

# Photopolymerization of Dendritic Methacrylated Polyesters.

## I. Synthesis and Properties

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### SYNOPSIS

The so-called starburst dendritic polyesters differ from classical polymers by their structural symmetry, high degree of branching, and high density of terminal functionality. The divergent synthesis of a series of polydisperse dendritic polyesters based upon pentaerythritol and 1,2,4-benzenetricarboxylic anhydride, modified by glycidyl methacrylate and methacrylic anhydride, is described, proceeding in a stepwise growth manner starting from an "initiator core," building branched arms. These materials have about eight (two samples), 12, or 16 methacrylate double bonds (indicated as D-1-OH, D-1, D-2, and D-3, respectively) at the chain extremities on each molecule. The rheological behavior was investigated by measuring the dynamic viscosity of the dendritic polyesters. The viscosities of the dendritic polyesters largely decrease in the order D-1-OH, D-1, D-2, and D-3 at lower frequency, but the viscosities of D-1-OH and D-1 decrease dramatically at higher frequency. Using a viscometric cup, the flow time of the dendritic methacrylated polyesters was compared with epoxy acrylate-modified unsaturated polyester of a linear type and it was shown that the flow time for the former is only one-third of that for the latter. The thermal mechanical properties and glass transition temperatures of the UV-cured films increase with the degree of terminal functionality. © 1996 John Wiley & Sons, Inc.

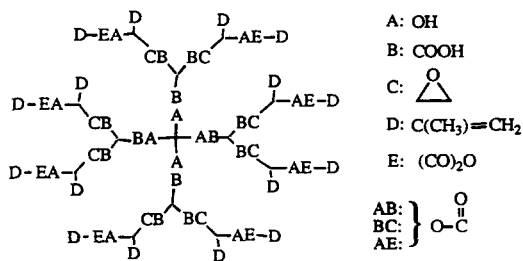
### INTRODUCTION

Radiation-curable resins are increasingly used in various industrial applications, replacing conventional thermally cured and solvent-based coatings and adhesives.<sup>1,2</sup> The radiation-curable resins have favorable properties, e.g., high-speed and low-energy consumption of cure, solvent-free formulations, room-temperature operation, and high-quality end products.<sup>3</sup> The principal components of a radiation-curable resin are oligomers (or prepolymers) and comonomers. The oligomers constitute the backbone of the three-dimensional polymer network formed by curing. Important types of oligomers commonly used for coatings are acrylated epoxies, acrylated polyurethanes, unsaturated

polyesters, and acrylated polyesters (or polyethers), which give the desired properties of the final cured films. However, those oligomers usually consist of linear molecular chains. The viscosity of the resin increases rapidly with increasing chain length of the oligomer. To obtain an operational viscosity of the formula for spraying, dipping, roll coating, etc., large amounts of multifunctional comonomer are required for the primary function of viscosity control. In addition, the comonomers have important effects on the cure reaction and the properties of the final product. Some of the comonomers have a low cure rate, cause shrinkage of the film during curing, or have a high cost or limited shelf life. Multifunctional acrylates are the preferred comonomers in radiation-curable systems because of their rapid curing rates and low prices. The common acrylate monomers are volatile and toxic and have a strong odor. Therefore, the trend is to use radiation-curable oligomers with a viscosity close to the required application viscosity in order to reduce or eliminate the use of comonomers.

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**Figure 1** Reaction scheme for the synthesis of the dendritic polyester.

Recently, a new family of oligomers with three-dimensional molecular architecture and possessing starburst topology has been attracting increasing interest for many applications, e.g., in agriculture, medicine, cosmetics, adhesives, and coatings, which is referred to as dendritic polyester or dendrimer.<sup>4-6</sup> An important structural difference between linear oligomers and dendritic polyesters is that a linear oligomer of sufficient molecular weight contains an entanglement of flexible molecular chains, while a dendritic polyester is a compact molecule with many branches which carry a high number of terminal functional groups on each molecule. Accordingly, dendritic polyesters can be used to reduce viscosity, increase reaction rate, and improve adhesion to substrates due to their very special molecular structures. This new kind of molecule modifies the physical and chemical properties both of the resin system and of the final product after curing. Therefore, high molecular weight dendritic polyesters with reactive (meth)acrylate double bonds at chain extremities would be of particular interest if they could be obtained in a simple process from readily available and inexpensive raw materials, thereby facilitating their use in coating and adhesive systems.

