Photopolymerization and the Related Properties of Dendritic Methacrylated Polyesters

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ABSTRACT: Three kinds of photopolymerizable dendritic polyesters have been synthesized based on 1,1,1-trishydroxymethyl-propanol, pentaerythritol, and dipentaerythritol as polyols and polycarboxylic acid anhydride, modified with glycidyl methacrylate and then esterified by acetic anhydride, which contain a maximum of 6, 8, and 12 methacrylic groups at the molecular chains, respectively. Their dynamic viscosity and UV-cure speed have been measured by a spinning viscometer and the tack-free time of the product, and the mechanical properties have been investigated by pendulum hardness and tensile strength of the UV-cured films. It is found by comparison with traditional linear epoxy (meth)acrylate oligomers with lower molecular weights that the dynamic viscosity of the dendritic methacrylated polyesters is only half of that for the linear oligomers. However, the UV-cure speed is about five times of that for the latter. The tensile strength of the cured films increases with the functionality of the polyester and a small amount of comonomer addition. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 499–504, 2001

Key words: dendritic polyester; photopolymerization; molecular mass distribution; rheological behavior; mechanical property

INTRODUCTION

Radiation curing has found a growing number of applications in recent years because of the unique advantages of this advanced technology, such as fast cure speed, conservation of energy, VOC minimization, high-quality products, and so forth.[1,2] The increasing use of curable materials for adhesives, inks, and coatings provides an incentive for the development of new varieties of photopolymers.[3]

The viscosity of a coating formulation should be low enough for easily spraying, dipping, and rolling. Therefore, a conventional radiation-cur-able resin formulation usually contains a large amount of multifunctional comonomers, up to 40%, except for oligomers. The comonomers used for decreasing the formulation viscosity play a key role because they influence the cure speed and the extent of polymerization, as well as the final properties, of the cured materials. However, the common multifunctional acrylate monomers are volatile and toxic, and have a strong odor. The various acrylated epoxies are the most important oligomers used for UV-coating systems because of their higher cure speed and excellent mechanical properties of the final cured products. But all (meth)acrylated epoxies usually have higher viscosity, which increases linearly with the molecular mass of epoxy resin.

Formulators always balance viscosity, cure speed, and final properties for a given UV formu-

lation. It is a difficult compromise to achieve both rapid cure speed and low viscosity for an oligomer by a conventional technique.[4] New dendritic hyperbranched polymers have provided a powerful technology in this field. Because of their multiplicity of end-groups and highly branched architecture they exhibit properties different from those of the linear counterparts.[5–7] In our previous series of investigations[8–10] we synthesized hyperbranched (meth)acrylated polyesters from pentaerythritol as a core molecule, and investigated their rheological behavior, photopolymerization characteristics, and mechanical properties of the composites in UV-radiation curing.

In this work, we synthesized a series of photopolymerizable dendritic polyesters, which contain a maximum of 6, 8, and 12 methacrylic groups at the molecular chains, respectively. The dynamic viscosity, the photopolymerization behavior of the resins, and the mechanical properties of the UV-cured films obtained from the dendritic methacrylated polyesters (DMAPE) have been compared with the linear epoxy (meth)acrylate resins.

EXPERIMENTAL

Materials

The polyesters were prepared from 1,2,4-benzenetricarboxylic anhydride (BTCA) as the polycarboxylic acid and pentaerythritol (PETL), 1,1,1-trishydroxymethyl-propanol (THMP), and dipentaerythritol (DPETL) as the polyols (supplied by Aldrich Chemicals, Germany). Glycidyl methacrylate (GMA; supplied by Luoyang Chemical, China) was used for modifying the polyesters with hydroxylic groups. 1,6-Hexanediol diacrylate (HDDA; supplied by Sartomer, Exton, PA) and α,α-dimethyl-(-phenyl acetophenone (I-651; supplied by Ciba-Geigy, Switzerland) were used as a comonomer and a photoinitiator, respectively. Epoxy (meth)acrylates E44-A, E44-MA, E20-A, and E20-MA were prepared from modifying bisphenol A epoxy resin E44 ($M_n \sim 500$) and E20 ($M_n \sim 1200$) with acrylic acid and methacrylic acid in our lab. The bisphenol A epoxy resins and all other chemicals for synthesis were purchased from the Third Reagent Company (Shanghai, China).

