Photopolymerizable Polyfunctional Methacrylated Polyesters

Hong Huang, Jiongzheng Zhang, Wenfang Shi

Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Three kinds of photopolymerizable polyfunctional polyesters were synthesized by polyesterification of polycarboxylic acid anhydride and polyols, modified with glycidyl methacrylate and then esterified by acetic anhydride. The modified dendritic polyesters contain a maximum of 6, 8 and 12 methacryl groups with approximately 2 of polydispersity, respectively. The dynamic viscosity measured using a spinning viscometer was compared with conventional linear epoxy (meth)acrylate oligomers with lower molecular weight, and it was shown that the viscosity of polyfunctional methacrylated polyesters is only half of that for the linear oligomers but the UV cure speed is about five times of that for the latter.

Keywords: photopolymerization, dendritic polyester, UV curing

1. Introduction

Radiation curing has found a growing number of applications in recent years due to the unique characteristics of this advanced technology, mainly its great speed, selective cure conservation of energy, solvent free VOC minimization and high quality products.[1,2]

The principle components of a radiation curable resin are oligomer and comonomer. The viscosity of the formulation should be low enough for easy spraying, dipping and rolling. The monomers used to lower the formulation viscosity play a key role, for it acts on both the cure speed and on the extent of polymerization, as well as on the final properties of the cured materials. The oligomers constitute the backbone of the cured three-dimensional polymer network. Important oligomers used for coating are acrylated epoxies, acrylated polyurethane, acrylated polyesters, and unsaturated polyesters which give desired properties of the final cured films.[3]

Rapid cure speed and low viscosity in an oligomer is a difficult combination to achieve by a conventional technique.[4] Comonomers are used as diluents to reduce the formulation viscosity, and also to affect the final properties. Thus formulators always balance viscosity, cure speed and final properties for a given UV formulation. The low

viscosity and high cure speed systems have been studied to meet this demand.

New dendritic photopolymerizable polyfunctional polyesters have provided a significant method in this regard. A dendritic polymer is a new kind of macromolecule. Due to their highly branched architecture they exhibit properties different from those of their linear counterparts.[5] Low melt viscosity, no inter-chain entangling and good solubility are some of their most intriguing properties. In this work, we synthesized a series of hyperbranched polyfunctional methacrylated polyesters with a maximum of 6, 8 and 12 double bonds on the surface of the molecules. The rheological properties of the resins, and their photo-polymerization behaviour were investigated.

2. Experimental

2.1. Materials

The polyesters were prepared from 1,2,4-benzenetricarboxylic anhydride (BTCA) as the polycarboxylic acid and pentaerythritol (PETL), 1,1,1-tris-hydroxymethyl-propanol (THMP), dipentaerythritol (DPETL) as the polyols. All the above chemicals were supplied by Aldrich, Germany. Glycidyl methacrylate (GMA), supplied by Luoyang Chemical Co., China, was used for modifying the polyesters. Acetic anhydride (AA) was

used to esterify the hydroxyl group formed by the reaction of epoxy with the carboxylic groups. 1,6-Hexanediol diacrylate (HDDA), supplied by Sartomer Co., USA, was used as a reactive diluent for UV curing formulation. 4-Methoxyphenol (MeHQ) was used as an inhibitor. Dimethylformamide (DMF) and 1,4-Dioxane were used as solvents. The α,α -dimethyl- α -phenyl acetophenone (I-651) supplied by Ciba Geigy Co., Switzerland was used as a photoinitiator for curing the polyfunctional methacrylated polyesters. Epoxy (meth)acrylates E44-A, E44-MA, E20-A and E20-MA were prepared from bisphenol A epoxy resins E44 (Mn=500) and E20 (Mn=1200) modified by acrylic acid and methacrylic acid, respectively.

All the solvents and reagents were obtained commercially and used without further purification.

2.2. General Directions

Infrared spectra (IR) of thin films were recorded on a Bruker Infrared Spectrometer using sodium chloride plates.

Thermogravimetric analysis (TGA) was performed on a Shimaduz TG-500, using a heating rate of 10 k/min in nitrogen.

Gel permeation chromatography (GPC) was performed on a Waters 244 GPC-LC Chromatograph, with connected 500, 10^3 , 10^4 , and 10^5 Å μ -styragel columns in series and a Waters Model R401 differential refractometer as a detector. The flow rate was kept at 1.0 ml/min and THF as an eluent at 25°C. THF was purified by a standard method for chromatography. The detection response was collected and recorded automatically by the Waters Model 730 microprocessor.