Dendritic polyester research is still fairly new, and, to date, no commercial products are available. The main difficulties in preparing three-dimensional dendritic polyesters are preserving the regularity and order in the structures, characterization of the products, and separating the products from the excess of reactants. Recently, it was announced that DSM Desotech Inc. is turning out multikilogram lots of the "new kind molecule"—the hyperbranched polyamine, portending commercial production by 2000.<sup>4</sup> Little work has been performed to prepare adhesive and coating systems with polyesters, especially for radiation-curing applications. A series of work on allyl ether maleate dendritic polyesters for UV-curing coatings by Hult and colleagues has been reported.<sup>7-10</sup>

In this work, we synthesized a series of dendritic methacrylated polyesters with different numbers of terminal double bonds per molecule and investigated rheological properties of the resins and the thermal mechanical properties of the UV-cured films. The polyesters synthesized in this work have "highly regular" branching and are "dendritic" according to Fréchet's nomenclature, while "hyperbranched" polymers are randomly branched.<sup>6</sup>

## EXPERIMENTAL

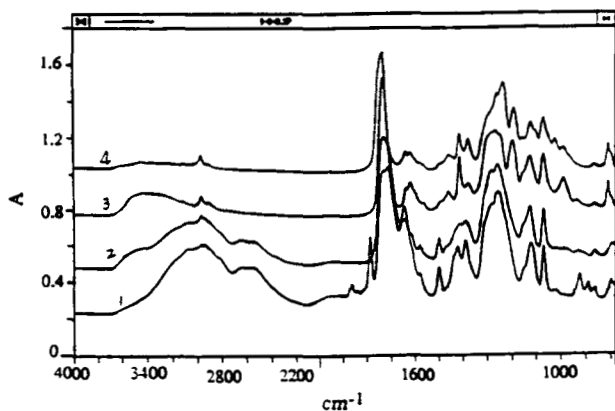
### Materials

Pentaerythritol and 1,2,4-benzenetricarboxylic anhydride are used for synthesis of the polyolester with carboxylic end groups. Glycidyl methacrylate and methacrylic anhydride are used for the end capping of the polyester with methacrylate groups and forming the star-shaped dendritic polyesters. Acetic anhydride is used to acetylate hydroxyl groups on the polyester chains. All the above materials were supplied by Aldrich, Germany, and used as received without further purification. The epoxy acrylate-modified unsaturated polyester (MUP) was synthesized from fumaric acid, phthalic anhydride, propylene glycol, and neopentyl glycol by a standard azeotropic polycondensation technique to a molecular mass of about 2200.<sup>1</sup> The multifunctional comonomer added to the polyesters was trimethylolpropane triacrylate (TMPTA) (supplied by Aldrich, Germany). Benzildimethylketal (BDK, Irgacure 651) from Ciba Geigy, Switzerland, was used as a photofragmenting initiator for curing the hyperbranched polyesters.

### Synthesis of Dendritic Polyesters

Two principally different methods have been developed for the synthesis of dendritic polymers: a convergent growth mechanism, where growth begins at chain ends, and a divergent growth mechanism, where growth begins at a central core.<sup>5,11</sup> In this work, the dendritic methacrylated polyesters were synthesized by a controlled stepwise divergent preparation, i.e., the synthesis started at the center of the dendritic polyester. At least two steps were needed to obtain dendritic polyesters with about 8, 12, or 16 terminal methacrylic double bonds located at the surface of the oligomeric sphere, as shown in Figure 1.