Irradiation

The resins without or with addition of comonomer HDDA in the presence of 2 wt % I-651 as a photoinitiator were used to cast the films of 0.1 mm thickness on glass plates as supports. The samples were then UV-irradiated with a high-pressure mercury lamp (1 kW, HPM-15; Philips, Holland), at a distance of 10 cm from lamp to specimen for different times at room temperature and under nitrogen atmosphere.

Measurements

Measurements of molecular weight distribution were performed on a Waters 244 GPC system. A Waters Model R401 differential refractometer was used as a detector and a Waters Model 730 microprocessor collected and automatically recorded the detection response. The columns used were μ-Styragel of pore sizes 500, 10^3, 10^4, and 10^5 Å with polystyrene standards for calibration and THF as the solvent. The flow rate was kept at 1.0 mL/min at 25°C.

The viscosities of the obtained DMAPE and epoxy (meth)acrylate resins were detected with a QNX Model spinning viscometer with the speed of 750 rpm.

The tack-free time was evaluated as the exposure time required to obtain a completely tack-free state by touching the surface after UV exposure under a nitrogen atmosphere with a cotton ball under a weight of 200 g for 30 s.

The pendulum hardness of the UV-cured films was determined using a QBY pendulum apparatus made by Tianjin Instrument Company. The films were prepared on glass plates (120 × 90 × 5 mm) by a coater with a 100-μm gap.

The tensile tests were performed on a Shimadzu Autograph Universal Tester with a jaw separation of 40 mm at an extending rate of 1 mm/min to failure. The final data were obtained after averaging the results from the five samples.

Synthesis

The DMAPEs were synthesized by a revised procedure based on the process published by authors, which was divided into three steps.[7] For comparisons a series of DMAPEs was prepared with the core molecule THMP, PETL, or DPETL, respectively. The reaction route for the synthesis of DMAPE with PETL as a core molecule is given in Figure 1. A stoichiometry of 1 : 1.05 was used instead of a 20–50 mol % excess of polycarboxylic anhydride to hydroxyl groups of core molecule; 1,4-dioxane was also used as a solvent in this study instead of DMF of the previous procedure in
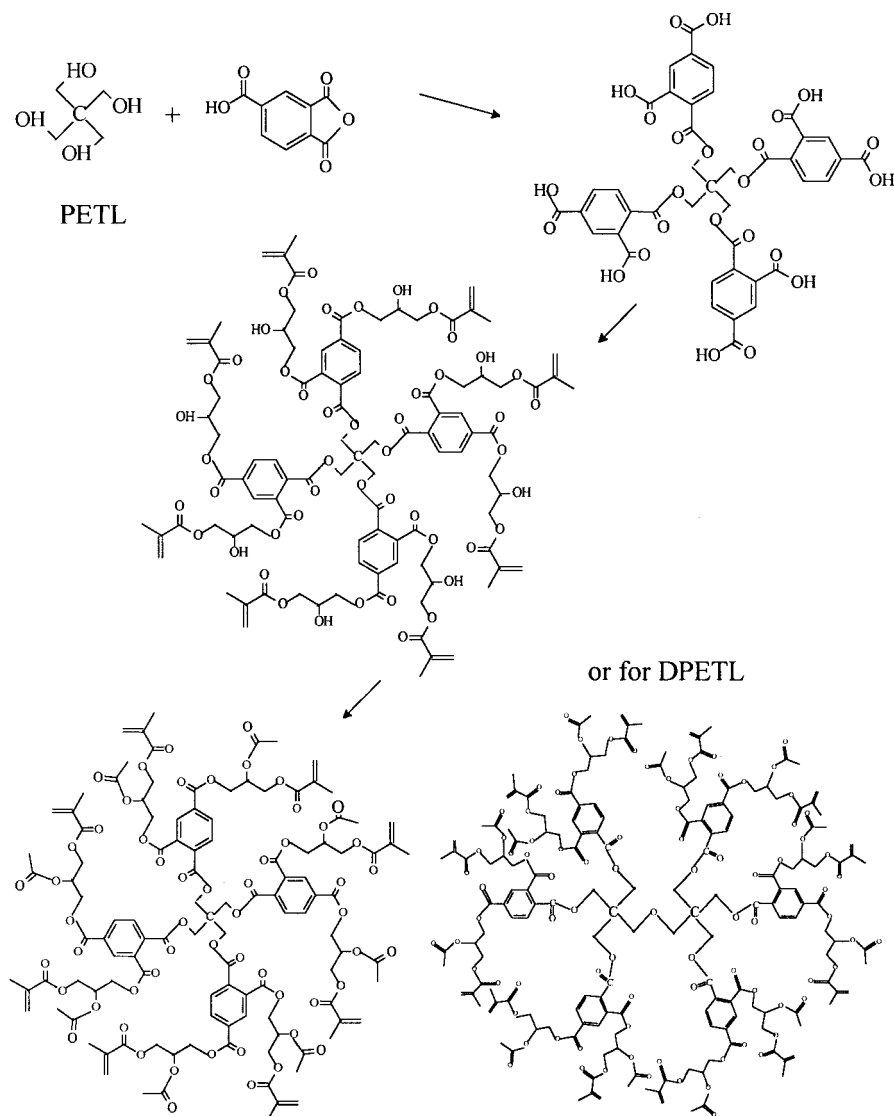
Figure 1 Reaction scheme for the synthesis of dendritic methacrylated polyester based on PETL as a core molecule.

