A Novel Dendritic Acrylate Oligomer: Synthesis and UV Curable Properties

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ABSTRACT: An dendritic acrylate oligomer with eight double bonds (DAO) was synthesized by Michael addition reaction of ethylene diamine (EDA) and trimethylolpropane triacrylate (TMPTA) under mild conditions, and was easily separated from the reaction system with methanol. The structure of DAO was characterized by IR, ^{1}H-NMR, and elemental analysis. DAO is UV curable oligomer with low viscosity and high curing speed. Its viscosity was 10.85% of that of the linear acrylic oligomers with similar molecule weight (EBECRYL Resin 285). With Darocure 1173 as the photoinitiator, the curing speed of DAO was respectively 7.5 and 10.3 times higher than that of EBECRYL Resin 605 and EBECRYL Resin 285. Furthermore, the effect of the photoinitiator and active diluent on curing speed of DAO UV curing system was studied. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1018–1022, 2004

INTRODUCTION

Because of their advanced characteristics, such as fast curing speed, conservation of energy, high efficiency, and less pollution, UV-curable resins are widely used for paints, coating, adhesives, and inks.[1–3] In the course of use, low viscosity and high curing speed are two important properties pursued for UV-curable oligomers. Acrylate oligomers are one of the most important UV-curable resins. However, traditional acrylate oligomers are commonly linear molecules containing two double bonds; their viscosity is usually higher, which causes difficulties in use so that reactive diluents must be used.[4,5]

Dendrimers have received great attention during recent years. They can be prepared with high regularity and controlled molecular weights, and a large number of functional terminal groups. The oligomers have unique shape and intrinsic properties such as high solubility, low viscosity, and high reactivity due to many available functional end groups on the periphery, leading to their potential applications in extensive fields like micelles, self-assemblies, liquid crystals, electroactive, or photoactive molecular devices, sensors, catalysts, biochemicals, pharmchemicals, and UV-curable systems.[6–8] However, synthesizing dendrimers is a hard work. In the divergent approach, excessive functional groups usually need to be protected in every step reaction, then deprotected before the next step reaction to get low polydispersities. Furthermore, divergent growth dendrimers are virtually impossible to purify as they have very similar structure to their byproducts.[9]

In this work, dendritic acrylate oligomers (DAO) with eight double bonds on the periphery have been prepared by Michael addition with ethylenediamine (EDA) and trimethylolpropane triacrylate (TMPTA) under mild conditions. EDA and TMPTA with four and three reactive groups respectively react directly without protection-deprotection; moreover, DAO can be easily separated from the reaction system with methanol. These two aspects facilitate the preparation and make obtaining a great quantity of DAO possible. DAO, in presence of a photoiniator, can be quickly cured under UV irradiation, and the effects of some factors on curing speed of DAO UV curing system have been studied.

EXPERIMENTAL

Materials

Ethylenediamine (EDA) and methanol were supplied by the Third Reagent Company of Shanghai (China), and purified by distillation before used. Trimethylolpropane triacrylate (TMPTA), tripropylene glycol diacrylate (TPGDA), bisphenol A epoxy diacrylate (EBECRYL Resin 600), 75% EBECRYL Resin 600 added 25%TPGDA (EBECRYL Resin 605), aromatic urethane diacrylate (EBECRYL Resin 210), aliphatic urethane diacrylate (EBECRYL Resin 270), 75% EBECRYL Resin 270 added 25%TPGDA (EBECRYL Resin 285) were products of UCB Chemicals. Company (Belgium). 1-Chloro-2-hydroxy-2-methyl-1-propanone (Darocur

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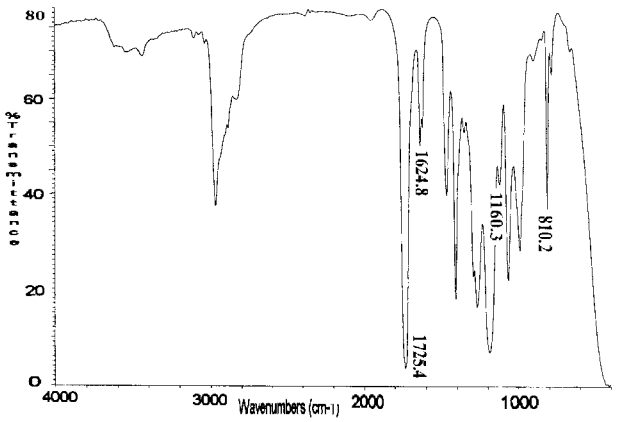

Figure 1 IR spectra of DAO.

