

# Photopolymer Morphology: Phase Separation During Polymerization

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## Synopsis

Morphology and phase structure were studied before and after photopolymerization for the binder-monomer system: poly(styrene/*sec*-butylmaleate)(50/50)-trimethylolpropane triacrylate (TMPTA)(75/25). Films supported on a suitable substrate were measured by dynamic mechanical analysis and by dielectric relaxation before and during photocrosslinking. Such film support techniques also allow a variety of physical and chemical treatments to be carried out to determine structure changes. Two phases and a secondary transition were identified. The shift in temperature of both  $T_g$ 's during photopolymerization and concurrent, fracture-surface electron photomicrography were consistent with a mechanism involving phase separation of TMPTA during polymerization. Probable composition of the phases is discussed.

## INTRODUCTION

A long-sought goal in this laboratory is to capture structure and morphology changes in polymer systems which occur during the course of chemical and physical manipulations which simulate or reproduce end use conditions. Classical techniques for measuring phase changes such as calorimetry are often insensitive in many polymer systems or such techniques may perturb the system under change and lead to erroneous results. In the system described below, DSC techniques gave ambiguous results which required additional characterization techniques. The development of torsion braid analysis by Gillham and co-workers<sup>1</sup> provided a useful tool to determine dynamic mechanical properties for many polymer systems. More recently, Starkweather and Giri<sup>2</sup> reported on a dynamic mechanical technique for measuring loss properties of supported polymers laminated on both faces of a substrate (brass, some stainless steels), which itself suffers no loss properties over the temperature range of interest. We have extended this technique to follow the phase structure of a simple monomer/binder/photoinitiator composition<sup>3</sup> during the course of photopolymerization. Dielectric relaxation spectra were also measured during polymerization stages from dry films of the polymer system coated on a single face of the substrate.

## EXPERIMENTAL

### Materials and Sample Preparation

Scripset 550 binder is a registered trademark of the Monsanto Company for the polymer composition: styrene/*sec*-butylmaleate (50/50) (molecular wt 10,000; acid no. 190).

\* Contribution No. 3381 from the Central Research and Development Department.

Trimethylolpropanetriacrylate (TMPTA) monomer was obtained from Polysciences, Inc. and was used without further purification. Brass shimstock (5 mil), Alinable, Inc. was pumice polished before coating.

Binder/monomer (75/25 w/w) with benzophenone/Michlers ketone (5.0/0.5 wt %) were dissolved in methylene chloride/methanol (95/5, w/w) and knife-edge cast from solution to give a 2-mil coating on brass. Samples for dynamic mechanical analysis were coated on each surface; samples for dielectric relaxation were coated on one face of the brass and sample buttons punched out with a 0.4375 in. diameter punch.

Samples were exposed in a nuARC platemaker, Model FT26UP, fitted with a mercury metal halide lamp. Lamp intensity was calibrated with an International Light probe standardized for 356 nm light. nuARC machine exposure units were related to intensity by

$$\text{mJ/cm}^2 = 8.62 (\text{exposure units}) + 2.1$$

### Dynamic Mechanical Analysis

Samples were evaluated using the DuPont Dynamic Mechanical Analyzer, Model 981, interfaced with a Hewlett-Packard 9825A Calculator.<sup>4</sup> Temperature was scanned from  $-50^{\circ}\text{C}$  to  $180^{\circ}\text{C}$ .

### Dielectric Relaxation Spectra

A Hewlett-Packard 4270A Automatic Capacitance Bridge with frequencies 1K, 10K, 100K, and 1000K was used with a DuPont 942 Thermal Mechanical Analyzer and a DuPont 990 Thermal Analyzer and Recorder.

### Electron Microscopy

TEM samples were prepared by freeze fracturing multiple layers of the polymer film in a vacuum evaporator at liquid nitrogen temperature. Fractured samples were coated with carbon/platinum while they were still cooled with liquid nitrogen. Dimethyl acetamide (DMAc) at room temperature for 1 h dissolved unexposed polymer; DMAc at  $60^{\circ}\text{C}/2$  h removed photocrosslinked material to leave clean replicas.

