

# Photopolymerization of Dendritic Methacrylated Polyesters.

## II. Characteristics and Kinetics

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### SYNOPSIS

The starburst dendritic polyester with about eight double bonds was found to polymerize rapidly in the presence of a 3% photofragmenting initiator, benzildimethylketal, at room temperature in air, reaching 75% conversion after 0.15 s UV irradiation of a  $\mu\text{m}$  film. The effects of a photoinitiator and comonomer on the photopolymerization process for methacrylated polyester resins were investigated by measuring the conversion of the unsaturation and physical properties. The degree of copolymerization of the unsaturation decreases in the case of resins with high functionality. A kinetic study of the UV-induced curing of the dendritic polyesters by evaluating gel content and belt speed has shown that the photopolymerization rate increases rapidly with increasing acrylic functionality of the dendritic polyesters, which is in favor of the theory of radical-chain polymerization. High pendulum hardness is obtained with dendritic polyesters of high functionality. However, the addition of 10–40 wt % multifunctional monomer trimethylolpropane triacrylate has a small effect on the curing efficiency after prolonged UV irradiation, which is different from conventional linear acrylated oligomers. © 1996 John Wiley & Sons, Inc.

### INTRODUCTION

Compared with conventional linear polymers, the recently developed dendritic polyesters are attractive for photocuring because of their unique molecular structure with many branches, a high number of functional groups on each molecule, and some degree of three-dimensional molecular architecture.<sup>1,2</sup> Consequently, the expected performance of these materials are lower viscosity, better adhesion to substrates, and a higher reaction rate in curing.

Although significant progress has been made in the research of dendritic polymer materials for various applications,<sup>3,4</sup> there is still not much information on their use as coating and adhesive systems. In a previous article, we synthesized dendritic methacrylated polyesters for radiation curing and

investigated their rheological behavior and the thermal mechanical properties of the UV-cured films.<sup>5</sup> The observed low viscosity of the polymers and the high glass transition temperature of the cured materials are important for the processing of glass fiber-reinforced polyester composites and also for coating and adhesive systems. The processing of such compounds occurs by complex free-radical chain-growth copolymerization between the dendritic polyester and the comonomer. More important is that the processing of the resins as composites and coatings involves two basic parameters, namely, the resulting degree of conversion of functional groups and the polymerization kinetics during curing, which determine the value for its intended end use.

It is well known that complete conversion of unsaturation is never obtained in UV curing of acrylate polyester systems. The residual unsaturated groups will further react, e.g., with oxygen, which is a source of aging of the end products. In the case of the dendritic polyesters, there are more terminal acrylate double bonds on each molecule than in conventional linear polyesters. Therefore, investigations of the rate and the final degree of polymerization for the

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dendritic polyester resins are very significant for the end uses.

The major object of this study was to examine the effects of the functionality of the dendritic polyester and the concentration of the comonomer and photoinitiator on the conversion of the unsaturation and to investigate the photopolymerization kinetics of the dendritic polyester resins by measurements of tack-free time, gel content, and pendulum hardness.

