Thermal and mechanical analysis of a photopolymerization process

J. G. Kloosterboer and G. F. C. M. Lijten
Philips Research Laboratories, PO Box 80.000, 5600 JA Eindhoven, The Netherlands
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Network formation by photopolymerization has been studied for tetra-ethyleneglycol diacrylate (TEGDA) using isothermal differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.). Owing to vitrification, the polymerization does not go to completion at room temperature. The ultimate conversion as measured by d.s.c. seems to depend on light intensity. This effect is not caused by self-heating. In thin layers as used with d.s.c. the temperature rise is less than 3 K. However, mechanical measurements show that especially at low intensities the photopolymerization process continues for a considerable time at a rate which cannot be detected by d.s.c. At equal doses the temperatures of maximum mechanical loss, $T(\tan \delta_{max})$, were observed to be the same. D.m.t.a. of partially polymerized samples of TEGDA reveals an increase of Young's modulus due to thermal postcure near 120°C. Parallel d.s.c.–extraction experiments show that this aftercure requires the presence of free monomer. Near the end of the polymerization the free monomer is exhausted and only crosslinks are formed. $T(\tan \delta_{max})$ then increases markedly with double-bond conversion. Trapped poly(TEGDA) radicals decay in the dark with the formation of radicals with a single-line electron spin resonance spectrum, presumably due to $-CH_2-CH_2-O^*$ radicals. After 21 h most of the radicals have disappeared.

(Keywords: network formation; dynamic mechanical thermal analysis; differential scanning calorimetry; electron spin resonance; photopolymerization; surface temperature; light intensity; tetra-ethyleneglycol diacrylate; diacrylates; isothermal vitrification; thermal aftercure)

INTRODUCTION

The bulk photopolymerization of multifunctional (meth)acrylates has a widespread application in various fields such as furniture finishing, printing, metal decorating and packaging[1-4]. More recent applications are the manufacturing of optical discs[5,6], of aspherical lenses[7,8] and the in-line coating of optical fibres[9,10]. In many of these applications glassy materials are required. Vitrification strongly reduces the rate of polymerization and therefore incomplete conversion of double bonds is often observed. Final extent of reaction and mechanical properties of the polymer are then strongly dependent on the temperature of polymerization. It has also been observed that the final extent of reaction, as measured with a differential scanning calorimeter (d.s.c.) under isothermal conditions, depends on the light intensity, that is on the rate of initiation[11,12]. This suggests that the mechanical properties of the polymer could also depend on the rate of formation of the polymeric glass at room temperature. In order to establish whether this indeed occurs we have studied the photopolymerization of tetra-ethyleneglycol diacrylate (TEGDA) at room temperature.

Dynamic mechanical thermal analysis (d.m.t.a.) was performed on photopolymer samples which had been exposed to various irradiation doses by variation of exposure time and light intensity. Temperatures of maximum mechanical loss at 1 Hz were determined for each sample.

However, with diacrylates there is no unique relation between extent of reaction and mechanical properties since unreacted double bonds may either be present in free monomer or as pendant groups on the network. In general, these will exhibit a different, conversion-dependent reactivity[13,14] as well as a different influence on the mechanical properties. Therefore we have measured the evolution of double-bond conversion with exposure time by combining isothermal d.s.c. with solvent extraction/liquid chromatography determination of unreacted monomer[15,16]. Using the results obtained with these different techniques we could evaluate the effect of unreacted monomer on mechanical losses and on thermal postcuring.

EXPERIMENTAL

Chemicals

Tetra-ethyleneglycol diacrylate (TEGDA) (Polysciences, Warrington, Pa., USA) was purified by washing several times with an aqueous NaOH solution (10%) followed by washing twice with an aqueous solution of $CaCl_2$. After centrifugation the extracted monomer was dried over anhydrous $CaCl_2$ and filtrated. The content of C=C double bonds was determined by bromination. The result was 97.6% of the theroretical amount.

1,6-Hexanediol diacrylate (HDDA) (Röhm, Darmstadt, FRG). Inhibitor and impurities were removed by solvent-free chromatography over basic alumina. The purity was checked with h.p.l.c. and by bromination of the double bonds. It was better than 99%.

Bis(2-hydroxyethyl)bisphenol-A dimethacrylate (HEBDM) (AKZO Chemie, Amersfoort, The Netherlands) had a double-bond content of 99.5% of the theoretical value.