the modification step by glycidyl methacrylate for easier distillation.

The (meth)acrylated epoxies were prepared by the reaction of acrylic acid or methacrylic acid with the epoxy resin E20 and E44 at the presence of *N,N*-dimethylbenzylamine (DMBA) (2.5 wt %) as a catalyst and MeHQ (1000 ppm) as an inhibitor in melt at 100°C under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Molecular Mass Distribution

Dendritic molecules exhibit the relationship between molecular mass and hydrodynamic radius (R_h) different from those of their linear counterparts of the same molecular mass. As R_h for a spherelike polymer is smaller than that for its linear counterpart of the same molar mass, it is expected that molecular mass determined by GPC calibrated with linear polystyrene will be lower. Figure 2 gives the GPC chromatograph for the three DMAPEs synthesized in this study, where linear polystyrene was used for the columns. As expected, the molecular weights determined experimentally were smaller than the theoretical molecular weights, which are listed in Table I.

The GPC analysis of the DMAPEs gives insight into the influence of the different core moiety on the molecular weight distribution. As shown in Figure 2, the elution curve of THMP-cored
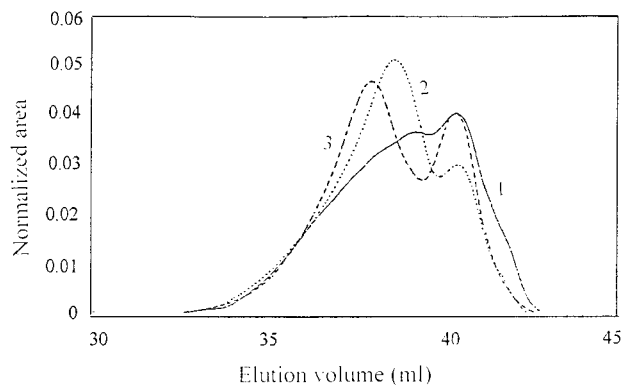
Figure 2 Polydispersity of dendritic methacrylated polyesters by GPC analysis. Curve 1, THMP; Curve 2, PETL; Curve 3, DPETL as a core, respectively.

DMAPE is likely monopeaked around the elution volume of 40.5 mL and other two samples have two peaks relating to the elution volumes of 34.5 mL, 40.5 mL, and 37.8 mL, 40.5 mL, respectively. It implies that THMP-cored DMAPE has one main product and the others have two. The wide and bimodal molecular weight distribution is related to irregularities in the synthesis, which is very similar to the result reported in the previous investigation.[8] The main components have the molecular structures shown in Figure 1. The components with low molecular weight are interpreted as resulting from the intramolecular cyclization of COOH and OH groups, whereas the high molecular weight tail is the result of secondary reactions of COOH groups in one polyester molecule with OH groups in another molecule, that is, an initial crosslinking.[8]

Rheological Behavior

Viscosity of an oligomer is an important parameter in UV-curing technology, which affects the curing process and the properties of the cured film. The viscosity of dendritic polymers at the molten state is markedly lower than that for their

Table I Molecular Mass Distribution of the Dendritic Methacrylated Polyesters with Different Core Molecules