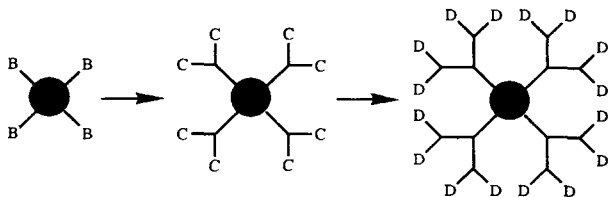
## EXPERIMENTAL

### Materials

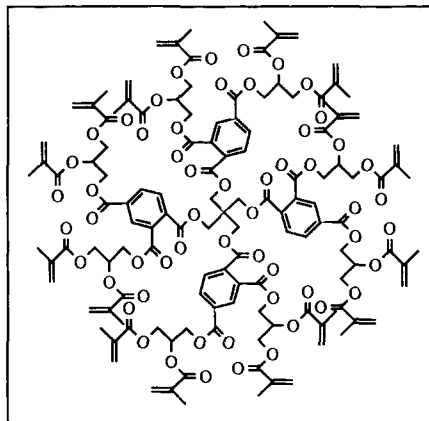
Three dendritic methacrylated polyesters were prepared from pentaerythritol and 1,2,4-benzenetricarboxylic anhydride and end-capped by glycidyl methacrylate and methacrylic anhydride via a controlled stepwise divergent preparation, as shown in Figure 1.<sup>5</sup> The dendritic oligomers with about 8, 12, and 16 terminal double bonds were numbered D-1, D-2, and D-3, respectively. The idealized formula of the polyester with 16 double bonds is shown in Figure 2. The multifunctional comonomer added to all formulations was trimethylolpropane triacrylate (TMPTA) (supplied by Aldrich, Germany). As the photoinitiator, benzildimethylketal (BDK, Irgacure 651), which produces two radical species upon irradiation with UV light, was used (supplied by Ciba Geigy). Each resin formulation contains 15 wt % TMPTA and 3 wt % BDK, unless otherwise stated.

### UV Curing

A Fusion UV Curing Systems, Model F300, was used in this study. Unless otherwise stated, the curing was accomplished by passing the test samples coated on a poly(ethylene terephthalate) (PET) sheet under 300 W/in. (120 W/cm) D bulb at variable conveyor speeds in air.



**Figure 1** Reaction scheme for the synthesis of the dendritic polyester: (B) hydroxyl groups; (C) carboxyl groups; (D) unsaturated groups.



**Figure 2** Idealized formula of the dendritic polyester with 16 double bonds.

### Measurements

#### Conversion of Unsaturation

The conversion of vinyl groups measured as residual unsaturation in the UV-cured films was determined with a Perkin-Elmer 1725X FT-IR spectrometer using the methacrylic double bond (out-of-plane deformation vibration) at  $810\text{ cm}^{-1}$  by a base-line method. The spectra were normalized using the carbonyl peak at  $1730\text{ cm}^{-1}$  as the internal standard to account for variations in sample thickness and instrument recording. The double-bond content of the uncured formulation was defined as 100%.

#### Gel Fraction

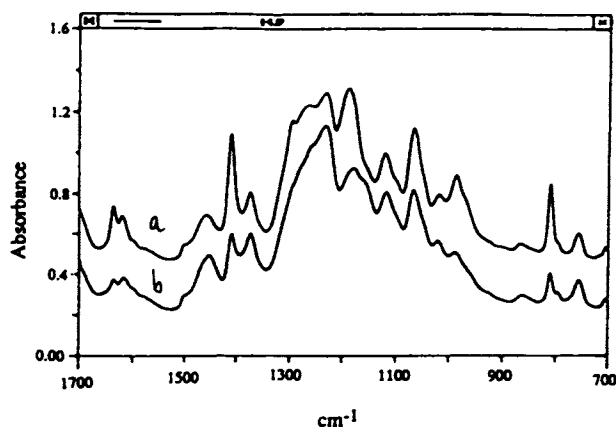
The gel content was determined by peeling the UV-cured films from the PET carrier sheets and extraction with boiling chloroform for 48 h. The solvent was renewed after the first 24 h of extraction. The films were dried in a vacuum oven at about  $50^\circ\text{C}$  to constant weight. The gel fraction in the film was given as percent insoluble residue of the initial weight.

#### Belt Speed and Irradiation Time

The belt speed under a Fusion F300 D bulb (300 W/in.) at which no cotton fibers adhered to the coating surface was recorded as the cure rate in meter per minute (m/min). The irradiation was performed in air. The belt speed varied from 20 to 35 m/min, which means irradiation times varied from 0.030 to 0.016 s.

#### Pendulum Hardness

The curing degree of the films was evaluated as "pendulum hardness" using a König pendulum ap-



**Figure 3** IR spectra of (a) the uncured dendritic polyester resin and (b) the UV cured film.

paratus. The films were prepared on glass plates (150 × 70 × 5 mm) by a coater with a 60 μm gap.