The photoinitiator α,α-dimethoxy-α-phenylacetophenone (DMPA) (Ciba Geigy, Basle, Switzerland) was used without further purification.

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Tetra-ethyleneglycol dibenzoate (TEGDB) was added in a concentration of 0.3% in order to monitor the extraction of unreacted monomer. It was synthesized by reacting the alcohol with benzoyl chloride.

Calorimetry

D.s.c. measurements were made with a Perkin–Elmer DSC-2C apparatus, modified for u.v. irradiation and proper control of oxygen content of the gas atmosphere[11].

Dynamic mechanical thermal analysis

D.m.t.a. measurements were made with a Polymer Labs instrument. Samples were clamped in the single cantilever mode in a frame of 22 mm using 6 mm clamps with 0.5 mm faces. The sample length between the clamps was 8 mm. Measurements were performed at a frequency of 1 Hz, a strain amplitude of 0.063 mm and a heating rate of 5 K min^{-1}. Clamping was checked by monitoring the strain amplitude on an oscilloscope. The measurements were carried out in air.

Sample preparation for d.s.c. and d.m.t.a.

When comparing results obtained with different techniques care should be taken to use equal sample thicknesses with relatively low absorbances at the wavelength of the irradiation since otherwise local differences in extent of reaction will preclude a correct interpretation. We have used thin coatings (60 μm) in order to allow comparison of d.s.c. and d.m.t.a. results. A solution of 3.36 wt% initiator and 0.302 wt% TEGDB in TEGDA was used for d.s.c. and d.m.t.a. measurements. D.s.c. sample weights were about 1 mg, corresponding to a thickness of about 60 μm when aluminium lids of standard sample pans are used. With thin samples, lids proved to be more suitable than pans. At the initiator concentrations used (3–4 wt%) the absorbance of such layers is 0.12–0.16 but the high reflection coefficient of aluminium smoothes the intensity gradient across the sample to less than 5%. The d.s.c. pans and d.m.t.a. substrates were cleaned before use by degreasing with chloroform for 15 min in an ultrasonic bath. After polymerization in the d.s.c. the samples were extracted with 2-propanol for one week and the extracts were analysed for unreacted monomer using liquid chromatography. This method has been described before[15,16].

D.m.t.a. samples were made by spreading the liquid sample on a metallic substrate. Aluminium (300 μm) and CrNi steel (200 μm) were tried. The dimensions were 7 × 25 mm and the layer thickness was controlled by the amount of liquid. CrNi steel gave the best results. Since its expansion coefficient matches that of the clamping arrangement no spurious increase of tan δ was observed.

The samples were contained in a vessel provided with a clear quartz window. Before and during irradiation the vessel was flushed with pure nitrogen (< 2 ppm O_2). Irradiation was performed with a 4 W fluorescent lamp (Philips TL08) mounted at a variable distance from the sample. The lamp emits at around 350 nm. Its spectrum and the absorption spectrum of the photoinitiator have been reported before[6]. Intensities were measured with an International Light 745A UV Curing Radiometer. Prior to irradiation the samples were flushed with nitrogen for 15 min. After the irradiation the samples were kept in the vessel overnight to allow for volume relaxation and decay of trapped radicals. Next a similar layer was prepared on the back of the substrate in order to obtain a symmetrical sample.

Thermometry

Maximum surface temperatures were measured during a few experiments using an AGA 782 infra-red camera with a calibrated detection system. Samples of varying thicknesses were used, the thinnest in d.s.c. lids, the thicker ones made by filling a machined recess in an aluminium block. Irradiation was performed in a similar vessel as used for d.m.t.a. but with a KBr window instead of quartz. Since there was some disturbance from the camera, two lamps were mounted aside the camera head at a variable distance from the sample. Samples for thermometry contained no extraction probe. The initiator concentration was either 4 or 0.25%.

Electron spin resonance measurements

Measurements were made at room temperature using a Bruker ER 220 D spectrometer with a TE 102 cavity at X-band frequencies. The preparation of e.s.r. samples has been described previously[17].