Viscosity of the final products was detected at 50°C by a spinning viscometer.

2.3. Synthesis

A three-necked glass reactor (250 ml) and a mechanical stirrer were used in synthesis procedure. The vessel was equipped with a stirring rod, a N₂ inlet and a reflux condenser with drying tube. A N₂ flow was used to remove O₂ to prevent oxidation. Temperature was controlled with a contact thermosensor and thermalsat equipped oil bath.

The polyfunctional methacrylated polyesters (PFMP) were synthesized after a revised procedure patented by B. Rånby and W. F. Shi which was divided into three steps.[6] During the first step, polycarboxylic anhydride BTCA was dissolved in DMF with a nitrogen protection. Then polyol THMP, PETL or DPETL was added as the

core molecule into the above solution. The DMF was distilled under reduced pressure at about 5 mmHg after 5 hours reaction. The obtained products were the so-called sphere-like polyol-esters. During the second step, the product from the first step was dissolved in 1,4-dioxane and warmed up to 100°C under a constant stream of nitrogen. Then glycidyl methacrylate with MeHQ(1000ppm) as an inhibitor and N,N-dimethylbenzylamine (DMBA) (2.5wt%) as a catalyst was added dropwise. The temperature was kept at 100°C for 2 hours and then at 70°C until the acid number lower than 3 mg KOH/g polyester was reached. Finally solvent 1,4-dioxane was removed at 75°C under vacuum. The obtained product was a yellow and transparent viscous liquid which was stored at room temperature until used.

A stoichiometry of 1:1.05 for hydroxyl groups of the core polyols to anhydride and carboxylic group to glycidyl group was used in this study.

Epoxy (meth)acrylates were synthesized by the following process: the acrylic acid or methacrylic acid with 2.5wt% DMBA and 1000ppm MeHQ was added into the epoxy resin E20 and E44 in melt stirred by a mechanical stirrer under nitrogen atmosphere. The reaction was carried out until the acid number reached zero.

2.4. UV Curing

PFMPs and epoxy (meth)acrylates were mixed with comonomer HDDA and 2wt.% of a photoinitiator (I-651) at 50°C. The resin with or without 15wt.%, 30wt.% of HDDA were prepared and used to cast films of 0.1 mm thickness on glass plate as a support,

Samples were exposed to a high pressure mercury Philip HPM15 lamp with a power output of 1000W. Irradiation was carried out with various times at room temperature and in a nitrogen atmosphere.

2.5. Tack-free Time

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

3. Results and Discussion

3.1. Esterification Process

The polyolesters obtained from the first reaction step were synthesized by the SnCl₂ catalyzed esterification of polycarboxylic acid anhydride and polyol. The esterification was carried out in DMF

as the solvent under N_2 for protection from oxygen. In order to increase the probability of reaction of the acid anhydride groups with the hydroxyl groups, an excess of the anhydride and medium temperature are necessary. After five hours esterification at $75^\circ C$ the acid number was determined by titration. During the second step, the carboxylic groups reacted with glycidyl groups of GMA and thus formed the ester bonds and hydroxyl groups. The above product obtained is photocrosslinkable but the viscosity and the compatibility with multifunctional comonomers are not preferable for UV curing due to the dense hydroxyl groups.[7] Therefore esterification of the hydroxyl group with acetic anhydride is needed.

The idealized formula of the PFMP with different core moieties are shown in Fig. 1. The maximum functionality increases in the turn THMP, PETL, DPETL as shown.

solved well in 1,4-dioxane. Therefore 1,4-Dioxane was used as a solvent in the second and the third steps.

3.2. Molar Mass

The architecture of dendritic substances involves some characterization problems, mainly because many methods are based on calibration with linear polymer standards of known molar mass as polydispersity index.[8] Dendritic molecules exhibit the relationship between molar mass and hydrodynamic radius (R_h) different from those of their linear counterparts of the same molar mass. As R_h is smaller for a sphere-like polymer than for its linear counterpart of the same molar mass, it is expected that molar mass determined with GPC, calibrated with linear polystyrene, will be lower. Since no adequate GPC standards are available, linear styrene was still used as the standard. As

Fig. 1 The idealized formula of the sphere-like multifunctional polyesters with (1) THMP; (2) PETL; (3) DPETL as a core moiety.