### Differential Scanning Calorimetry

DSC scans were carried out using the Mettler TA2000 System at  $10^{\circ}\text{C}/\text{min}$  and chart speed 20 mm/min.

## RESULTS AND DISCUSSION

### DSC Spectra

Figure 1 compares DSC scans of unexposed through 40 exposure units. Unexposed film showed a  $T_g$ -like transition around  $45^{\circ}\text{C}$  and a strong exotherm at  $150^{\circ}\text{C}$  due to thermal polymerization of monomer. The low temperature transition persisted through photopolymerization stages with a

gradual shift in onset temperature to around 55–60°C. The exotherm became less pronounced at higher photopolymerization exposure and was replaced by a broadened exotherm with decomposition above 180°C. Persistence of the exotherm indicated that unpolymerized vinyl groups survived the highest photopolymerization conditions (40 units; 350 mJ/cm<sup>2</sup>).

### Electron Microscopy

TEM microscopy of fracture surfaces shows that unexposed dry film is at least biphasic, with average diameter 365 Å of the spherical domains [Fig. 2(A)]. Although the composition of the phases was not identified, it seems likely that the spherical domains which constitute a smaller portion of the surface than the disperse phase, should be richer in monomer which is present at only one-third of the binder-polymer weight. After 10 units exposure (88 mJ/cm<sup>2</sup>), these domains measured 450 Å; and after 20 units exposure, they had increased to 1000 Å. This behavior appears to be a diffusion-controlled ripening process. After 40 units exposure, phase coalescence was complete, and it was not possible to distinguish between disperse and discontinuous phases.

### DMA and Dielectric Loss Spectra

Figure 3 shows the DMA plot of loss modulus vs. temperature through photopolymerization. Peaks are identified as  $\alpha, \beta, \gamma$  in descending order from highest temperature to lowest without morphological assignment. The  $\alpha$  peak was well defined through all stages of polymerization. The  $\beta$  peak at low exposure was a weakly defined shoulder on the  $\alpha$  peak which acquired better definition at the higher exposures. The  $\gamma$  peak diminished in intensity and disappeared at high light exposure. The  $\alpha$  loss modulus peak of unexposed composition appeared at about 120°C but rapidly shifted to 160°C as photopolymerization proceeded. The  $\beta$  peak initially appeared as a poorly defined shoulder at about 65°C and shifted to 90°C with polymerization as the peak became better defined. The  $\gamma$  peak showed no apparent shift before it disappeared.

Analogous conclusions regarding peak definition were made from the dielectric relaxation spectra (Fig. 4). Both  $\alpha$  and  $\gamma$  dielectric loss (dissipation factor) peaks were well defined through all polymerization stages; a well-defined  $\beta$  peak was evident after 20 exposure units. Characterization of a  $\beta$ -transition is difficult because of the absence of unequivocal peaks by dielectrics except for that shown on Figure 4, 20 units exposure. Support for the presence of such a transition is based upon the following qualitative evidence:

1. At least two phases are present from electron microscopy.
  2. DSC indicates at least one persistent glass transition over the photopolymerization history whose temperature range (40–55°C) is consistent with a transition intermediate in temperature between the  $\alpha$ - and  $\gamma$ -peaks.
- Since activation energies (below) showed the  $\gamma$ -transition to be a secondary transition and the  $\alpha$ - to be a glass transition, it seemed likely that a  $\beta$ -transition was buried in the low temperature shoulder of the  $\alpha$ -peak in the dynamic mechanical loss spectra and either under the  $\gamma$  peak (e.g., Fig. 4:

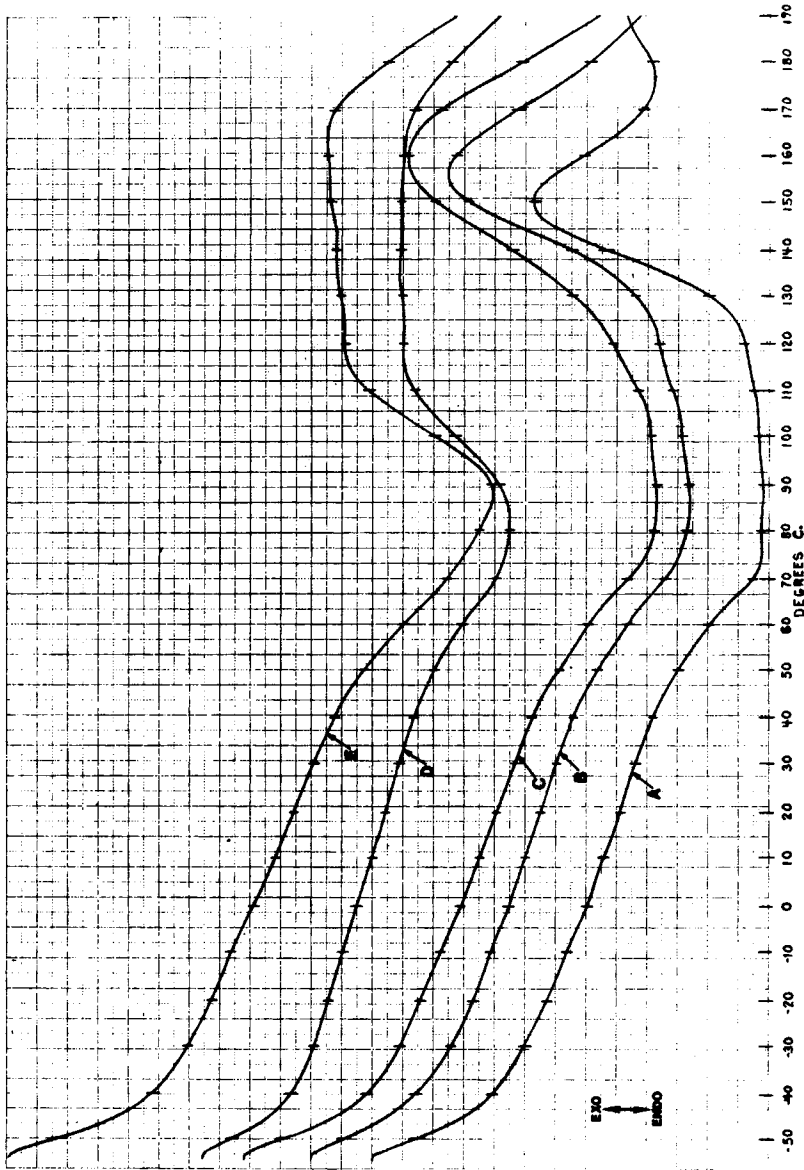


Fig. 1. DSC of Scripset 550/TMPA (75/25): (A) unexposed; (B) 5 units; (C) 10 units; (D) 20 units; (E) 40 units.