RESULTS AND DISCUSSION

Calorimetry

In *Figure 1a* the maximum extents of double-bond conversion, x, obtained at various light intensities, are indicated for polymerizations of TEGDA at 20 and 80°C, respectively. The increase of ultimate conversion with light intensity is observed at both temperatures. In *Figure 1b* the heat effects observed during heating in the dark of samples polymerized at 20°C are depicted as a percentage of additional conversion. Samples heated under nitrogen immediately after photopolymerization exhibit an overall exothermic effect, but samples which had been stored in air overnight and then heated under nitrogen exhibited an endothermic effect. Typical d.s.c. traces are shown in *Figure 2*. The heat effects were determined from the

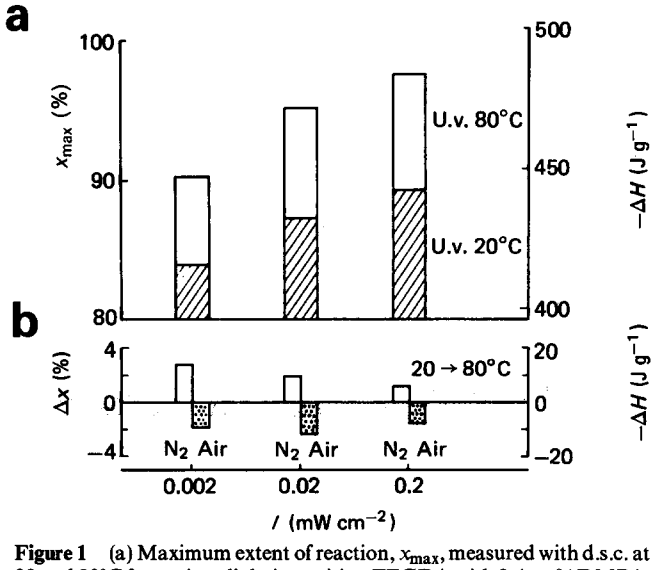

Figure 1 (a) Maximum extent of reaction, x_{max}, measured with d.s.c. at 20 and 80°C for various light intensities. TEGDA with 3.4 wt% DMPA. Intensities are shown at the bottom. (b) Heat effects observed upon heating from 20 to 80°C. Left: in N_2, just after polymerization. Right: the same but after one night storage in air