In order to imitate an industrial batch, the process without purification or washing of the products was done and 5% excess of BTCA was chosen. The first step was performed at a relatively low esterification temperature, with the range of $70\sim 80^\circ C$ chosen to suppress unwanted side reaction and trans-esterification.

The complete removal of solvents from the final products with dense chain structure always takes a long time. The crosslinking reaction may take place during distillation. So the solvent with lower boiling point, and good solubility is preferable. DMF is a good solvent except for its high boiling point (above $150^\circ C$). 1,4-Dioxane with a boiling point of $100^\circ C$ has been found to be a suitable solvent. Products obtained from all steps dis-

expected the molecular weights determined were smaller than the theoretical molecular weights. Fig. 2 gives the GPC chromatograph for the three PFMPs synthesized in this study. A summary of the molecular characteristics of PFMPs is listed in table 1.

The incomplete reaction between BTCA and polyols is the main factor contributing to the wide molecular distribution. The esterification of polyols with BTCA is the key stage that affects the following reactions and polydispersity of the final products. The GPC analysis of the PFMPs gives insight into the influence of the different core moiety on the molecular weight distribution. The microvolume occupied by the surface groups accumulates with the functionality of the PFMP. Thus

the surface stoichiometry leads to more branch defects and wide weight distribution. As can be seen from Fig. 2, the elution curve of THMP-cored PFMP is mono-peaked around the elution volume of 40.5 ml and two other samples have bi-peaks relating to the elution volumes of 34.5ml, 40.5ml and 37.8ml, 40.5ml, respectively. It implies that THMP cored PFMP has one main product and the others have two. The polyester relating to the elution volume of 40.5 ml can be interpreted as the 3-BTCA-branched product.

tive -OH group of the core polyols. At the sterical point THMP is easily completely esterified by BTCA. It is difficult to completely esterify PETL, which can be seen from the bi-peaked curve 2 of GPC. It is implied that the sterical effect limits the conversion of a 3-BTCA-branched polyester to a 4-BTCA-branched one. But the main product is still 4-BTCA-branched molecules. As to DPETL as a core the complete esterification is rather difficult as the surface congestion develops with an increasing esterification extent. The full-filled

Fig. 2 Molecular weight distribution of PFMPs with different core moiety by GPC: THMP, PETL and DPETL refer to the core moieties.

Table 1 The molecular weight and polydispersity of the PFMPs with different core moieties.

Core	M_T	Mw	Mn	P (Mw/Mn)
THMP	1700	912	450	2.02
PETL	2200	1028	506	2.03
DPETL	3400	1013	487	2.08

M_T is the theoretical molecular weight of the ideal formula.

It is well known that the microvolume occupied by surface BTCA cells accumulates with the conversion of the hydroxyl group when THMP, PETL or DPETL with 3, 4, and 6 hydroxyl groups in their molecules reacts with BTCA respectively. Sterically induced stoichiometry is manifested whenever the summation of surface group volume and incoming reagent BTCA volume approaches the available exterior volume surrounding the reac-

space leads to inaccessible buried hydroxyl groups. Thus the molar mass distributes as the bi-peaked shape. The molecule related to the peak at elution volume of 37.8ml may be 5 or 6-BTCA-branched polyfunctional polyesters.

Considering the intricacies involved with the PFMPs synthesis, we can conceive of a variety of other defects that would lead to a divergence from ideality and broaden the molecular weight distribution. Generally, these are of 2 types: those involving intra-molecular events such as intra-molecular cyclization and those leading to intermolecular bridging or looping[9]. These all lead to more polydispersed systems.

3.3. Thermal Property

The product obtained from the first step is a white solid powder but the products obtained from the second and third steps are viscous liquids under room temperature. The melting point is

strongly affected by the polarity of the terminal groups[10,11]. The thermogravimetric analysis (TGA) was performed to investigate the thermal-stability and volatile content of the final product. The result of TGA analysis of PETL-cored PFMP is shown in Fig. 3. Upon heating, PFMP gradually lost 1% of its weight up to the very onset temperature of 120°C, probably due to the volatility of solvents. Then PFMP quickly experienced thermal decomposition by another 0.2% weight loss up to 160°C, probably due to the decomposition of the acetic ester bonds.

