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# OPTIMIZATION OF THE PHOTOCURING OF A TERNARY MIXTURE OF METHACRYLIC MONOMERS USING DSC

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## ABSTRACT

DSC was used for optimization of the photocuring conditions of an unusual ternary mixture of methacrylic monomers. Effects of the surrounding atmosphere, temperature and concentrations of the $O_2$ scavenger and the initiator on the curing profile and conversion were investigated. We demonstrate that TBPT is a very effective $O_2$ scavenger for this system, having its maximum effect at concentration of ca. 2 wt.%.

## INTRODUCTION

The use of DSC (Differential Scanning Calorimetry) as one of the methods of choice for the characterization of photopolymerization reactions is documented in the literature [1] . Most of the studies deal with the photocuring behaviour of acrylates or methacrylates, used commercially as coatings and inks. In this study we have used DSC for optimization of the curing parameters of a complex mixture of methacrylic monomers. We found DSC to have many advantages for such purposes, since it is accurate, reproducible, versatile and makes use of very small samples. These enable the user to easily monitor the effects of oxygen, wavelength, light intensity and relative concentrations of the reactive components in the system on the photocuring process.

## EXPERIMENTAL

Methacrylic monomers were obtained from commercial sources. Polyethylene glycol 600 dimethacrylate (SR-252, Sartomer Company) was used as received. Ethylene glycol dimethacrylate (EGDMA, Sigma Chemical Company) and

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heptafluorobutyl methacrylate (HFBMA, PCR-SCM Company) were repeatedly washed with 10% NaOH solution and water, dried over molecular sieves and filtered prior to use. Tri-n-butyl phosphite (TBPT, Aldrich Chemical Company) and 1-hydroxycyclohexyl-phenyl ketone (I-184, Ciba-Geigy) were used as received.

Polymerizations were conducted in the sample cell of a Perkin-Elmer DSC-4 instrument, using an empty reference cell. The original cover of the oven was removed, and the two cells were covered using pyrex half spheres of 12 mm. diameter. The U.V. source was a UVL-56 lamp (UV Products), equipped with one or two 6-watt mercury-vapour tubes, with peak emission at 365 nm. The original filters were removed from the lamp, which was mounted on a lift, enabling the adjustment of its distance from the DSC cell. Approximate light intensity of 5 $mW/cm^2$ was calculated when one tube was used at a distance of 6.5 cm. from the cell. The cells were flushed during the experiments with $N_2$ or $O_2$ at a flow rate of 25 cc/min. Most of the experiments were conducted isothermally at 50°C, turning the lamp on 1 min. after the beginning of the run. A reference run of the methacrylate mixture, excluding the initiator, revealed a negligible change in the baseline upon turning the U.V. light on and off. In most cases, samples of 18-20 mgs. were used.

## RESULTS AND DISCUSSION

The formulation used in our studies consisted of an equimolar mixture (based on the methacrylic moiety) of EGDMA, SR-252 and HFBMA. I-184 was used as initiator and TBPT as oxygen scavenger. This specific methacrylic mixture was designed to achieve maximum control on the refractive index and the shrinkage of the final film, along with optimal curing time and conversion: HFBMA enables the system to acquire the desired range of the refractive index, whereas EGDMA contributes rigidity to the system. SR-252 is used as a mediator, enabling the system to reach relatively high conversions, which are rarely encountered in radical polymerization of pure methacrylic monomers [2]. Moreover, SR-252 has the ability to reduce to a minimum the shrinkage during cure, which is a serious drawback of EGDMA containing systems [3]. TBPT is very effective as an oxygen scavenger: It has the ability to decompose peroxy radicals or hydroperoxides, formed in the presence of oxygen during the initiation step, to give phosphates while regenerating the initiating radicals [4].