## RESULTS AND DISCUSSION

### Photopolymerization Characteristics

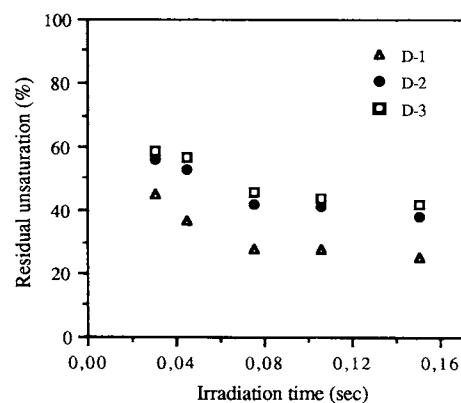
The dendritic methacrylated polyesters containing a small amount of multifunctional comonomer are rapidly crosslinked by a free-radical polymerization mechanism in the presence of an effective photoinitiator. The photocrosslinking process includes three major curing reactions which are the same with linear and dendritic oligomer systems: monomer–monomer, monomer–polyester, and polyester–polyester.<sup>6</sup> The curing reactions include intermolecular crosslinking, branching growth, polyester chain extension, intramolecular cyclization, and comonomer homopolymerization. It can be assumed that the comonomer molecules added to the dendritic polyester resin surround the dendritic polyester molecules and react largely with the methacrylic double bonds on the spherical surface and form crosslinks between neighboring dendritic polyester molecules and also homopolymerization. However, a small amount of the double bonds of the comonomers and dendritic polyesters may be buried inside the crosslinked networks of the cured resins and remain unreacted during the curing.

Infrared spectroscopy has been widely used to investigate the photopolymerization behavior of radiation-curable resins. Infrared spectra of coatings give quantitative measurements of functional groups. IR spectra of an uncured dendritic methacrylated polyester resin and a UV-cured film are shown in Figure 3. The decrease of the IR absorption

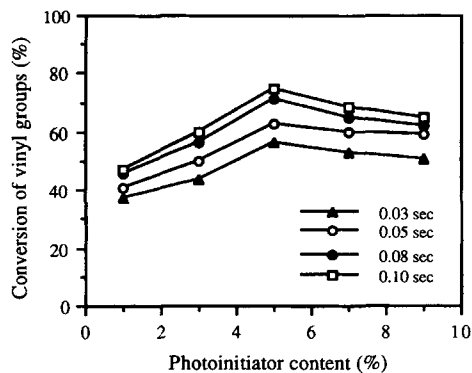
band (out-of-plane deformation vibration) at 810  $\text{cm}^{-1}$  as a function of the irradiation time allows an evaluation of the number of methacrylic double bond in the resin during curing.

Plots of residual unsaturation vs. irradiation time are shown in Figure 4 for the dendritic methacrylated polyester D-1, D-2, and D-3 resin systems, respectively. All three resin systems show rapid initial reaction rates and D-1 has the lowest residual unsaturation ( $\sim 25\%$ ) after prolonged irradiation. After curing, there still remain certain amounts of methacrylic double bonds in the film substrate. At increasing functionality of the dendritic polyester, the maximum degree of curing decreases. There are numerous reports showing that about 30% unreacted C=C double bonds remain in acrylate prepolymer films after UV curing. Complete conversion is never obtained, especially when multifunctional monomers are used.<sup>7,8</sup> In our case, this is interpreted as due to the reduced mobility and accessibility of the reactive groups with increased functionality of the dendritic methacrylated polyester molecules, i.e., some residual methacrylic double bonds will be trapped in the three-dimensional polymer matrix formed and unable to react.<sup>9</sup> A more compact network of crosslinked polymer is expected at higher crosslinking density of the cured resin. As a result, the conversion of double bonds in the resin system with high functionality of the polyester molecules is lower.

The conversion of vinyl groups in the UV-cured resin films of D-1 polyester at different photoinitiator concentrations is shown in Figure 5. The degree of conversion increases to a maximum at a concentration of 5 wt % Irgacure 651 photoinitiator and reaches a conversion of 78% after 0.1 s irradiation. A further increase of the amount of photoinitiator



**Figure 4** Conversion of unsaturation in the cured films of three dendritic polyesters as a function of irradiation time measured by FTIR.