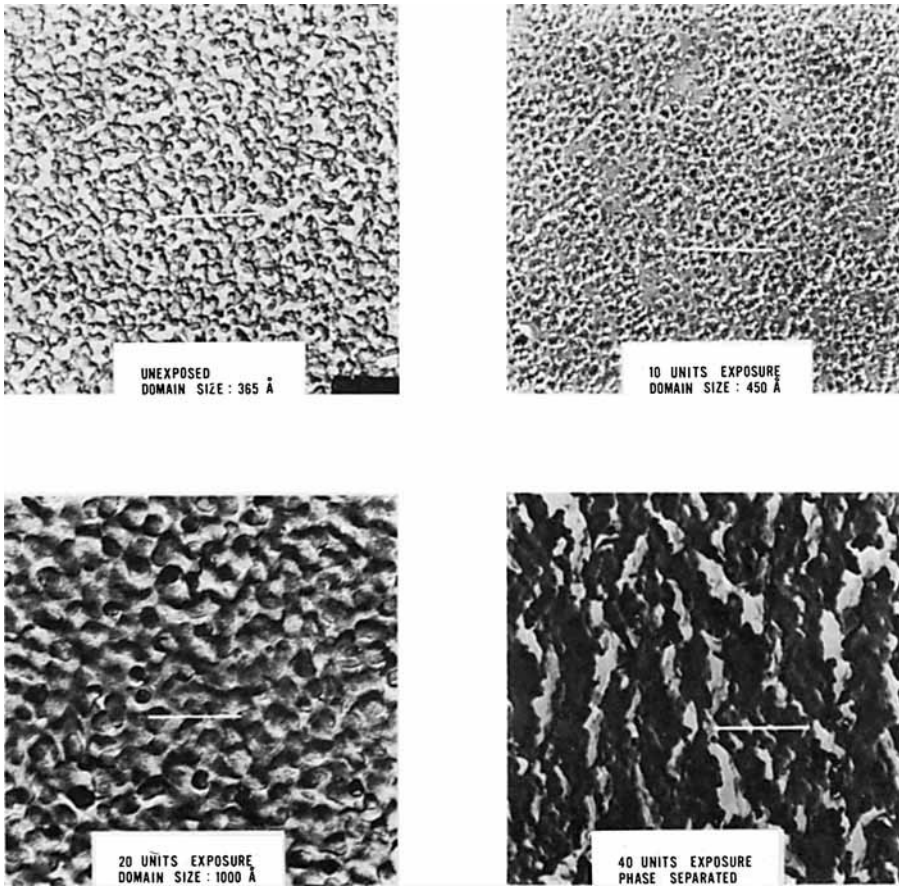


Fig. 2. Fracture surface electron photomicrographs with increasing photopolymerization. The marker bars represent 0.5 μm.

20 units at 1 MHz) or under the  $\alpha$  peaks at 5, 40 units in the dielectrics spectra. The  $\beta$  peak was resolved by curve fitting by least squares using the modeling equation:

$$Y = A[e^{-(T - T_0)/B}]^2 - 1] + c$$

where  $y$  = loss modulus or dielectric loss of  $\beta$  peak and  $T_0$  = measured  $\alpha$ -transition temperature.

### Assignment of Peak Morphology

Table I summarizes transition temperature peaks observed from the loss modulus (DMA) and dielectric loss (dissipation factor) spectra. Activation energies were used to assign morphology to the transitions<sup>5</sup> from the Arrhenius equation:

$$E_{ACT} = -R \cdot \frac{d(\ln f)}{d(1/T)} = -2.303R \cdot \frac{d(\log f)}{d(1/T)}$$

