56, −10, and 60°. However, only two transitions appeared at −7 and 58° when the dose was 0.05 Mrad; at this dosage, gel started to form rapidly (Figure 1). The 0.06-Mrad specimen also yielded two transitions, but at slightly higher temperatures. The 0.08- and 0.15-Mrad samples each showed two transitions in the regions 60 and 90°,

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(5) T. Hattori, K. Tanaka and M. Matsuo, submitted for publication.

(6) D. N. Bort, Y. Y. Rylou, N. A. Okladnov, B. P. Shtarkman, and V. A. Kargin, *Vysokomol. Soedin.*, 7, 50 (1965).

(7) S. Loshaek, *J. Polym. Sci.*, **15**, 391 (1955).

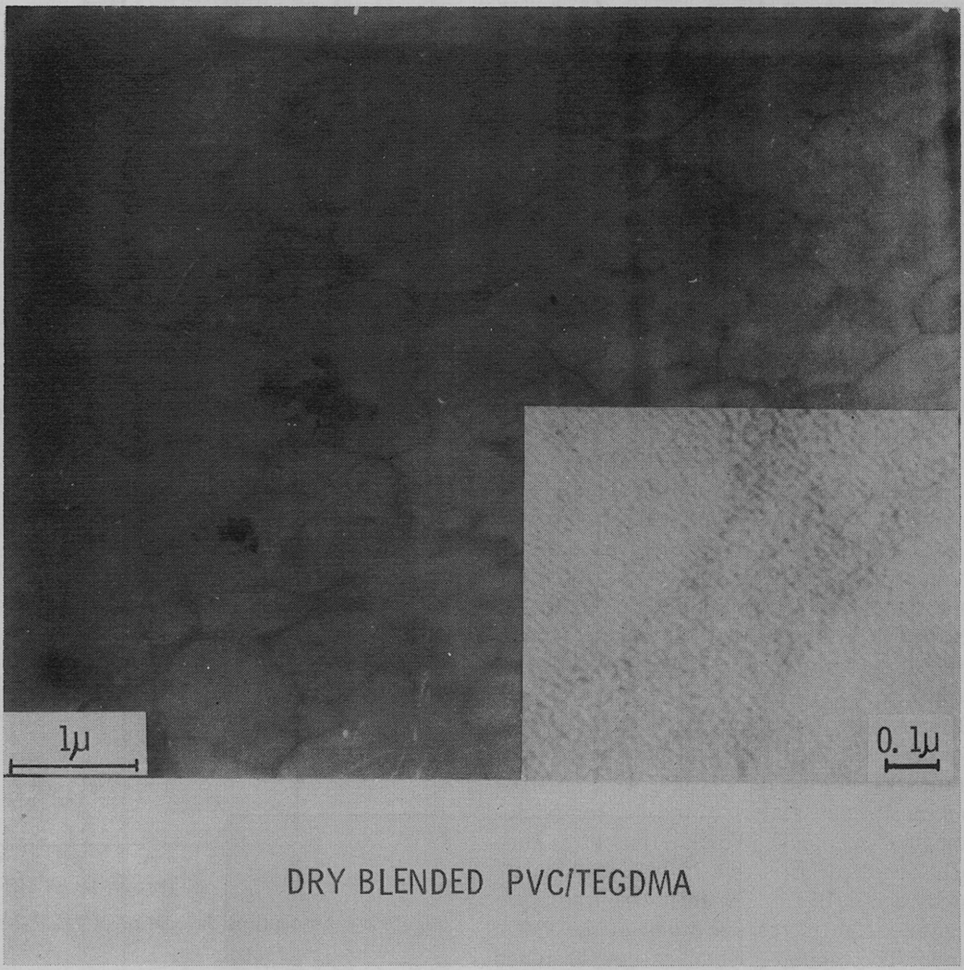

Figure 3. Electron micrograph of unirradiated PVC–TEGDMA mixture.