Fig. 1 shows the observed ΔH of curing per equivalent of methacrylic moiety for each monomer as compared to the ternary system. The data retrieved from Fig. 1 are summarized in Table 1:

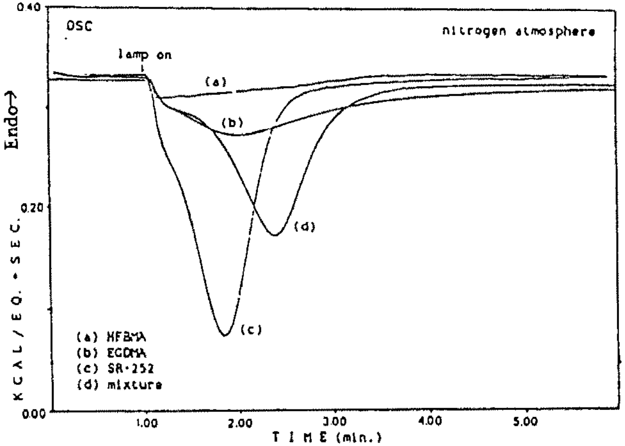

Fig. 1: Curing profiles of HFBMA, EGDMA, SR-252 and their equimolar mixture.

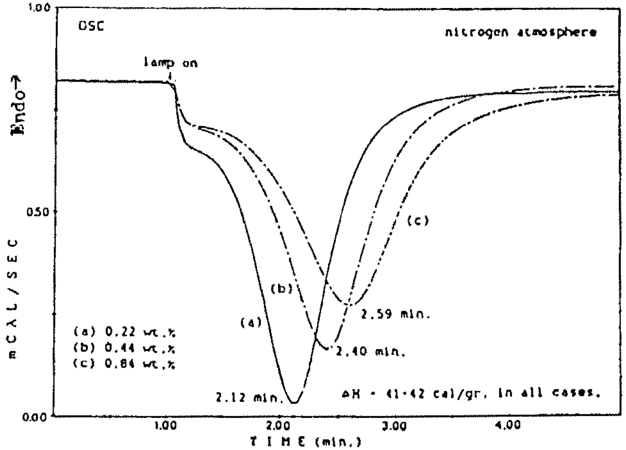

Fig. 2: Effect of initiator concentration on the curing behaviour of the ternary mixture.

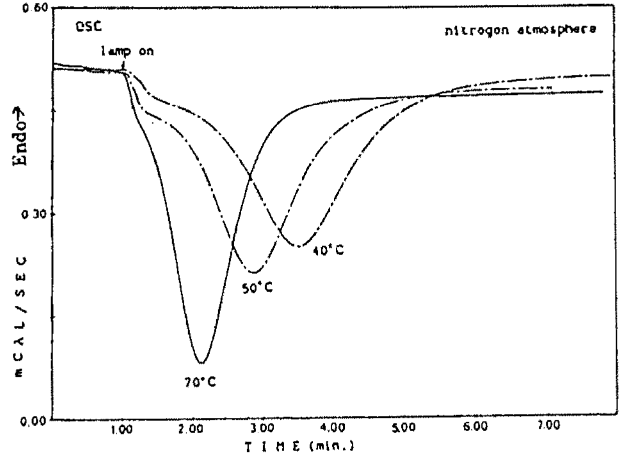

Fig. 3: Temperature effect on the curing behaviour of the ternary mixture.

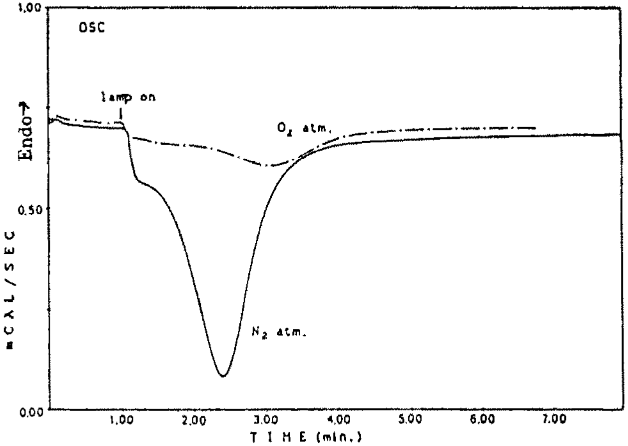

Fig. 4: Effect of the atmosphere on the curing behaviour of the ternary mixture.

**Table 1**

**DSC analysis of curing reactions of methacrylic monomers*:**

| monomer | ΔH - Kcal/eq. (cal/gr.) | % cure** | time to max. reaction rate (sec.) |
|---|---|---|---|
| EGDMA | 7.5 (75.8) | 54 | 63 |
| SR-252 | 12.5 (34.0) | 91 | 48 |
| HFBMA | 2.0 ( 7.5) | 15 | 9 |
| mixture | 10.2 (41.0) | 74 | 84 |

*) All experiments were run using constant equivalent ratios of 65:1 of the methacrylic monomer/s to the initiator and 15:1 of the monomer/s to the phosphite.