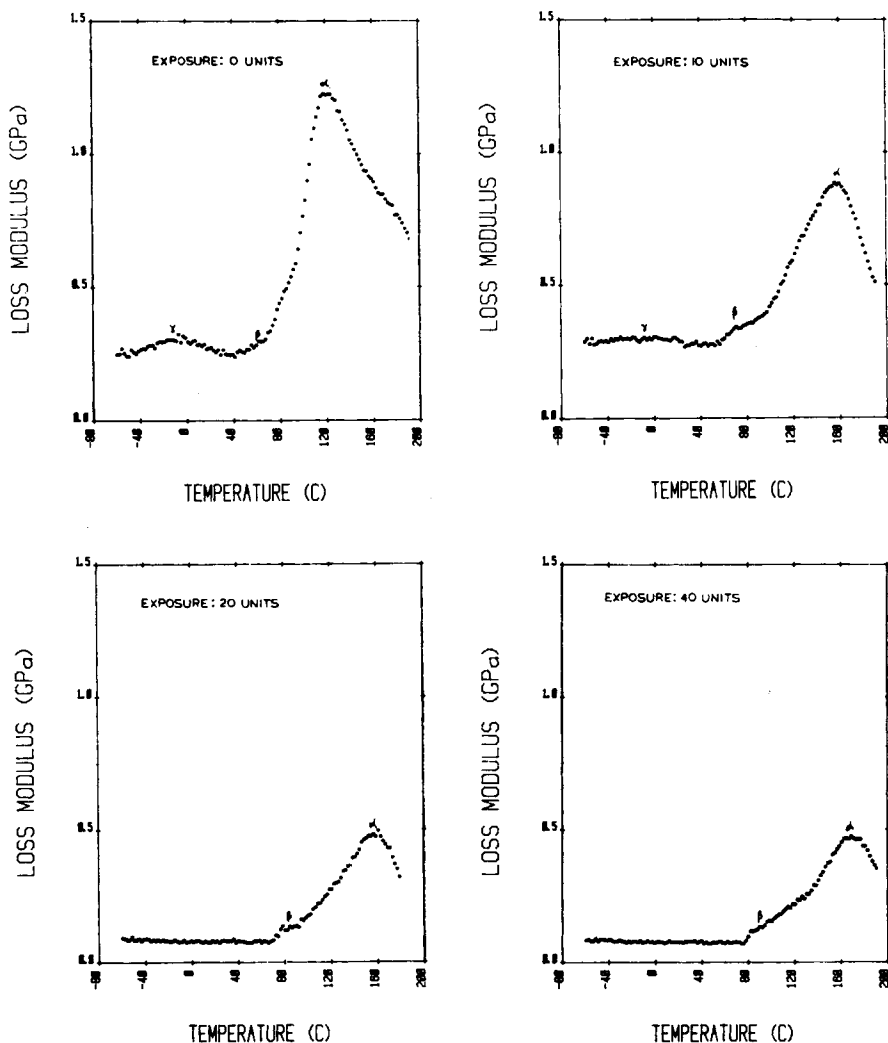


Fig. 3. DMA loss modulus vs. temperature.

where  $f$  = the frequency (Hz),  $T$  = temperature (K),  $R = 1.99$  kcal/mol/K. The activation energy  $E_{ACT}$  has the units in kcal/mol.

Figure 5 shows the Arrhenius plot for the system after 5 units exposure. Extrapolated temperatures for the  $\beta$ -transition were less precise because of fewer data points in the dielectric region. The data, exemplified by Figure 5, were consistent over the exposure range which was studied. Table II summarizes  $E_{ACT}$  and the transition temperature extrapolated to 1 Hz from the Arrhenius plots. Peaks labeled  $\alpha$  and  $\beta$  were assigned as glass transitions because activation energies ranged around  $-100$  kcal/mol.<sup>5</sup> Peak  $\gamma$  is a secondary type transition because of activation energies around  $-30$  kcal/mol.<sup>5</sup>

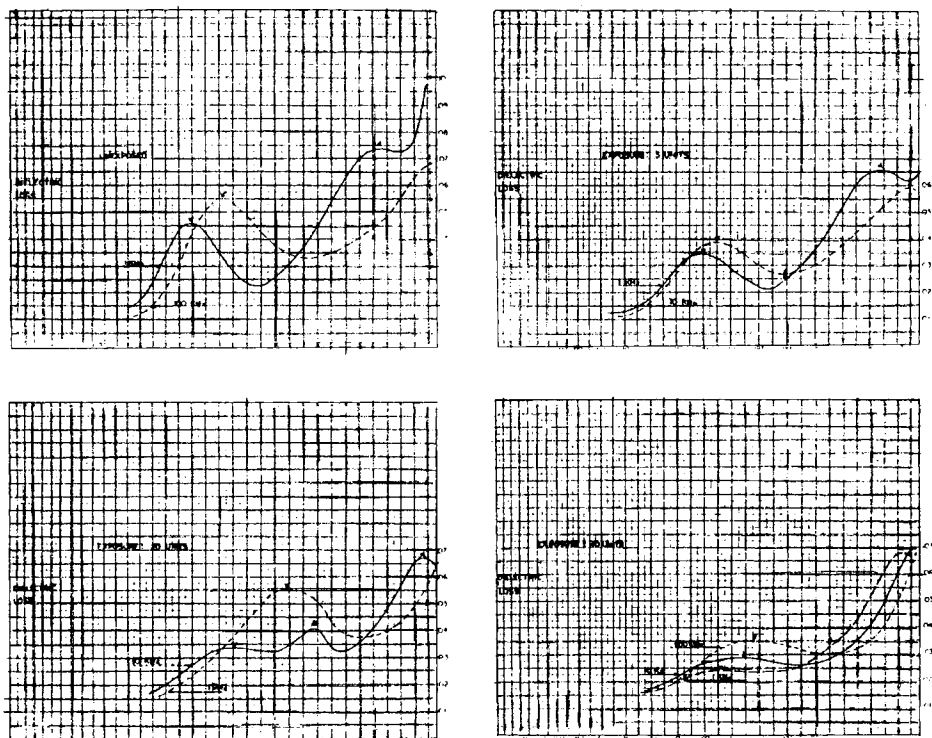


Fig. 4. Dielectric loss vs. temperature.