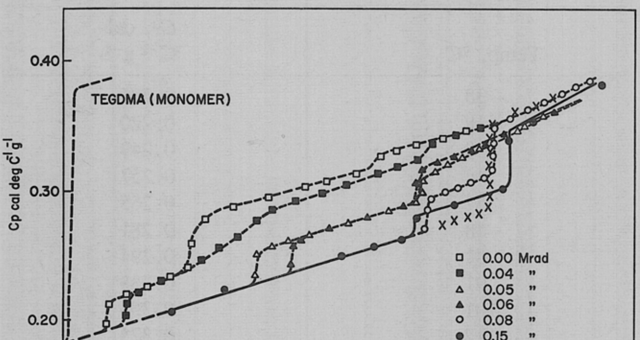

Figure 4. Differential scanning calorimetry curves.

respectively. Further increase in dosage to *ca.* 1 Mrad resulted in the occurrence of only one transition at 84° which appeared to be unreasonably low when compared with the higher T_g of 92° for the 0.15-Mrad sample. The low value is probably attributable to radiation-induced degradation of PVC, as suggested by the extensive discoloration of the specimen. The transition temperatures for each specimen are listed in Table II together with ΔC_P values for each transition.

It was also found that when the 0.06-Mrad sample, with two transitions at 8 and 55°, was extracted in ether to remove soluble materials, subsequent calorimetric experiment revealed a single transition at 52° (Figure 5). The change in C_P was about the same magnitude as the sum of the two prior ΔC_P values at 8 and 55° (Table II). It appears that low molecular weight polymer and/or residual monomer are still present in the 0.06-Mrad sample. This is consistent with the results of gelation studies (Figure 1) which indicate that cross-linked network begins to form at 0.05 Mrad and is not yet extensive at 0.06 Mrad.

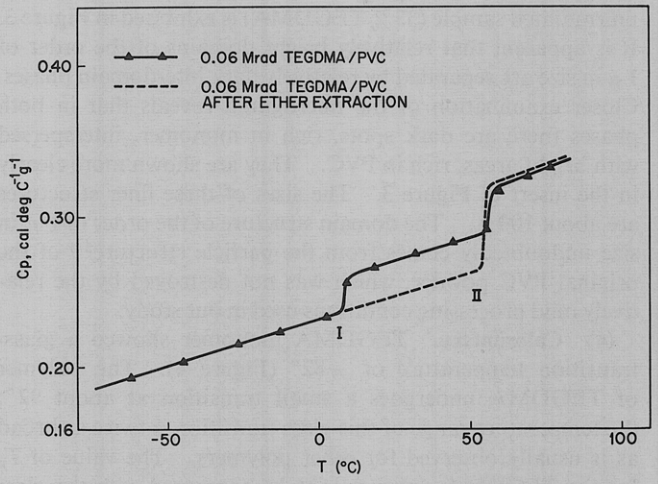

Figure 5. Effect of solvent extraction on the thermogram of the 0.06 Mrad sample.

(5) Viscoelastic Measurements. The loss tangent (tan δ) and loss modulus (E'') curves are shown in Figures 6–8.

TABLE II
TRANSITION TEMPERATURES

		Calorimetry			Viscoelasticity	
Sample	Dose	T_g, °C	ΔC_P	Remarks	T_g, °C	Remarks
TEGDMA		−82	0.198			
Poly(TEGDMA)[a]		92	0.050	Broad	110 ± 10	Broad
PVC		84	0.055		84	
TEGDMA–PVC	0	−64	0.024		−50	Estimated by separating the E'' peak
		−33	0.045		−20	
		40	0.010			
	0.04	−56	0.022		−45	
		−10			−5	
		60	0.023			
	0.05	−7	0.022			
		58	0.017			
	0.06	8	0.022		45	(Shoulder)
		55	0.031		75	
	0.06	52	0.062	After ether extraction		
	0.07				50	(Shoulder)
					80	
	0.08	60	.025			
		87	.036			
	0.15	55	0.014		70	(Shoulder)
		92	0.045		90	
	1.0	84	0.065		94	
	5.0				105	

[a] Polymerized at 80° overnight with benzoyl peroxide as catalyst.

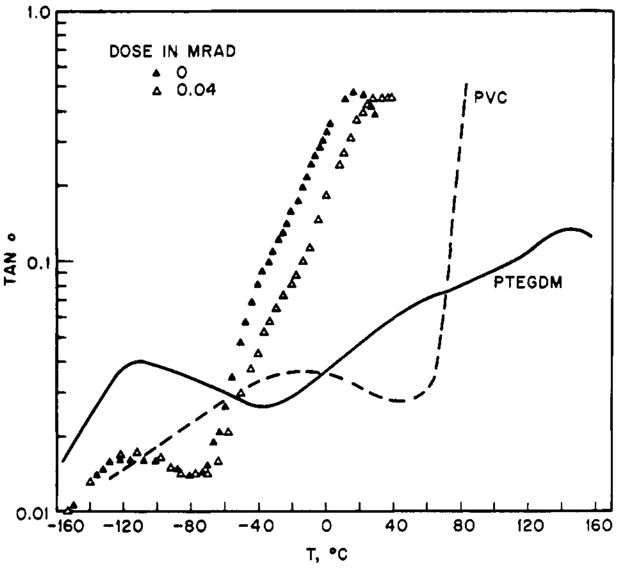

Figure 6. Loss tangent curves of PVC, Poly(TEGDMA), unirradiated mixture, and the 0.04 Mrad sample.