1173), 1-chloro-4-propyloxy-thiosantone (CPT) and 2-benzyl-2-dimethylamino-1-(4-malinophenyl)-butanone (Irgacure 369) were purchased from Ciba Geigy (Switzerland).

Synthesis

Methanol (15 mL), trimethylolpropane triacrylate (TMPTA) (29.6 g, 0.1 mol), and ethylenediamine (EDA) (1.2 g, 0.02 mol) were added in turn into a three-necked flask equipped with a mechanical stirrer, a themometer, and a condenser. The mixture was kept at 30°C for 6 h with stirring and poured into 150 g of stirred methanol. After some time the lower phase was separated and washed twice with 200 g methanol again, dried in vacuum at 30°C to yield a colorless, transparent, viscous liquid product (DAO). Its IR spectrum, as shown in Figure 1, could be analyzed as follows: 1725.4 cm^{-1}, carbonyl of ester; 1624.8 cm^{-1} and 810.2 cm^{-1}, C═C; 1160.3 cm^{-1}, C—N. Figure 2 is the ^{1}H-NMR spectrum of DAO, from which all expected signals appeared as follows: 6.38, 6.12, 5.88 ppm (CH_2═CH—); 4.14 ppm (CH_2═CH—COO—CH_2—); 3.49 ppm (—COO—CH_2—); 2.76 ppm (—CH_2—COO—); 2.45 ppm (—CH_2—N—); 1.65 ppm (—CH_2—); 0.91 ppm (—CH_3). Results of element analysis were 59.80% (C), 7.08% (H), 2.95% (N), which is consistent with the theoretical value 59.80% (C), 7.07% (H), 2.25% (N).

Measurements

Infrared (IR) spectra were carried out with a Magna-550 Fourier-transform infrared spectrometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on an INOVA 400 MHz using $CDCl_3$ as a solvent. Elemental analysis was carried out with a Shimadzu EA-1110 CHNSO. High-pressure liquid chromatography (HPLC) was performed on a Shimadzu LC-6A using C_{18} column (4 × 250 mm) and mixture of CH_3CN and H_2O (volume ratio 4 : 1) as an eluent at 0.7 mL/min. Viscosity was measured by a NDJ-1 Rotation viscometer.

UV curing

A mixture of DAO, Darocur 1173 (or CPT or Irgacure 369, mass percent was 1.42–5.68%), and TPGDA (or TMPTA, mass percent was 0–30%) was smeared on a NaCl prism to form a thin film. Then the sample was exposed to a UV lamp (80 W, made by Shanghai Yaming Bulb Factory, China) for a certain time.

RESULTS AND DISCUSSION

Preparation of dendritic acrylate oligomer

Dendritic acrylate oligomers with eight double bonds on the periphery (DAO) were prepared according to Figure 3.

The mol ratio of TMPTA and EDA, the amount of methanol, the reaction temperature, and reaction time all have great influence on the product, as shown in Table I.

The mol ratio of TMPTA and EDA

From the chemical reaction equation, the theoretical mol ratio of TMPTA and EDA is 4.0 : 1.0. However, it can be seen from Table I that the reaction system gels if the mol ratio of TMPTA and EDA is below 5.0 : 1.0. Moreover, from 5.0 : 1.0 to 4.0 : 1.0, the smaller the mol ratio, the shorter the sustainable reaction time. This is because TMPTA and EDA are both monomers with multifunctional groups. But when TMPTA was in large excess the product could not be separated from the system with CH_3OH. Therefore, the suitable mol ratio of TMPTA and EDA is 5.0 : 1.0.

Amount of methanol

Comparing run 9 to 12 in Table I, we find that the reaction system may gel when the methanol content is

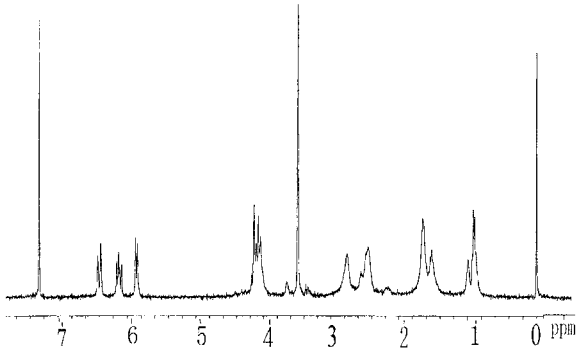

Figure 2 ^{1}H-NMR spectra of DAO.