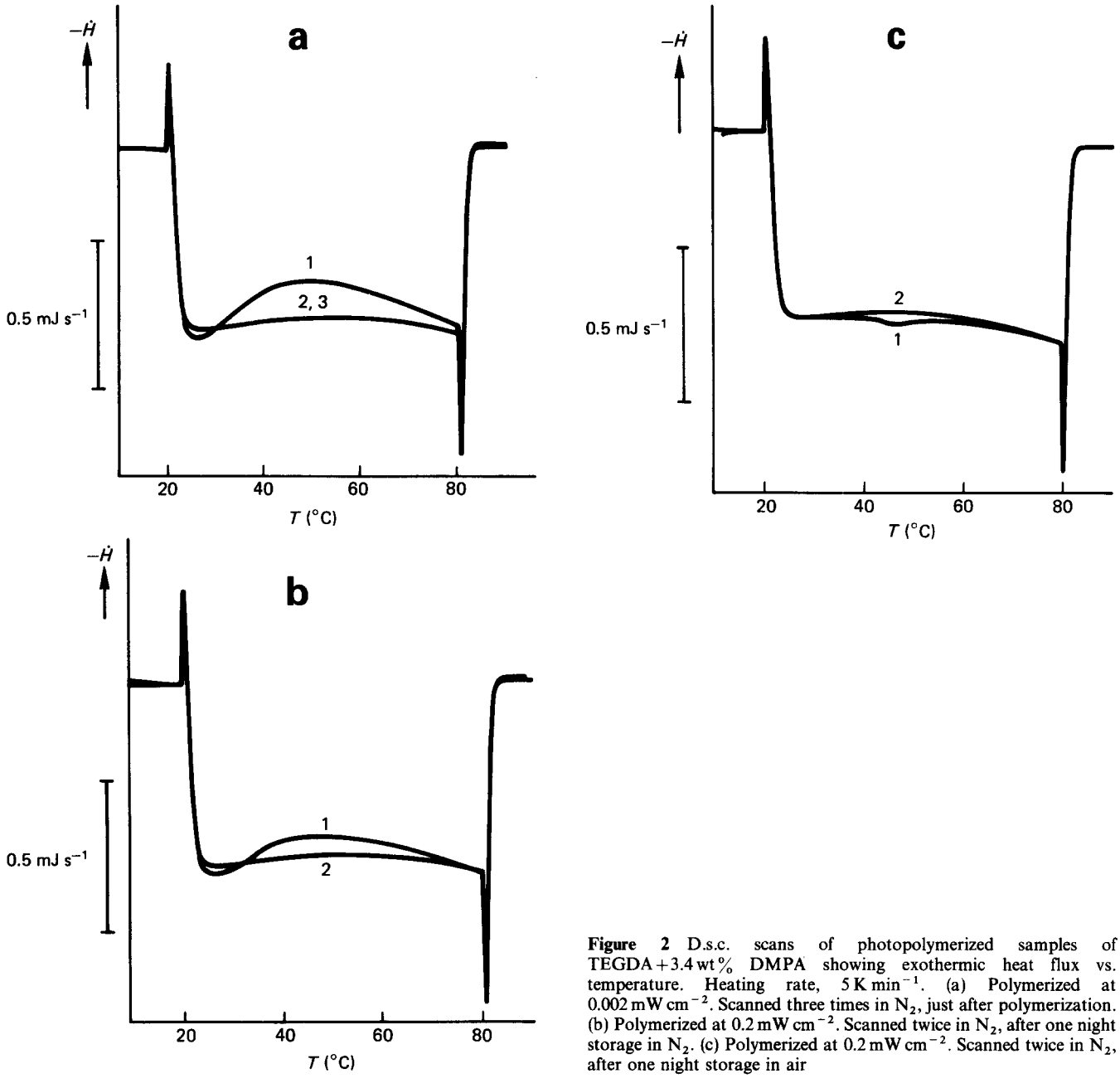

Figure 2 D.s.c. scans of photopolymerized samples of TEGDA + 3.4 wt% DMPA showing exothermic heat flux vs. temperature. Heating rate, 5 K min^{-1}. (a) Polymerized at 0.002 mW cm^{-2}. Scanned three times in N_2, just after polymerization. (b) Polymerized at 0.2 mW cm^{-2}. Scanned twice in N_2, after one night storage in N_2. (c) Polymerized at 0.2 mW cm^{-2}. Scanned twice in N_2, after one night storage in air

difference between the first and the second scan. During a third scan (*Figure 2a*) no further changes were observed. The exothermic effect in *Figures 2a* and *2b* is preceded by a small endothermic effect; in *Figure 2c* only an irreversible endothermic effect is observed. Owing to the high crosslink density of the samples the glass transition is broadened to such an extent that it cannot be detected by d.s.c.

The exothermic effect must be due to additional polymerization caused by mobilization of trapped radicals[16,17] which are absent in aerated samples. The interpretation of the endothermic effects is less straightforward. Their occurrence may be understood by comparison with the thermal behaviour of linear glassy polymers. Far below the glass transition temperature T_g these materials are not in thermodynamic equilibrium. The departure from equilibrium is determined by the rate of cooling during vitrification and, to a lesser extent, by the period of ageing. A rapidly cooled glass will be farther removed from equilibrium than a slowly cooled glass. When the rapidly cooled glass is heated slowly, relaxation towards equilibrium will occur upon approaching T_g. Relaxation causes shrinkage and hence an exothermic heat effect will be observed[18]. If on the other hand a slowly cooled glass is heated rapidly, expansion and disentanglement of the chains cannot keep up with temperature until, beyond T_g, the mobility has increased sufficiently. Then a sudden expansion, accompanied by an endothermic heat effect will occur[18,19].

Our glasses have been vitrified isothermally and the rate of vitrification is determined by the rate of polymerization. However, this rate is difficult to compare with a rate of cooling: the latter may be kept constant but the first is strongly influenced by the self-decelerating character of the polymerization process after the onset of vitrification[14]. Perhaps a coupling with cooling rates might be established through the use of fictive temperatures obtained from density measurements[20]. At the present stage, however, these are not available and we will assume that the subsequent heating proceeds faster

than the initial vitrification. This applies to all intensities used. This means that the exothermic reaction observed during dark heating of samples which contain trapped radicals is superimposed on an endothermic process (*Figures 2a* and *2b*, 20–30°C) and that the extent of additional conversion is somewhat higher than depicted in *Figure 1b*. Accurate splitting up of the observed heat effect into exothermic and endothermic contributions is not feasible, however.