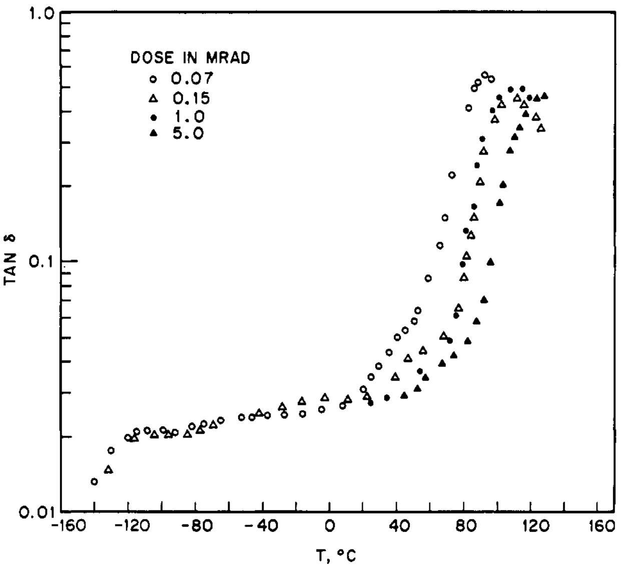

Figure 7. Loss tangent curves of the 0.07, 0.15, 1.0, and 5.0 Mrad samples.

In the ensuing discussion, the temperature of the E'' maximum (Figure 8) is taken as the peak-dispersion temperature. The peak temperature of the main transition in PVC occurs at 82°; the secondary transition extends from −120 to 40°, with a maximum located at about −30°. These results are in good agreement with earlier investigations.[8] The TEGDMA polymer shows a γ dispersion peak at −115°, a broad β dispersion from −30 to about 100°, and an α dispersion from 100 to 160° with a peak temperature estimated between 100 and 120°.

The unirradiated mixture of PVC and TEGDMA shows a low-temperature dispersion near −115°, undoubtedly due to the presence of a $(CH_2CH_2O)_4$ group in the monomer.[9] A broad asymmetric dispersion extends from −70° to 10° in the E'' curve (Figure 8). In the same temperature range, the loss tangent curve (Figure 6) appears to consist of two lines of different slopes, one from −70 to −40° and the other from

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[8] M. Takayanagi, H. Harima, and Y. Iwata, *Mem. Fac. Eng., Kyushu Univ.*, 23, 1 (1963).

[9] A. H. Willbourn, *Trans. Faraday Soc.*, 54, 717 (1958).

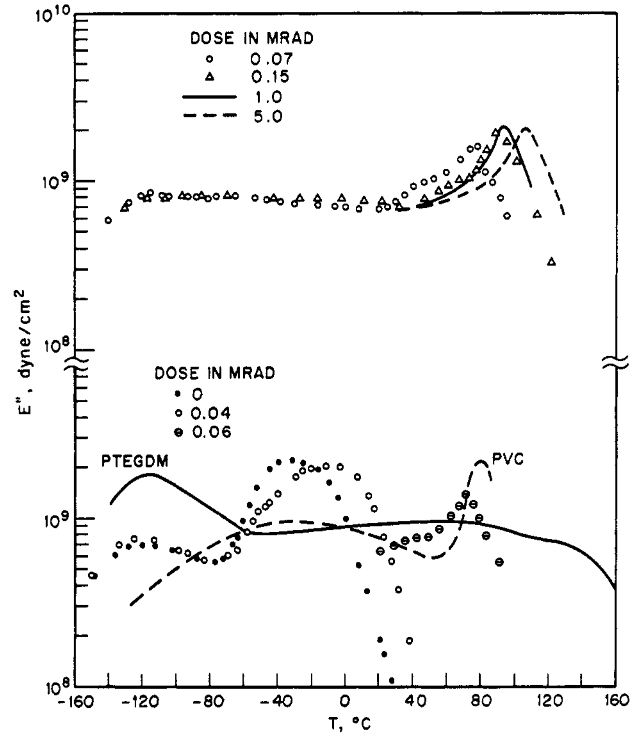

Figure 8. Loss modulus curves.