Fig. 3 Thermogravimetric analysis of PETL-cored PFMP.

3.4. Viscosity

The viscosity in melt is markedly lower for sphere-like polymers than that for their linear analogues due to their highly branched structures.[6] The PFMPs are viscous liquids under room temperature while the epoxy (meth)acrylates are still in the solid state. For easy comparison the viscosity was detected at a raised temperature of 50°C. As shown in the Fig. 6, the viscosity of PFMP is much lower than epoxy (meth)acrylates without HDDA as a diluent. When diluted with HDDA, the viscosity of PFMPs reduces sharply. The viscosity of PFMPs with added 10% HDDA is only 1/6 of those without HDDA added while the viscosity of epoxy acrylates E44-A and E44-MA with the same amount of HDDA added is about 1/3~1/2 of those without HDDA added. The viscosity of an oligomer is related to the dynamic extension of the molecules 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. Due to the highly branched sphere-like structure of PFMP, there will

be little entanglement between molecular chains, thus resulting in a rather lower viscosity. This is promising for its applications in radiation curing formulations for easily controlling leveling time and processability.

3.5. UV Curing

The cure rate of the resin system is of great importance as time and energy consuming con-

Fig. 4 Viscosity of the sphere-like PFMPs and epoxy-(meth)acrylates with similar molecular weight.

cerns in applications. The PFMPs with and without HDDA as a comonomer are all rapidly crosslinked by a free radical polymerization mechanism in the presence of the effective photoinitiator I-651 (2wt.%) due to their polyfunctionality. The tack-free times for PFMP resins were measured using a high-pressure mercury lamp (1kW) (table 2). As seen from the table 2, the cure speed for the PFMP resins without HDDA addition is 5~6 times higher than that for linear epoxy (meth)acrylate resins. And with HDDA addition, the cure speed for the former is 4~5 times higher than the latter. Adding a great amount (30wt.%) of HDDA to the PFMP system had little effect on the tack-free time.

Table 2. Tack-free time for PFMP resins

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

4. Conclusions

Sphere-like polyfunctional methacrylated

polyesters have been synthesized by divergent growth beginning at the center in this study. The resulting polymers were polydispersed. The choice of the polyol core is of great importance. In order to obtain a high degree of conversion of the hydroxyl group on the core, changing the reaction temperature and time, and adding suitable catalysts are necessary. For easy industrial application, 5% excess of BTCA was chosen, and no purification was done but the solvent of DMF was replaced with 1,4-Dioxane for easy distillation from the final products. These sphere-like polyfunctional methacrylated polyesters synthesized in this study have low viscosity but high cure speed compared to traditional UV-curable linear oligomers of similar molecular weight. The PFMP in resin applications needs only a small amount of polyfunctional comonomers or none at all. The PFMP may take the place of conventional oligomers used in coating, adhesive, and ink formulations.

Acknowledgment

The research work is supported by a grant from the Natural Science Foundation of China,

which is gratefully acknowledged.

Reference

1. C. Decker, *J. Coating Technol.*, **59** (1987) 97.
2. J. Suurland, *RadTech Europe'95 - Conference Proceedings*, (1995) p281.
3. G. E. Green and B. P. Stark, *J. Macro. Sci. vs Macro. Chem.*, **C21(2)** (1987) 187.
4. R. R. Kemmer, *RadTech Europe'95- Conference Proceedings*, (1995) p306.
5. D. A. Tomalia, A. M. Mayler and W. A. Goddard, *Angew. Chem. Int. Ed. Engl.*, **29** (1990) 138.
6. W. F. Shi and B. Rånby, Patent WO96/07 688.
7. W. F. Shi and B. Rånby, *J. Appl. Polym.*, **59(12)** (1995) 1945.
8. W. F. Shi and B. Rånby, *J. Photopolym. Sci. Tech.*, **4** (1996) 173.
9. G. R. Newcome, J. K. Young and J. K. Baucker, *Macromolecules*, **26** (1993) 2394.
10. Y. H. Kim and R. Beckerbauer, *Macromolecules*, **27** (1994) 1968.
11. C. J. Hawker, P. J. Farrington and J. F. J. Fréchet, *J. Am. Chem. Soc.*, **117** (1995) 4409.