**) Conversions were calculated based on the lit. value of 13.8 Kcal/mole as the heat of polymerization of MMA [5].

The complex nature of the ternary mixture can be deduced from Table 1. All three monomers reach maximum reaction rate in a shorter period of time than the combined mixture. The ternary system has a pronounced gel-effect, clearly observed in Fig. 1. The total conversion in the mixed formulation is much higher than expected according to the data listed for all the three monomers separately. This finding could be explained by the presence of SR-252 monomer in the polymer backbone. SR-252 is a good cross-linker, but still induces some flexibility because of its long etheral chain. These two facts result in good incorporation of EGDMA and HFBMA into the polymeric structure, allowing the system to reach such high conversions.

Fig. 2 shows the effect of the initiator concentration on the curing behaviour of the ternary system. Changing its concentration from 0.22 to 0.84 wt.% had no effect on the observed heat of cure.

Turning off the light while the reaction is still in progress, resulted in additional 10-15% of propagation, as measured by DSC, until the reaction ceased. However, the initiator concentration was sufficient to bring the reaction to completion once it was resumed by turning the U.V. source on again.

Fig. 3 shows the temperature effect on the curing behaviour of the ternary system comprising 2.2 wt.% of TBPT and 0.4 wt.% of I-184. It was shown that up to 70°C there is no effect on the heat of reaction due to volatilization of some of the components. No reproducible results could be obtained beyond this temperature.

Curing under $O_2$ atmosphere demonstrated the high sensitivity of the system to oxygen inhibition. The heat of reaction dropped considerably to 15-20% of the value obtained for the reaction run under $N_2$ atmosphere (Fig. 4), even though the same concentration of TBPT was present in the sample. Secondly, the reaction exotherm is shallower, reaching its maximum rate after a much longer period of time.

The role of TBPT in preventing oxygen interference in the curing reaction is shown in Fig. 5. Both experiments shown in this Figure were performed under nitrogen atmosphere, having 2.2 wt.% or no TBPT in the mixture. In the latter case a lag period of 30 seconds was observed until the reaction was initiated, and the conversion did not exceed 25% of the value obtained in the presence of TBPT. In this case, the drastic effect is mainly attributed to the oxygen dissolved in the system. Degassing the sample prior to its irradiation, in an attempt to eliminate the dissolved oxygen , was only partially successful: The conversion reached only ca. 50% of its ultimate value. The degassing procedure has two disadvantages when applied to our system: (a) Having relatively high initial viscosity, it is hardly possible to obtain a completely deoxygenated system, and (b) Extensive degassing can possibly alter the system composition, changing the end properties of the film obtained.

Using an oxygen scavenger turned out to be more successful. It can either trap $O_2$ to form an unreactive peroxide, or decompose a reactive peroxide formed upon reaction of the cleaved initiator with oxygen. The most effective class of oxygen scavengers for our system proved to be the phosphites. Fig. 6 shows the net exotherm caused by U.V. irradiation of the system I-184/TBPT/dissolved oxygen in $\gamma$-butyrolactone, used as an unreactive solvent instead of the methacrylates. The peroxide decomposition exotherm is negligible as compared to the polymerization exotherm. Fig. 7 shows profiles of the photocuring reactions performed in the presence of different TBPT concentrations. Increasing TBPT concentration, results in an increase in the conversion (measured by the heat of reaction) and a decrease in the time needed to reach the maximum reaction rate (Fig. 8). In both cases a plateau is reached at a TBPT concentration of ca. 2 wt.%. Measurements were carried out up to 5 wt.% TBPT without any

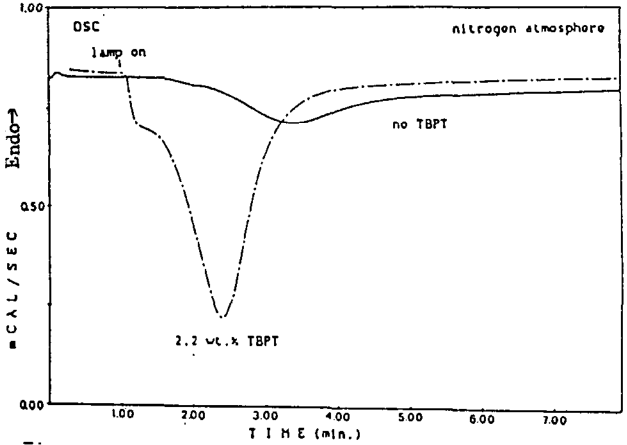

Fig. 5: Effect of TBPT on the curing behaviour of the ternary mixture.