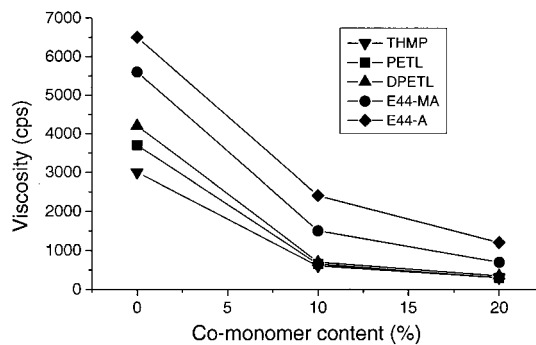| Core Molecule	M_T	M_w	M_n	$P\ (M_w/M_n)$
THMP	1750	910	450	2.02
PETL	2230	1030	510	2.03
DPETL	3410	1010	490	2.08

Figure 3 Viscosity comparison of dendritic methacrylated polyesters with traditional epoxy (meth)acrylate.

linear analogs as a result of their highly branched structures.[7] For easy comparison the viscosity was detected at a raised temperature of 50°C. As shown in the Figure 3, the viscosities of DMAPE samples with the core molecules THMP, PETL, and DPETL are only about one-half to one-third of that for E44-modified epoxy (meth)acrylates E44-MA and E44-A ($M_n \sim 700$) without addition of HDDA. The viscosity of DMAPEs sharply decreases with addition of the comonomer HDDA. The viscosity of DMAPEs with 10% HDDA is only about one-sixth to one-fifth of those without HDDA added, whereas the viscosity of epoxy (meth)acrylates E44-MA and E44-A with the same amount of HDDA added is about one-third to one-half of those without HDDA added. Moreover, the addition of 20% HDDA into the DMAPEs results in approximately equal viscosity.

The viscosity of an oligomer is related to the dynamic extension and the segment density within the volume of a molecule, and intermolecular chain entanglement. The melting viscosity for a linear polymer increases rapidly with molar mass because of the development of chain entanglements with increasing chain length. Because of the highly branched spherelike structure of DMAPE, there will be little entanglement between molecular chains, thus resulting in a rather lower viscosity. Easy control of the viscosity and leveling time, and processability of a formulation are the main intriguing properties for its application in radiation-curing coating systems.

Photopolymerization Rate

The DMAPEs without and with HDDA added as a comonomer are all rapidly crosslinked by a free-

Table II Tack-Free Time (s) Comparison of the Dendritic Methacrylated Polyesters with the Traditional (Meth)acrylated Epoxies under UV Irradiation

Oligomer	Monomer Content (wt %)		
	0	15	30
THMP	<1	<1.5	<1.5
PETL	<1	<1.5	<1.5
DPETL	<1	<1.5	<1.5
E44-MA	6	7	9
E20-MA	—	6	7
E44-A	5	6	8
E20-A	—	5	7

Figure 4 Pendulum hardness comparison of dendritic methacrylated polyesters with traditional epoxy (meth)acrylate.

radical polymerization mechanism in the presence of the effective photoinitiator I-651 (2 wt %). The tack-free times for DMAPE and E44-MA/A, E-20-MA/A resins under the irradiation of a high-pressure mercury lamp are given in Table II. It can be seen that the cure speed for the DMAPE resins without HDDA addition is about five- to sixfold higher than that for linear epoxy (meth)acrylate resin E44-MA/A and E20-MA/A. It can be interpreted as resulting from their polyfunctionality and accessibility of the reactive groups presented on the surface of the DMAPE molecule. With addition of HDDA, the tack-free time increases with the amount of the HDDA for the epoxy (meth)acrylate resins, although not obvious with the DMAPE resins with the core molecules THMP, PETL, and DPETL. It can be interpreted that the comonomer molecules added to the resin surround the DMAPE molecules and largely react with the methacrylic double bonds on the spherical surface and form crosslinks between neighboring DMAPE molecules, which is very favorable to forming films and also homopolymerization.