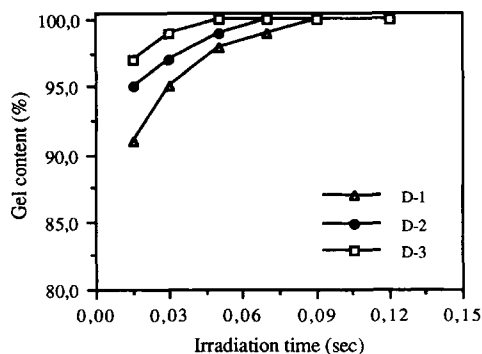


**Figure 5** Conversion of vinyl groups in cured films of D-1 polyester at different photoinitiator concentrations measured by FTIR.

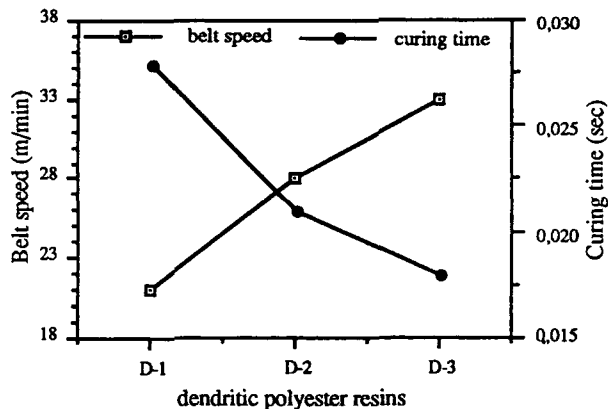
gives a lower conversion. This is interpreted as due to an increased radical combination which is a second-order reaction, resulting in termination of the polymerization, while initiation is of first order. Photocured coatings always contain a certain amount of unreacted vinyl groups.

### Photopolymerization Kinetics

A property of great importance is the cure rate for the resin system. The rate of photopolymerization was found to increase with increased oligomer functionality. The gel content measurements of the cured film can be used to determine the amount of cross-linked polymer formed after UV irradiation. The inextractable part in wt % as cure time is shown in Figure 6 for three dendritic polyesters. At irradiation times longer than 0.09 s for D-1 but 0.075 s for D-2 and D-3, plateau values of gel fractions approaching 100% for all three dendritic polyester systems are obtained. This indicates that the samples are highly crosslinked, even though their FTIR spectra



**Figure 6** Pendulum hardness of the three dendritic polyester resins D-1, D-2, and D-3.

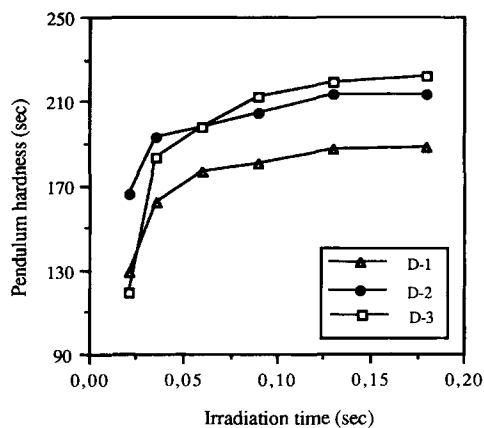


**Figure 7** Effect of comonomer contents on pendulum hardness of the dendritic methacrylated polyester D-3 resins after increasing curing times.

indicate that they contain significant residual unsaturation, as shown in Figure 4. It also means that loss of mobility of the reactive groups during curing effectively limits the degree of conversion after essentially all of the low molecular weight species have been incorporated into the network.

The irradiation time is varied by changing the speed of the conveyor belt. The polymerization rate of the dendritic polyester resins was determined by measuring the irradiation time required to obtain a fully tack-free state for the cured film using a cotton bar. The data are given in Figure 7. The resin with oligomer D-3 needs the shortest curing time to obtain a tack-free state.

Measurement of pendulum hardness is a convenient method to monitor the UV-curing process of a resin. Figure 8 shows the pendulum hardness of the three dendritic polyester resins vs. irradiation time. The pendulum hardness increases rapidly at



**Figure 8** Gel fraction in the cured films of D-1, D-2, and D-3 dendritic polyesters as a function of irradiation time.