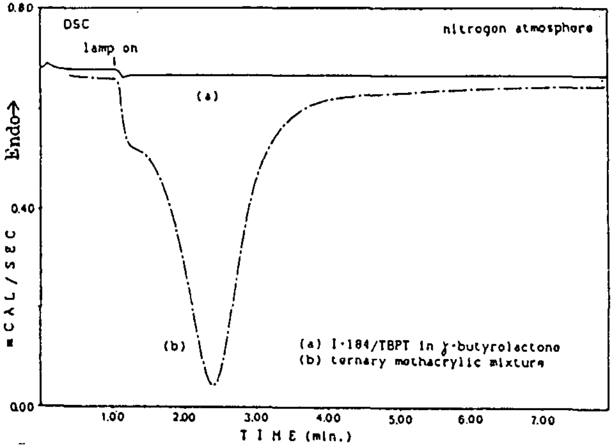

Fig. 6: Phosphite oxidation exotherm as compared to the overall polymerization exotherm.

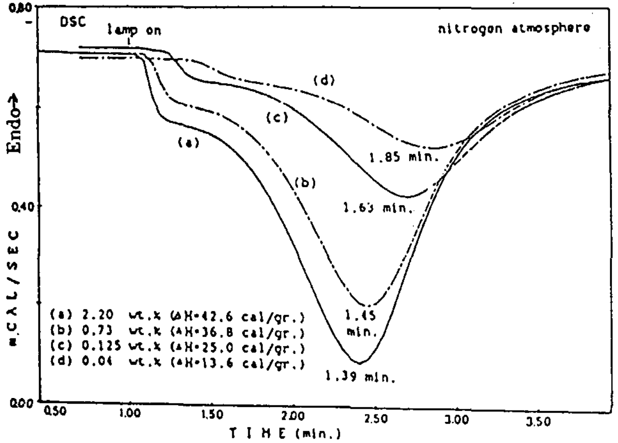

Fig. 7: Effect of TBPT concentration on the curing behaviour of the ternary mixture.

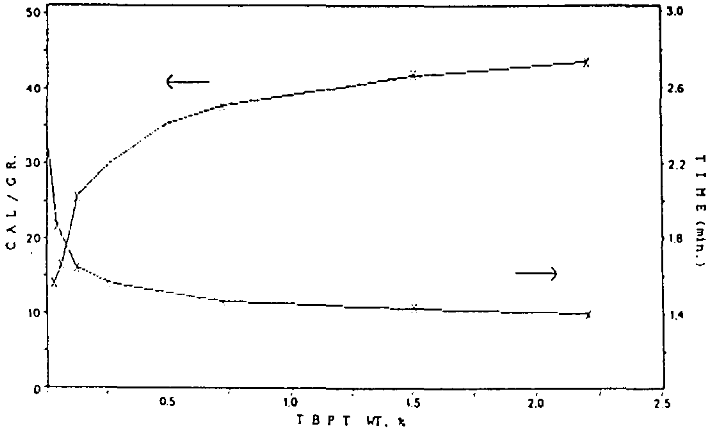

Fig. 8: The influence of TBPT concentration on the heat of curing and time to max. reaction rate.

further effect on the conversion. It is also of interest to note that a lag period for initiation exists at low TBPT concentrations. This lag period is eliminated when TBPT concentration reaches the optimal value of 1.5-2 wt.%. Nevertheless, the time needed for the reaction to achieve its maximum rate after initiation is constant (ca. 1.4 min.), and is independent of the TBPT concentration.

## CONCLUSIONS

In this study we have shown that the photocuring conditions of a methacrylic ternary system based on EGDMA, HFBMA and SR-252 can be optimized using DSC. This system was found to be extremely sensitive to dissolved oxygen. TBPT was proven to be an effective oxygen scavenger, and its optimal concentration was found to be ca. 2 wt.%. Initiator concentration as low as 0.22 wt.% is used in order to achieve the maximum conversion (74%), providing the right TBPT concentration is present in the system.

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