Pentaerythritol, a 20–50 mol % excess of 1,2,4-benzenetricarboxylic anhydride to hydroxyl groups

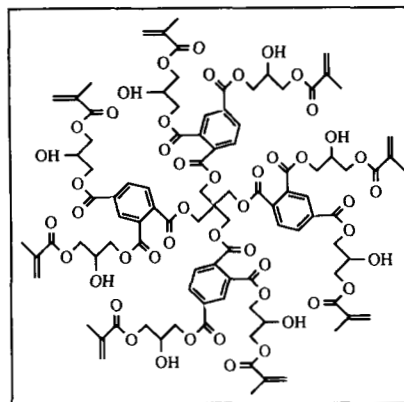


**Figure 2** IR spectra of the products at different reaction stages.

of pentaerythritol, and a catalytic amount of stannous chloride as the activating agent were heated for 16 h to temperatures below 100°C in the presence of *N,N*-dimethylformamide (DMF) as the solvent under a nitrogen atmosphere. DMF is then distilled off in a vacuum as well as possible. The IR spectrum of the product mixture with residual 1,2,4-benzenetricarboxylic anhydride is shown by curve 1 in Figure 2.

Toluene was used to wash the reaction products to remove the excess of 1,2,4-benzenetricarboxylic anhydride until no peaks at 1760 and 1850  $\text{cm}^{-1}$  for anhydride groups could be observed by IR measurement, as shown as curve 2 in Figure 2. The wide absorption bands at around 3150  $\text{cm}^{-1}$  in the IR spectrum indicate the terminal carboxylic groups on the benzene ring. The polyolester of the poly(carboxylic acid) anhydride is a white powder after completely removing the solvents.

The polyolester was further reacted with a 5 mol % excess of glycidyl methacrylate to the carboxyl group of polyolester in a mixture of DMF and toluene at 70°C in the presence of 2.5 wt % benzyldimethylamine as the basic catalyst and hydroquinone as the inhibitor for radical polymerization until no carboxyl groups could be detected by end-group titration. The IR spectrum of the product is shown as curve 3 in Figure 2. The appearance of the wide absorption at around 3460  $\text{cm}^{-1}$  indicates the formation of hydroxyl groups on the molecular chains due to the reaction of epoxy-carboxylic groups. Finally, the solvents were removed by evacuation at low temperature. The final "starburst" dendritic polyester products with about eight double bonds at the end groups and one hydroxyl group at each branched chain are translucent viscous liquids,

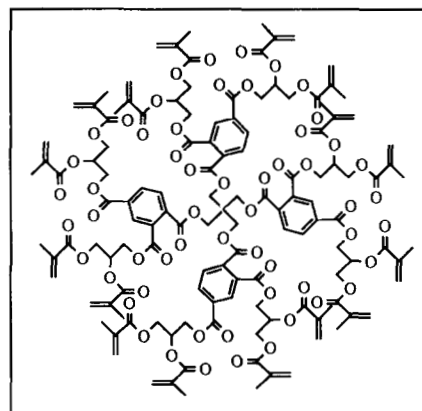


**Figure 3** Idealized formula of the dendritic polyester with eight double bonds at the chain ends and eight hydroxyl groups on the chains.

numbered D-1-OH. The molecular structure is ideally spherulike, with the principal formula shown in Figure 3.

The hydroxyl groups of the dendritic polyester were reacted further by ester formation with methacrylic anhydride in order to prepare the dendritic polyester molecules with about 12 and 16 end-double bonds. The idealized formula of the obtained product with 16 double bonds in each molecule is shown in Figure 4. The IR spectrum of the dendritic polyester with about 16 double bonds is shown by curve 4 in Figure 2. Almost no peak for the hydroxyl group could be observed.

Given amounts of acetic anhydride were added to esterify a part of the hydroxyl groups on the molecular chains in order to decrease the molecular polarity of the dendritic polyester with about 8 and 12 double bonds and improve their compatibility



**Figure 4** Idealized formula of the dendritic polyester with 16 double bonds at the chain ends.

with multifunctional comonomers. The modified dendritic polyester products with about 8, 12, and 16 terminal double bonds prepared in this study are fairly transparent colorless viscous liquids, numbered D-1, D-2, and D-3, respectively.

### Sample Preparation

For measuring the thermal mechanical properties, samples of the dendritic methacrylated polyesters with only a photoinitiator added were weighted into the plastic mold (length 10 mm, width 4 mm, and thickness 300  $\mu\text{m}$ ) and irradiated with an ultraviolet lamp system (Fusion UV Curing Systems, 120 W/cm, Model F300 D bulb). The samples were removed from the mold and analyzed without further treatment.