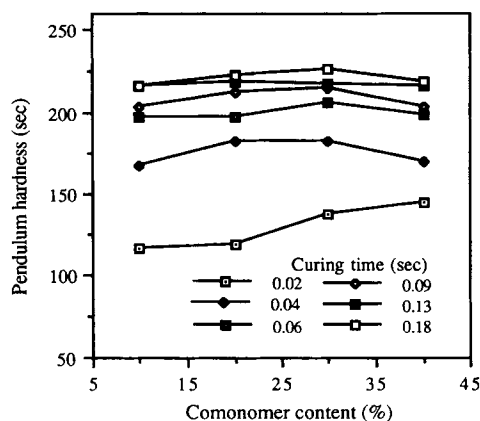
UV irradiation times up to about 0.05 s and then levels-off at about 0.10 s irradiation. The resin with the D-2 oligomer shows the highest increase of initial hardness, while the resin with D-3 reaches the highest final pendulum hardness. These differences are related to the crosslinking density of the polyester resins.

The amount of monomer (TMPTA) added has a significant effect on the pendulum hardness of the cured film only at low irradiation dose. Figure 9 gives the pendulum hardness of the cured resin with D-3 oligomer containing 10–40 wt % of TMPTA. It can be seen that the addition of large amounts of TMPTA results in higher pendulum hardness of the cured film at the beginning of irradiation. This could be interpreted as due to the reactivity of the small TMPTA molecules which are highly reactive and are rapidly homopolymerized or copolymerized at lower UV irradiation dose in the presence of a photofragmenting initiator. However, after 0.04 s of irradiation, a slight increase of hardness can be observed for the cured films containing 10–30 wt % TMPTA. There is a small decrease of hardness of the cured films containing above 30 wt % TMPTA, which means that pendulum hardness in this case is related to the aromatic dendritic polyester.

The higher cure speed with the higher functionality of dendritic polyester can be interpreted with the kinetic theory of radical polymerization. With benzildimethyketal used as the photoinitiator, two radicals per molecule are produced by UV irradiation, and the rate of photochemical initiation should be given by  $R_i = 2\phi I_a$ . Therefore, the rate of radical polymerization reaction ( $R_p$ ) as a function of monomer concentration  $[M]$  and initiation and termination rates is

$$R_p = -\frac{d[M]}{dt} = K_p \left( \frac{\phi_d I_a}{K_t} \right)^{0.5} [M]$$

where  $K_p$  is the polymerization rate constant;  $\phi_d$ , the quantum yield of photodecomposition of initiator;  $I_a$ , the intensity of absorbed light in moles of light quanta per liter-second; and  $K_t$ , the termination rate constant. The polymerization rate,  $R_p$ , is a linear function of monomer concentration ( $[M]$ ).<sup>10</sup> The term monomer concentration  $[M]$  indicates the number of double bonds contained in the system. It has been seen from Figure 6–8 that the observed dependence of the curing behavior on the molecular structures of the polyesters is in favor of the theory involving radical chain polymerization. The dendritic polyester D-3 has the highest photopolymer-



**Figure 9** Curing time and belt speed to tack-free state for UV-cured dendritic polyester films.

ization rate due to its high functionality of double bonds per acrylated oligomer molecule.

## CONCLUSION

Dendritic oligomers end-capped with methacrylated groups are very reactive compounds which undergo fast photopolymerization by a radical mechanism with a photofragmenting initiator also in air. All three dendritic polyesters studied with about 8, 12, and 16 methacrylate groups per molecule have a high cure rate and form crosslinked polymers containing amounts of residual unsaturation which are on an acceptable level compared with conventional linear acrylate oligomers. The addition of 10–40 wt % multifunctional monomer trimethylolpropane triacrylate has small effect on the curing efficiency after prolonged UV irradiation.

Dendritic acrylated polyesters are promising for the development of coatings and adhesives in industrial applications. Dendritic resins are expected to compete with or even replace some of the existing radiation-curable products.

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