Thermometry

In order to verify that the intensity-dependent maximum extent of reaction (*Figure 1* and ref. 11) was not caused by self-heating of the sample a few measurements of the maximum surface temperature were made under conditions similar to d.s.c. and d.m.t.a. Two extreme cases were investigated, HDDA and HEBDM. HDDA has a high rate of polymerization, a high concentration of double bonds and a large heat of polymerization, as compared with HEBDM. Results presented in *Table 1* show that indeed high surface temperatures may develop with the first but not with the second monomer. However, with thin layers as used with d.s.c. the increase of temperature does not exceed 3 K. In TEGDA the concentration of C=C double bonds is lower than in HDDA and their rates of polymerization are almost the same. Hence lower temperature rises will occur.

D.m.t.a. measurements

Figure 3 shows the d.m.t.a. curves measured after various irradiation times. On reducing the exposure time from 600 s to 0 s the maximum in tan δ shifts progressively towards lower temperatures. For exposure times of 5 s and less, thermally induced polymerization occurs around 120°C, together with an increase in E'. (Since all samples were coated on a metallic substrate and since it is difficult to control the thickness very accurately the changes in E' are more significant than their absolute values.)

The repeated scan in *Figure 3c* shows that the maximum in tan δ shifts towards even higher temperature than in *Figure 3a*. This can be readily explained since before the d.m.t.a. experiment the sample in *Figure 3a* has not been subject to as high a temperature as the one in *Figure 3c*. Repetition of the scan of *Figure 3a* caused a shift of the maximum to 48°C. The thermally induced polymerization is even more important in *Figures 3d* and *3e*, as can be seen from the jump in E'. Moreover, the low-temperature maximum in tan δ splits up into two peaks, one at a rather constant position around −50°C, the other at a steadily decreasing value. It is tempting to attribute the low-temperature peak to unreacted monomer (see below). In *Figure 3f*, finally, our attempt to measure unreacted monomer is depicted. However, this is very difficult to accomplish, since upon melting the sample starts flowing off the substrate. The thermal reaction shown in the figure is caused by the unquantified remainder of liquid sample on the substrate. From the low-temperature maxima it can at best be concluded that these occur in the vicinity of −50°C. No satisfactory explanation for the splitting can be offered at the present stage, although delamination of the sample might well contribute to the complicated picture. With d.s.c. a glass transition was observed at −70°C. Since the d.s.c. experiment is carried out on a much longer timescale this may well be the same transition as was observed with d.m.t.a. near −60°C.

Table 1 Maximum surface temperatures during photopolymerization

Sample	Initiator, DMPA (wt%)	Light intensity ($mW\,cm^{-2}$)	Maximum temperature (°C) at thickness: 1 mm	0.25 mm	0.05 mm
HDDA	0.25	0.2	73	27	
HDDA	0.25	1.5	137	45	
HDDA	4	1.5	>100		<25
HEBDM	4	1.5	32		

Initial temperature 22°C

Combination of calorimetric and mechanical results

We now turn to a correlation of the d.m.t.a. results with d.s.c. measurements. In *Figure 4* the extent of C=C double bond conversion, x, as measured with d.s.c., is plotted *versus* exposure time. Also plotted is the amount of monomer M extracted afterwards from the d.s.c. samples. It can be seen that for exposure times longer than 6 s the rate of polymerization decreases suddenly to a much lower value, but not to zero. At the same time the free monomer is exhausted so further reaction necessarily means further crosslinking by reaction of pendant double bonds. According to our mechanical measurements thermal postcuring also ceases to have an observable effect on E' (*Figures 3a* and *3b*). From this we conclude that significant thermal postcuring requires the presence of unreacted monomer. In its absence only a change in $T(\tan \delta_{max})$ was observed upon repetition of the thermal scan. This change may either be caused by volume relaxation or by some additional polymerization which is insufficient to cause an observable increase of Young's modulus.

During prolonged exposure only little conversion takes place, but since mainly crosslinks are formed the temperature of maximum loss continues to change considerably. This is illustrated in *Figure 5*, where we have plotted the position of the maximum of tan δ as a function of double-bond conversion as measured with d.s.c. Beyond 75% conversion ($t_{exp} \geq 6$ s) a very steep increase in the position of the maximum is observed. The increase in transition temperature is much steeper than that observed with epoxide networks[21,22], possibly because of the inhomogeneous nature of the networks formed by bulk polymerization of diacrylates[16]. It could be argued that in the final stage of the reaction the microgel particles formed in the beginning[23] are connected more tightly, thereby reducing the internal mobility in a rather abrupt way.