### Measurements

#### IR Spectra

Infrared spectra of the polyesters at different reaction stages were recorded on a Perkin-Elmer 1725X Fourier transform spectrometer prepared as a pressed KBr solid disk or smeared as an acetone solution of the resin on a NaCl prism to form a thin film.

#### Molecular Weight Distribution

Measurements of molecular weight distribution were performed on a WATERS 410 GPC system equipped with a WISP 712 automated injector. The columns used were  $\mu$ -Styragel of pore sizes 500,  $10^5$ ,  $10^4$ ,  $10^3$ , and 100  $\text{\AA}$  with polystyrene standards for calibration and tetrahydrofuran as the solvent.

#### Dynamic Mechanical Spectroscopy

The dynamic mechanical properties of the dendritic polyesters were measured by shear rheometry (dynamic analyzer RDAII). Viscous liquid samples were examined at 25°C using two parallel plates of 12.5 mm radius with a 0.62–0.76  $\mu\text{m}$  gap over a wide range of frequencies.

#### Flow Time

The flow time of the resins with multifunctional comonomer TMPTA added was measured using a viscometric cup of number 68 for comparison of the viscosity of the dendritic polyesters with that of modified linear unsaturated polyester.

### Thermomechanical Analysis

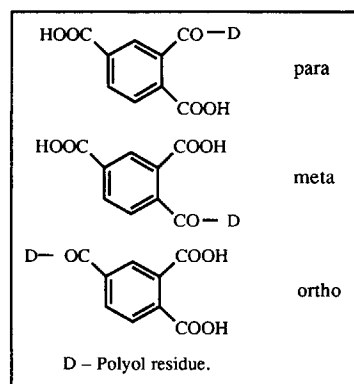
A dynamic mechanical thermal analyzer (DMTA, Polymer Laboratories MK II) was used to measure the glass transition temperature ( $T_g$ ) and tensile loss factor ( $\tan \delta$ ) of completely UV-cured films at the range of 40–250°C and 1 Hz frequency.

## RESULTS AND DISCUSSION

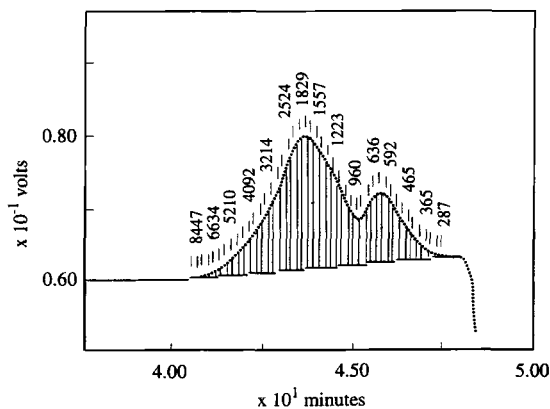
### Preparation of the Dendritic Polyesters

Three isomeric products could be obtained in the esterification reaction stage of pentaerythritol with 1,2,4-benzenetricarboxylic anhydride, and the molecular structures are shown in Figure 5. The product is largely a mixture of *meta* and *para* isomers of pentaerythritol ester according to the relative reactivity of the anhydride and the carboxyl groups at a low reaction temperature. A small amount of the *ortho* isomer is expected to be polyolester from the hydrolysis product of 1,2,4-benzenetricarboxylic anhydride or the hydrolysis product of polyolester formed from the reaction of carboxyl-hydroxyl groups. Those reactions are favored at elevated temperatures and in the presence of water in the system.

The polydispersity measured by GPC analysis varied from 1.4 to 1.9 at different reactant molar ratios and reaction temperatures. The molecular mass distribution of the dendritic polyester D-1 with molecular weight at the maximum of 2180 theoretically is shown in Figure 6. The wide and bimodal molecular weight distribution is related to irregularities in the synthesis. The main component has the molecular structure shown in Figures 3 and 4, giving the molecular weight of 2180. The low mo-