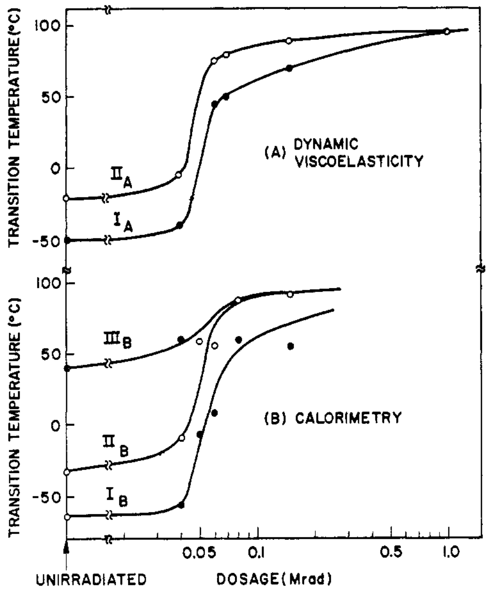

Figure 9. Dependence of transition temperature on radiation dosage.

−40 to 10°. It is most likely that two overlapping mechanisms of motion participate in this dispersion. While it is difficult to resolve the broad E'' peak into two components, a comparison of the tan δ and E'' curves with those for the 0.04-Mrad sample gives some idea as to the locations of the component peaks. Our best estimates of the positions of the component peaks are −50 and −20°. It is noted that the peak area for the latter component forms the major contribution of the total peak area.

All the irradiated samples retain the low-temperature γ dispersion at about −115 . The γ dispersion is not of primary interest in this investigation and will not be discussed further. The sample with the dose of 0.04 Mrad shows tan δ and E'' curves similar to those of unirradiated samples, but the two peaks are separated more clearly. The positions of the two peaks are estimated to be −45 and −5°. The main dispersion of the 0.06-Mrad sample jumped to 75°, which was preceded by a small shoulder at around 45°. The loss curve for the 0.07-Mrad sample showed a maximum at 80°, with a shoulder at 50°. The curve for the 0.15-Mrad material has similar shape except that the main dispersion is located at 90°; a small shoulder also seems to exist near 70°. At still higher dosages, only one dispersion is seen at 94° for the 1.0-Mrad sample and at 105° for the 5.0-Mrad sample, which is intensely discolored. The dispersion temperatures are also listed in Table II.

Discussion

We have observed multiple transitions occurring for most of the specimens both in the calorimetric and the dynamic-mechanical measurements. This indicates the presence of multiple phases. The ensuing discussion will focus on two main points of interest: (1) how the transitions observed in the above two measurements correlate with each other, and (2) how they are related to the results of the electron microscope study.

For these purposes, all the transition temperatures obtained with dynamic viscoelasticity were plotted against the irradiation doses. Assuming that the low-temperature transitions of the irradiated samples are derived from the same phase which gives rise to the low-temperature transition of the unirradiated sample, one obtains curve $\mathrm{I_A}$ in Figure 9A. Similarly, the high-temperature transitions are represented by curve $\mathrm{II_A}$. It is noted that the transitions in both the $\mathrm{I_A}$ and $\mathrm{II_A}$ series begin to shift rapidly to higher temperatures at a dosage of about 0.05 Mrad, the critical gelation dose. It is also seen that both curves converge to a limiting temperature of about 94° at a dosage of 1.0 Mrad.

The same procedure has been applied to the transitions in the calorimetric measurements, and the results are shown in Figure 9B. Three transitions can be discerned when the doses are small. They are designated as transitions $\mathrm{I_B}$, $\mathrm{II_B}$, and $\mathrm{III_B}$, in order of increasing temperature. Transitions $\mathrm{I_B}$ and $\mathrm{II_B}$ are seen to behave in a quite similar manner as transitions $\mathrm{I_A}$ and $\mathrm{II_A}$, respectively, of the viscoelastic measurement. This suggests that the phases responsible for transitions $\mathrm{I_A}$ and $\mathrm{I_B}$ are closely related; similarly, the phases responsible for transitions $\mathrm{II_A}$ and $\mathrm{II_B}$ are also related. Transition $\mathrm{III_B}$, which was not observed in the viscoelastic measurement, seems to merge with transition $\mathrm{II_B}$ soon after the dosage exceeded the critical gelation dose.