Next we turn back to the original question, i.e. whether or not variations in light intensity show up in the mechanical properties of photopolymers. *Figure 6* shows the d.m.t.a. curves that were obtained from samples polymerized at different light intensities under the same conditions and during the same time as in the d.s.c. experiments. The latter were stopped at the time where the rate of polymerization fell below the limit of detection of the d.s.c. apparatus (about 0.2% of the maximum rate observed during an experiment). There is a clear increase of the tan δ_{max} temperature with light intensity and, therefore, with conversion. However, the applied doses also increase with light intensity. When the doses are kept

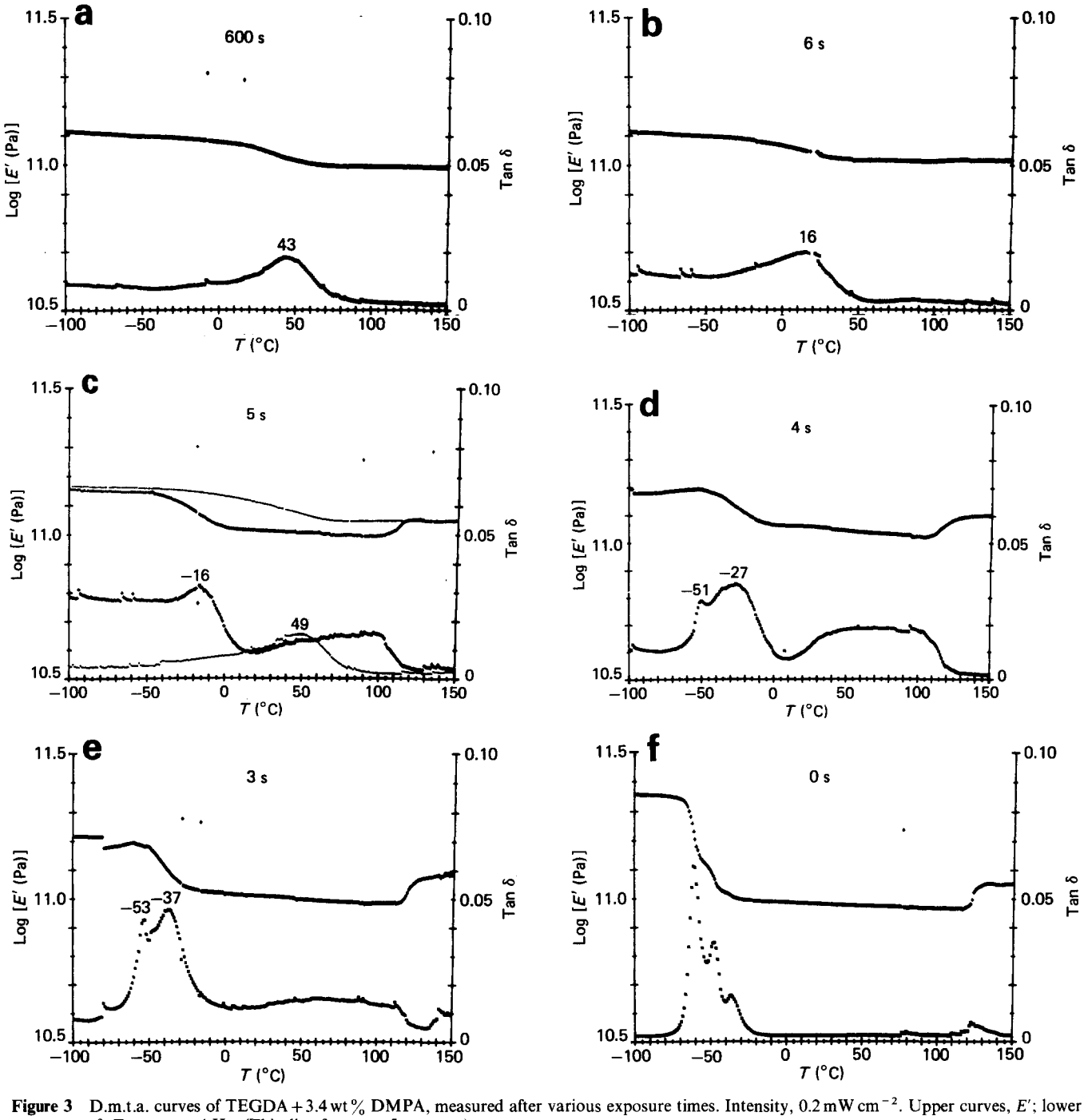

Figure 3 D.m.t.a. curves of TEGDA + 3.4 wt% DMPA, measured after various exposure times. Intensity, 0.2 mW cm^{-2}. Upper curves, E'; lower curves, tan δ. Frequency, 1 Hz. (Thin line for $t_{exp} = 5$ s: repeat)

equal (*Figure 7*) the difference between the samples vanishes within experimental error. This shows again that, especially at low light intensities, reaction continues at an extremely low rate when the vitreous state is approached. This rate cannot be measured with isothermal d.s.c.