**Figure 5** Molecular structure of the three polyolester isomers.



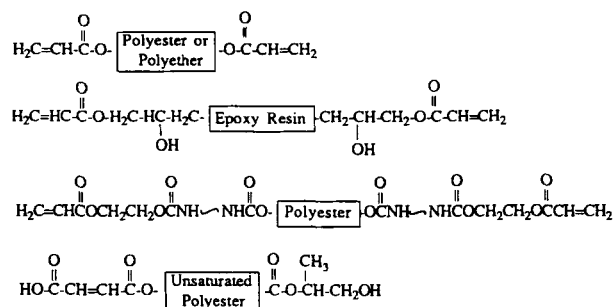
**Figure 6** Polydispersity of the dendritic methacrylated polyester D-1 by GPC analysis.

lecular component at about 600 is interpreted as due to intramolecular cyclization of COOH and OH groups, while the tail of high molecular weight is due to secondary reactions of COOH groups in one polyester molecule with OH groups in another molecule, i.e., an initial crosslinking. All polyester molecules of different molecular weight have carboxyl end groups which react with glycidyl acrylate and methacrylic anhydride. The double bonds introduced are at the chain ends of the molecules and will, therefore, be located at the surface of the oligomeric spheres, which is highly favorable for UV cure.

### Rheological Behavior

Low viscosity is particularly important in controlling the leveling time of a coating and for evaluation of the processability of a radiation-curable coating and adhesive. This is especially the case for 100% solid coating systems for thin films. The oligomer is the principal constituent of the resin and primarily responsible for the basic properties of the coating. The viscosity of the oligomer is, therefore, an important parameter since it determines the amount of oligomer required in the final product. For control of the viscosity of the radiation-curable resin, we have only two parameters: the viscosity of the oligomer and the amount of comonomer added.

The rheological behavior of a viscous liquid is determined by the elasticity and viscosity of the material. The principal rheological difference between the branched and linear polyester molecules lies in the smaller spatial extension of the branched molecule at a given molar mass. The generalized structures of conventional oligomers with acrylate functions at the end groups of the backbone, which is

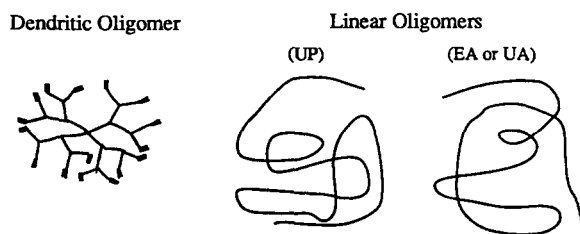


**Figure 7** Generalized structures of conventional radiation-curable oligomers.

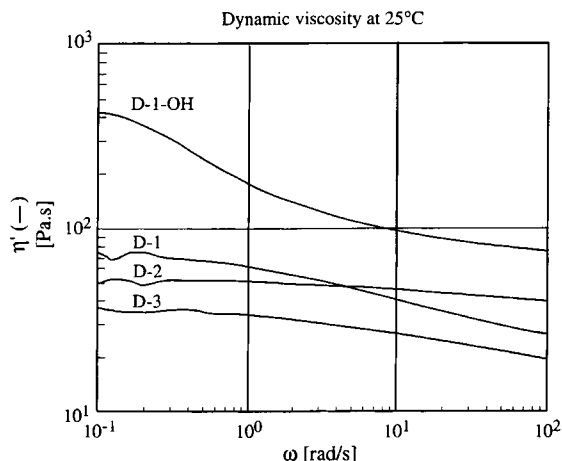
mainly a polyester, epoxy resin, or a urethane polyester, and with vinylene double bonds at the middle chain, which is an unsaturated polyester, are shown in Figure 7. The idealized structures of dendritic polyesters studied are starlike branched molecules as shown in Figure 3 and 4.

The architectural features of the dendritic polyesters studied in this work and the conventional linear polyesters are compared in Figure 8. It can be considered from Figures 4 and 5 and Figures 7 and 8 that the segment density within the volume occupied by a dendritic molecule in solution is higher than for a linear molecule with the same number of monomer units, as indicated in the literature.<sup>12</sup> The viscosity of the resin is related to the dynamic extension in space and the segment density within the volume of the molecule. Therefore, the spherulike starburst polyester has a lower viscosity than that of a corresponding linear polyester.