### Phase Composition

Figure 6 shows the plot of transition temperature at 1 Hz vs. temperature.  $T_g$ 's of both the  $\alpha$ - and  $\beta$ -phases increased at lower exposures and levelled off at higher exposure. Temperature of the secondary transition,  $\gamma$ , did not change significantly over the exposure range consistent with motion of some pendant group on the main chain or of some pendant segmental motion in the main chain. No assignment of the chemical structure of the  $\gamma$ -transition has been made.

Unexposed  $\alpha$  and  $\beta$  phases are believed to be, respectively, the binder-rich phase of Scripset 550 polymer plasticized with TMPTA and the TMPTA-rich phase containing dissolved Scripset 550. The initiator, which is primarily benzophenone (BP), is distributed through both phases with the TMPTA monomer, since solubility studies showed high compatibility of BP for TMPTA.

In separate studies, we found the  $T_g$  by DMA of molded bars of Scripset 550 to be 150–155°C and the  $T_g$  (by DSC) of photopolymerized and solvent extracted poly(TMPTA) to be around 40°C.

During photopolymerization, the  $\alpha$  phase  $T_g$  increased to approach that of Scripset 550. Similarly, the  $T_g$  of the  $\beta$  phase increased as an interpenetrating polymer network of poly(TMPTA) formed containing entrapped Scripset 550. Such an IPN should show a  $T_g$  elevated over that of

TABLE I  
DMA and Dielectric Spectra Peaks

No.	Exposure units	1000/T	log f	No.	Exposure units	1000/T	log f
1	0	2.51	0.80	26	10	2.36	3.0
2	0	2.97	0.80	27	10	3.51	4.0
3	0	3.75	0.82	28	10	2.27	4.0
4	0	3.68	3.0	29	10	3.14	5.0
5	0	2.46	3.0	30	10	3.14	6.0
6	0	3.45	4.0	31	20	2.30	0.75
7	0	2.35	4.0	32	20	2.815	0.75
8	0	3.39	5.0	33	20	3.29	3.0
9	0	3.105	6.0	34	20	2.32	3.0
10	5	3.49	0.79	35	20	3.30	4.0
11	5	2.915	0.78	36	20	2.77	4.0
12	5	2.39	0.80	37	20	2.28	4.0
13	5	3.44	3.0	38	20	3.10	5.0
14	5	2.83	3.0	39	20	2.92	6.0
15	5	2.375	3.0	40	40	2.73	0.75
16	5	3.31	4.0	41	40	2.26	0.75
17	5	2.26	4.0	42	40	3.32	3.0
18	5	3.125	5.0	43	40	2.30	3.0
19	5	2.93	6.0	44	40	3.10	4.0
20	10	3.52	0.815	45	40	3.25	4.0
21	10	2.75	0.815	46	40	2.24	4.0
22	10	3.77	0.84	47	40	3.03	5.0
23	10	2.84	0.84	48	40	2.88	6.0
24	10	2.30	0.80				
25	10	3.44	3.0				

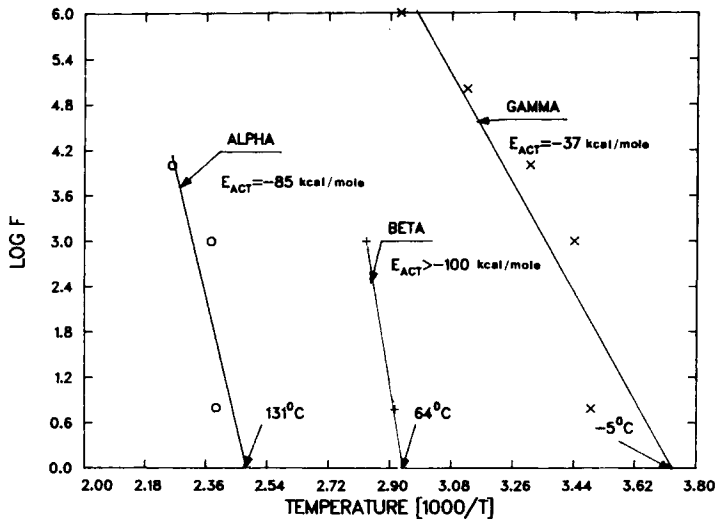


Fig. 5. Activation energies from Arrhenius plot after 5 exposure units.