Electron spin resonance measurements

After photopolymerization trapped radicals were observed with e.s.r., just as in HDDA[16,17]. However, with increasing exposure times their concentration stabilized at a level of about 2×10^{-4} M, much lower than in HDDA (3×10^{-3} M). Furthermore, the radicals are far from being as stable as in the case of HDDA. In HDDA the radicals have a lifetime of several months at room temperature and under vacuum but with TEGDA the spectrum of the radicals changes rapidly from a three-line polyacrylate spectrum into a single-line spectrum. Shortly after the irradiation the height of the central peak increased with respect to the two outer peaks. Even in the first spectrum the central line was already more pronounced than in the case of HDDA and many other acrylate radicals[17,24–26]. This suggests that the observed spectrum is a composite of the normal three-line polyacrylate spectrum and a single-line spectrum. Since the two polymers differ only in the composition of the bridges between their acrylate moieties, it seems appropriate to attribute the reduced stability of the radicals to the presence of the tetra-oxyethylene moiety in TEGDA.

Low-temperature u.v. irradiation of poly(oxyethylene) in the presence or absence of compounds capable of

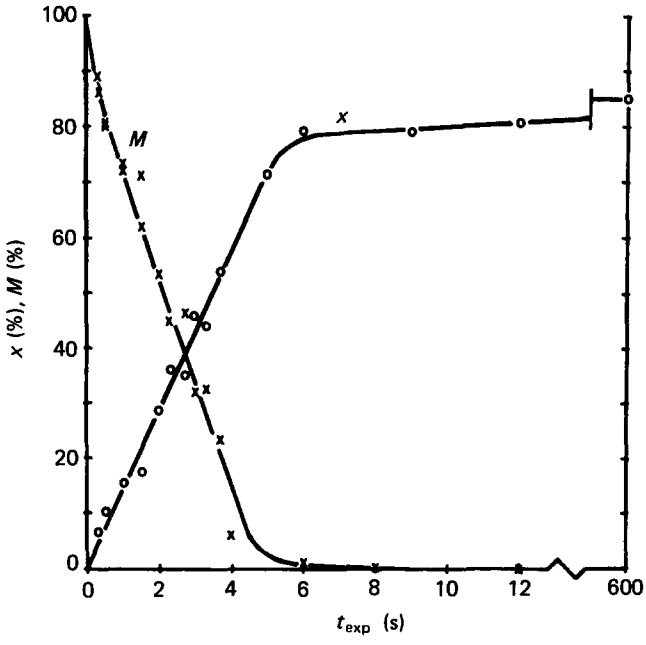

Figure 4 Extent of C=C bond conversion, x, measured with d.s.c. and fraction of extractable monomer, M, vs. exposure time. TEGDA with 3.4 wt% DMPA. Intensity, 0.2 mW cm^{-2}

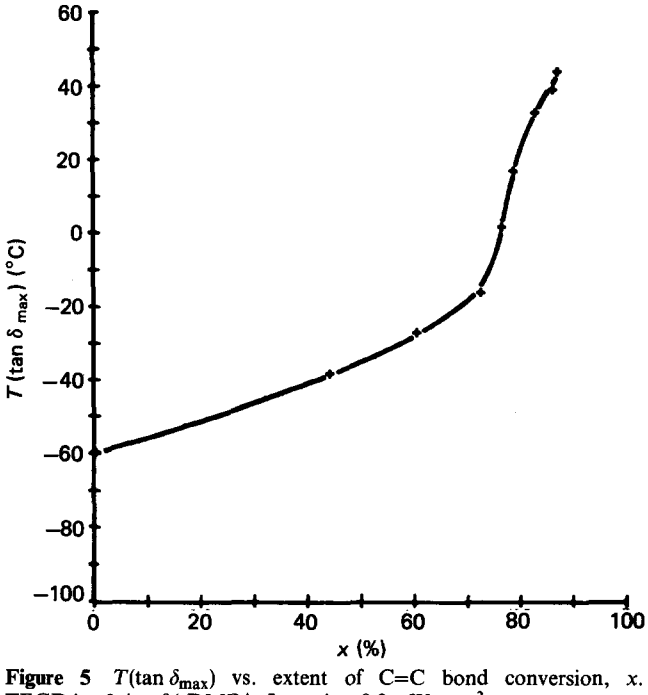

Figure 5 $T(\tan\delta_{max})$ vs. extent of C=C bond conversion, x. TEGDA + 3.4 wt% DMPA. Intensity, 0.2 mW cm^{-2}