The dynamic viscosity and complex shear modulus were measured as a function of frequency for the dendritic polyesters with a different number of double bonds, as shown in Figures 9 and 10. The dendritic polyester D-1-OH with about eight double bonds without acetic anhydride modification has the highest viscosity due to the many hydroxyl groups in the system (about eight hydroxyl groups per molecule), forming intermolecular hydrogen bonding



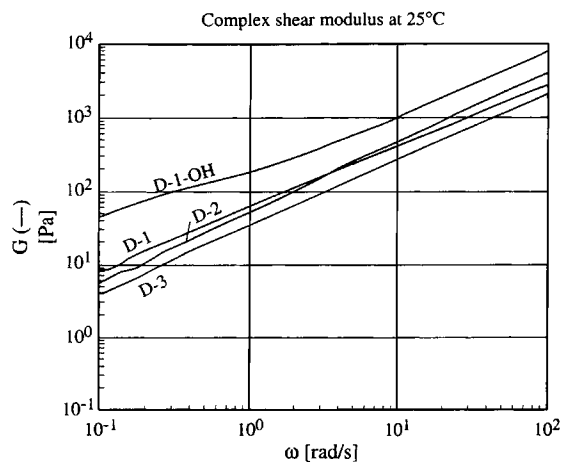
**Figure 8** Structural schemes of dendritic and two linear oligomers.



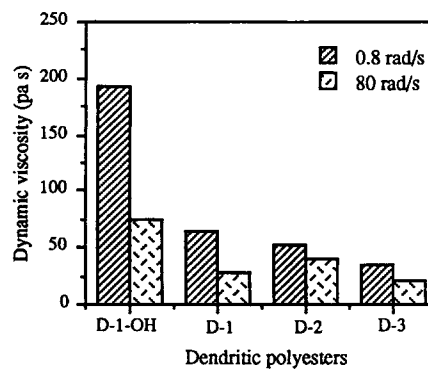
**Figure 9** Dynamic viscosity of the dendritic methacrylated polyesters with DMTA.

(dendritic polyester aggregation). At decreasing hydroxy functionality and increased symmetry of the polyester molecule, on the average, two hydroxyl groups per D-1 and D-2 molecules, the dynamic viscosities of the dendritic polyesters at lower frequency largely decrease in the order D-1, D-2, and D-3. The complex shear modulus decreases in the same order, as seen from the decrease in dynamic viscosity at low frequency.

However, the dynamic viscosities of the D-1-OH and D-1 decrease dramatically, and the moduli of D-1-OH and D-1 increase at lower rates than do those of D-2 and D-3 at higher frequency. The changes in dynamic viscosity at two frequencies is compared in Figure 11. The dynamic viscosities of D-1-OH and D-1 both decrease more than 50% when



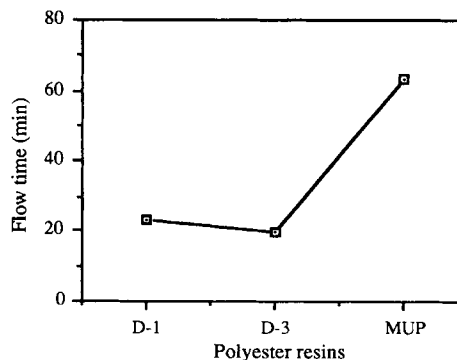
**Figure 10** Complex shear modulus of the dendritic methacrylated polyesters with DMTA.



**Figure 11** Dynamic viscosity of the dendritic polyesters at varying frequencies.

the frequency is increased 100 times. For D-2 and D-3 polyesters, the decrease is smaller. It can be explained as an effect of hydrogen bonding. When the shear force becomes big enough to overcome the intermolecular hydrogen bonding at high frequency, the viscosity of the systems decreases. Because polyesters D-1-OH and D-1 have more hydroxyl groups per molecule and less molecular symmetry than do polyesters D-2 and D-3, the influence of increased rotation frequency on the dynamic viscosity of the former is bigger than that of the latter. That is the reason why the viscosity curves for D-1 and for D-2 cross (Figs. 9 and 10). It is not surprising that D-3 has the lowest viscosity compared with D-1 and D-2 because of the high number of double bonds (no remaining hydroxyl groups) at the surface of the spherical molecule, which results in increasing symmetry of the dendritic molecule, apart from less influence from the hydrogen bonding.