Mechanical Properties

The pendulum hardness increases rapidly at exposure times up to about 10 s and then levels off at about 20-s exposure for DMAPEs. However, for E44-MA and E20-MA resins, the pendulum hardness increases sharply at exposure times up to about 10 s, and then a slight increase of hardness can be observed for the cured films up to 30-s exposure. Moreover, the pendulum hardness increases with the functionality of DMAPE as a result of increasing crosslinking density (see Fig. 4).
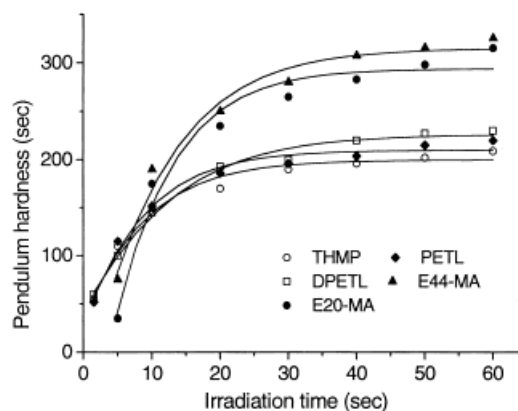
The addition of comonomer HDDA affects the pendulum hardness and curing rate of the DMAPE resins. The pendulum hardness of the UV-cured DMAPE resin films containing different HDDA content is shown in Figure 5. The pendulum hardness of the PETL-cored DMAPE with 30 wt % HDDA comonomer is the highest when compared with 15 wt % and without HDDA addition. It is well known that the hardness is related to the crosslinked network density and the conversion of the double bonds at the molecular chains. As the polyfunctional DMAPE resins cure to a nontacky solid state very quickly under UV irradiation, chain propagation stops before the reaction is completed because of the dense network formed, thus resulting in restriction in mobility of the reactive sites in the cured materials. In the cured DMAPE films without HDDA
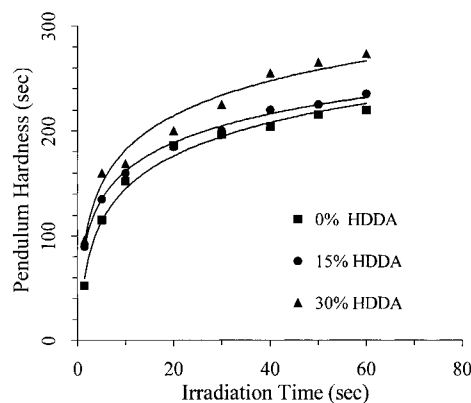

Figure 5 Pendulum hardness of dendritic methacrylated polyesters based on PETL as a core with different HDDA content.
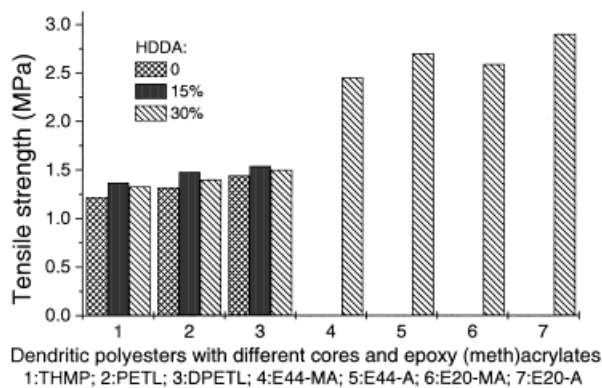
Figure 6 Tensile strength of dendritic methacrylated polyesters based on different cores without and with HDDA addition.

added, a certain amount of methacrylic double bonds may remain unreacted and buried in the crosslinked network as a result of reduced mobility. The added HDDA not only acts as a diluent for reducing the viscosity but also assists in forming the crosslinking network by copolymerization with methacrylic groups of DMAPE.

The architecture of dendritic polymers implies that crystallization is not likely to occur and no interchain entangling has been observed. This gives rise to poor mechanical properties.[6] Figure 6 shows the tensile strength of the cured films obtained from two types of seven oligomer resins without and with HDDA added. It was found that the tensile strength of the epoxy (meth)acrylates is higher than that of DMAPEs in all cases. Moreover, the tensile strength of the cured PFMAP films increases at first but then slightly decreases with the comonomer HDDA addition. It may be assumed that the crosslinking structure is changed by the comonomer addition.

CONCLUSIONS

Spherelike DMAPEs synthesized by divergent growth in this study have wide and bimodal mo-lecular weight distribution. The dynamic viscosity of the polyesters decreases rapidly with a small amount of comonomer addition. Moreover, high cure speed for the DMAPE resins can be observed compared with that for traditional UV-curable linear epoxy (meth)acrylates. However, the tensile strength of the cured DMAPE films increases with not only the functionality of the polyester but also a small quantity of comonomer addition.

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