In the next step, we shall extend the discussion to the correlation of these transitions with the morphology of the unirradiated sample. At first glance at the electron micrograph (Figure 3), one may conclude that the system consists mainly of two phases: PVC-rich, domain phase and monomer-rich, interdomain phase. It is tempting, therefore, to identify the domain and interdomain regions with transitions $\mathrm{II_A}$ and $\mathrm{I_A}$, respectively. However, we have also found two transitions in a well-milled sample in which no large domain structure (~1 μ) is noticeable.[10] Thus, a different assignment must be undertaken. We will tentatively attribute transitions $\mathrm{I_A}$ and $\mathrm{II_A}$ to the dark fine spots, rich in monomer, and the bright fine spots, rich in PVC, respectively, in Figure 3. It is quite possible that both phases maintain some degree of

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[10] M. Matsuo and T. K. Kwei, to be published.

mechanical continuity in the specimen. As a result, the dynamic moduli E' at temperatures intermediate between two transitions remain quite high *e.g.*, $E' = 1.88 \times 10^{10}$ dyn/cm^2 at −30°.

In the calorimetric studies, three transitions were found for the unirradiated mixture. Transitions I_B and II_B, as mentioned previously, are related to transitions I_A and II_A in viscoelastic measurements. We therefore assign these two transitions also to the dark and bright spots in the micrograph, respectively. The origin of the third transition, III_B, at 40° is not clear at this time. Whether a minor amount of a more rigid phase is present in the bright region but not identified in the micrograph is open to speculation.

We would also like to call attention to the intensities of the transitions in calorimetry. We have estimated the weight fraction of the phase (or phases) responsible for each transition from the ratio of the observed ΔC_P for a given transition to the total change in ΔC_P for all the transitions in a given specimen. The results are plotted in Figure 10. It is apparent that the weight fraction for phases II_B plus III_B increases, and that for phase I_B decreases as the dose increases, until finally the former reaches 100%. These results clearly imply that the monomer-rich phase (phase I_B) not only increases its transition temperature but also is converted continuously to phases having much higher transition temperature as the dose increases. Finally, all the phases converge to show one transition, because the completely polymerized phases are all expected to have transition temperatures within the narrow range of 84° (PVC) and 92° (poly(TEGDMA)) and are thus indistinguishable in dsc measurements. We did not estimate the weight fractions for the samples with higher monomer content, *i.e.*, 0- and 0.04-Mrad samples, because there is a large difference in the ΔC_P values for TEGDMA and its polymer and a large error will be introduced by the same calculation.

A final point of interest is that the increase in T_g is rapid at low doses. At 0.15 Mrad, the temperature of the major transition already approaches the limiting value and network formation is near completion. Further increase in radiation dosage and cross-link density does not raise T_g substantially, as has been demonstrated by Loshaek.[7] These conclusions are in excellent agreement with the results of unsaturation and gelation studies (Figure 1) which indicate that essentially all the monomer has undergone polymerization and insolubilization at a dose of 0.1 Mrad.

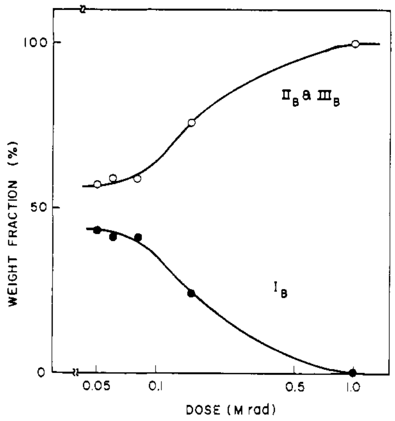

Figure 10. Estimated weight fractions of the microphases.

Conclusions

(1) The TEGDMA-PVC mixture consists of more than one phase.

(2) Both calorimetry and dynamic viscoelasticity measurements appear to be capable of detecting minute phases as small as *ca.* 100 Å in diameter.

(3) The transition temperatures of the phases increase with increasing radiation dosage and are closely related to the extent of polymerization reaction. At a dose of about 1 Mrad, the polymerization reaction is essentially complete and only a single transition is observed.

(4) Reasonable correlation between the calorimetric or viscoelastic transitions and the microscopic phases can be established.

(5) We wish to reiterate the importance of applying more than one technique in the study of ultrafine dispersion of phases.

Acknowledgment. The authors wish to acknowledge L. D. Loan for his suggestions and many stimulating discussions.