Flow-time measurements are another evaluation of the relative viscosity of various coating and adhesives, using a viscometric cup, which is common

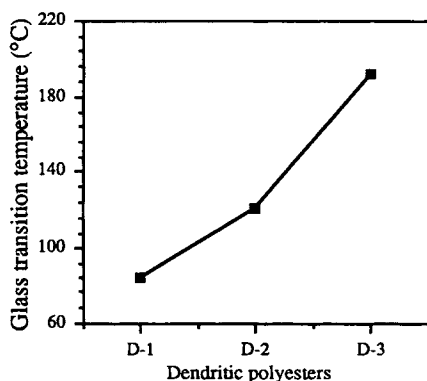


**Figure 12** Flow time of dendritic polyesters and MUP using a viscometric cup.

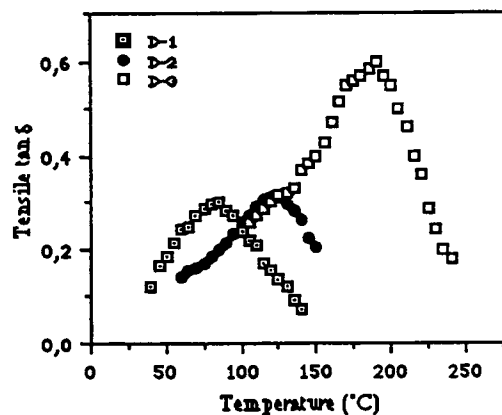
practice in industry. The viscosities of the dendritic methacrylated polyesters containing 15 wt % TMPTA with MUP containing 35 wt % TMPTA at 21°C are compared in Figure 12. It can be seen that the flow times through the viscometric cup for dendritic polyester resins are three times shorter than for MUP resin. This means that the viscosity of MUP is three times higher than that of dendritic polyester. A practical consequence is that the processibility of dendritic polyester-containing resins is improved due to their lower viscosities.

### Thermal Mechanical Properties of the UV-cured Films

The physical properties of the cured material are related to the structure of the crosslinked network. The glass transition temperature,  $T_g$ , is a function of the flexibility of the polymer chains. If the flexibility decreases, the transition temperature increases. Flexibility is a function of chain structure, crosslink structure, and crosslink density.<sup>13</sup> For the starburst dendritic polyesters, the spherical shape of the molecules and the high crosslink density after curing due to the high functionality decrease the flexibility of the cured films. Therefore, crosslinked dendritic polyesters give higher glass transition temperatures than do crosslinked linear oligomers as an effect of the structural difference. The glass transition temperatures of the crosslinked dendritic polyesters D-1, D-2, and D-3 measured by dynamic mechanical thermal analysis (DMTA) are given in Figure 13. It can be seen that the glass transition temperature increases rapidly with increasing functionality of the cured dendritic oligomer. Undoubtedly, there is a higher crosslinking density in the UV cured D-2 and D-3 polyester films than in the



**Figure 13** Glass transition temperatures of the UV-cured dendritic polyesters.



**Figure 14** Tensile loss factor  $\tan \delta$  for the UV-cured films of dendritic polyesters.

cured D-1 film, although residual double bonds are retained in the cured D-2 and D-3 polyester films in relatively large amounts. The tensile loss factor  $\tan \delta$  for the cured dendritic polyester films vs. temperature is given in Figure 14. These results indicate that the crosslinking density is increasing from D-1 to D-3, which can also be derived from the increase in  $T_g$ .

### CONCLUSION

Starburst dendritic oligomers endcapped with methacrylic groups have been synthesized by divergent stepwise growth beginning at the center of dendritic polyester, with a wide molecular weight distribution that varied from 1.4 to 1.9. These dendritic polyesters have a low viscosity which is a function of the functionality of the polyester due to their dendritic structure. The cured films from dendritic polyesters of high functionality have high glass transition temperatures.

The dendritic methacrylated oligomers, synthesized in this study, may open up a new line of radiation-curable products. They may be modified to meet particular application requirements for coating, lamination, and adhesive systems.

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