photogeneration of radicals has also produced single-line spectra[27]. The reported singlet spectrum did not change shape upon heating but decayed at 20°C. It has been assigned to $-CH_2-CH_2-O^*$ radicals, generated by chain scission[27]. The formation of such radicals would certainly increase the mobility of the radical sites as compared with acrylate groups and thereby reduce their lifetime and saturation level. The high internal mobility in poly(TEGDA) as compared with poly(HDDA) is likely to amplify this difference. The abstraction of tertiary hydrogen atoms from the polyacrylate chain, as has been demonstrated for HDDA[17], could also contribute to the radical mobility and thereby to the dark polymerization observed after irradiation.

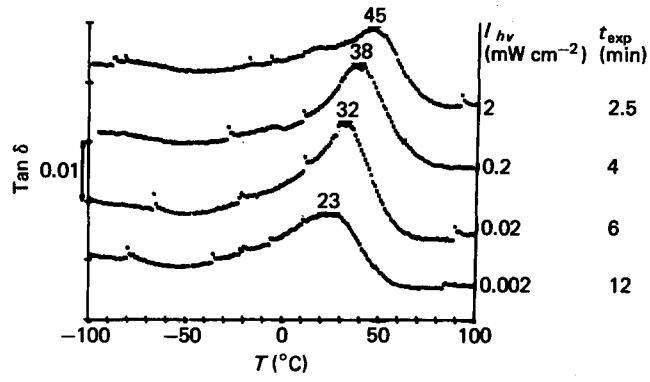

Figure 6 D.m.t.a. scans of TEGDA samples polymerized at different light intensities. Exposure times as with d.s.c. Initiator, 3.4 wt% DMPA

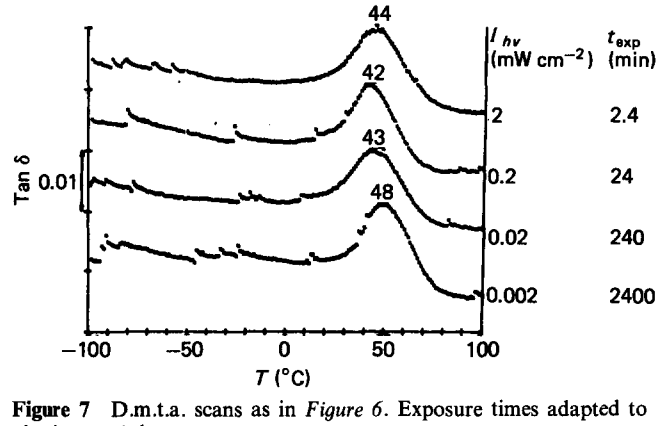

Figure 7 D.m.t.a. scans as in *Figure 6*. Exposure times adapted to obtain equal doses

CONCLUSIONS

The rate of photopolymerization of TEGDA shows a sudden decrease when free monomer is exhausted and only crosslinking can still occur. The maximum extent of double-bond conversion in TEGDA as measured with d.s.c. increases not only with temperature but also with light intensity. Mechanical measurements show, however, that the intensity dependence vanishes when equal doses are applied. This means that at low intensities the polymerization continues for a considerable time at a rate which is imperceptible with d.s.c.

Heating in the dark of partially polymerized d.s.c. samples yields an exothermic effect when oxygen is absent (polymerization due to mobilization of trapped radicals) but an endothermic effect in its presence. This is presumably caused by fast heating of slowly vitrified samples. With decreasing u.v. dose, $T(\tan\delta_{max})$ also decreases. When free monomer is still present additional polymerization causes a stepwise increase of E' and $T(\tan\delta_{max})$ during a thermal scan. In the presence of sufficient monomer the $\tan\delta$ peak splits up into two peaks: one at a constant and the other at a dose-dependent position, representing monomer and network, respectively.

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