TABLE II  
Transition Temperature (1 Hz) and Activation Energy

Peak designation	Unexposed		5 units		10 units		20 units		40 units	
	T (°C)	E <sub>ACT</sub>	T	E <sub>ACT</sub>	T	E <sub>ACT</sub>	T	E <sub>ACT</sub>	T	E <sub>ACT</sub>
α	114	-84	131	-85	144	-145	154	-90	158	-105
β	54	> -100	64	> -100	74	> -100	81	> -100	88	-85
γ	-23	-33	-5	-37	-19	-32	-11	-31	-12	-29

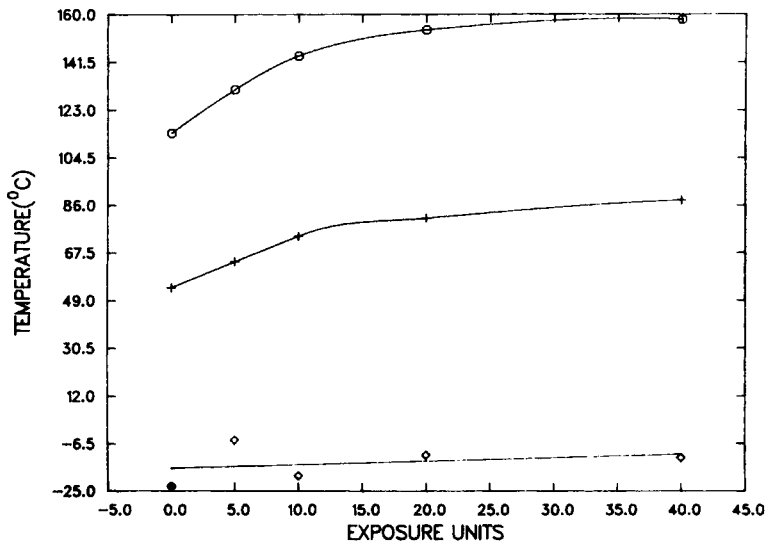


Fig. 6. Transition temperatures (extrapolated to 1 Hz, from Arrhenius equation plots) vs. exposure units: (○)  $\alpha$ -transition; (+)  $\beta$ -transition; (◇)  $\gamma$ -transition.

poly(TMPTA), consistent with studies of other crosslinked systems.<sup>6</sup> Kwei and co-workers,<sup>7</sup> for example, found multiple phases in the system: poly(vinyl chloride)/tetraethylene glycol methacrylate. After crosslinking, the  $T_g$  of these phases increased with increasing doses of electron irradiation until only a single transition was observed when a highly grafted and interpenetrating polymer network was achieved. Although grafting between polymerizing TMPTA and binder polymer is less likely in these studies, formation of an IPN appears sufficient to explain the increasing  $T_g$  of the  $\beta$  phase.

## CONCLUSIONS

Phase separation as shown by electron photomicroscopy must involve migration of TMPTA primarily from the  $\alpha$  phase during polymerization. Evidence for this is the large increase in  $T_g$  which eventually became identical with the measured  $T_g$  of Scripset 550.

If phase separation had occurred from the  $\beta$  phase, we would expect the  $T_g$  of  $\beta$  to decrease as it approached that of poly(TMPTA). Similarly, if migration of TMPTA had occurred from both initial phases, we would have expected to see information of a separate poly(TMPTA) phase with a  $T_g$  between 40°C and 90°C especially at the highest exposure levels. Since no evidence for a separate poly(TMPTA) phase was found, TMPTA migration must occur almost entirely from the  $\alpha$  phase.

The author thanks Dr. M. Panar for many helpful discussions. T. F. Johnson and C. F. Osier carried out DMA and Electron Microscopy evaluations, respectively.

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Received June 5, 1984

Accepted August 6, 1984