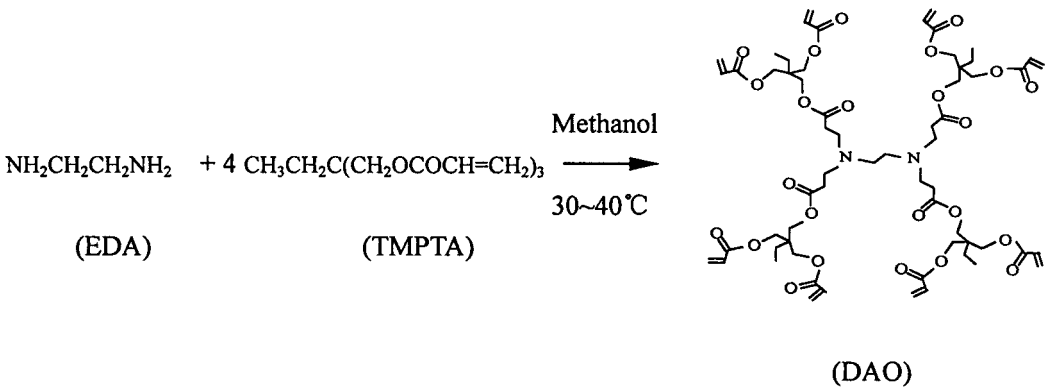

Figure 3 Reaction scheme for the synthesis of Dendritic acrylate oligomers (DAO).

lower, for example, 11.39%. The reaction systems with less methanol have higher concentration of reactants, the contact of reactive groups becomes easy, and the reactions are accelerated. Additionally, the reaction systems with less methanol are rather viscous so that heat cannot transferred effectively; as a result, the reaction is out of control and gels. When methanol content is higher, the amount of product decreases while the mass percent of DAO in the product increases. The experiments indicate that higher methanol content can prevent gelation, but is not beneficial to the separation of product. The proper mass of methanol is 27.84% of the total reaction system.

Reaction temperature

It can be seen from Table I that at reaction temperatures from 25 to 35°C, the amount of product does not vary greatly, but the mass percent of DAO in the product changes remarkably. When the reaction temperature was 40°C, the reaction system gelled after 1.0 h, because when the reaction temperature rises, the system becomes more reactive and more prone to gelation. The experiments showed that 30°C is suitable for DAO.

Reaction time

Runs 1 to 5 in Table I indicate that when the reaction time increases, the amount of product changes very slightly, but the mass percent of DAO in the product first increases then decreases. When the reaction time was 6 h, both the amount of product and the mass percent of DAO are the highest. This can be interpreted that many kinds of reactions, for example, reactions of one EDA molecule with one, two, three, or four TMPTA molecules, and reactions of two mole-

TABLE I
Influence of Reaction Conditions on Yield and Purity of DAO

Run	*n* (TMPTA) : *n* (EDA)	w (CH_3OH),[a] %	Temperature, °C	Time, h	Product, g	w (DAO),[b] %
1	5.0 : 1.0	27.84	30	3.0	22.38	81.24
2	5.0 : 1.0	27.84	30	6.0	22.45	97.57
3	5.0 : 1.0	27.84	30	10.0	22.43	97.43
4	5.0 : 1.0	27.84	30	24.0	22.07	75.62
5	5.0 : 1.0	27.84	30	28.0	22.30	60.30
6	5.0 : 1.0	27.84	25	6.0	21.69	75.43
7	5.0 : 1.0	27.84	35	6.0	25.69	66.20
8	5.0 : 1.0	27.84	40	1.0[c]		
9	5.0 : 1.0	11.39	30	5.5[c]		
10	5.0 : 1.0	20.45	30	10.0	23.23	66.69
11	5.0 : 1.0	33.96	30	10.0	18.32	72.31
12	5.0 : 1.0	39.13	30	10.0	16.38	79.52
13	4.7 : 1.0	27.79	30	3.5[c]		
14	4.4 : 1.0	27.74	30	2.0[c]		
15	4.0 : 1.0	27.64	30	0.5[c]		

[a] Refers to mass percent of methanol in the reaction system.
[b] Refers to mass percent of DAO in the product, which is obtained from HPLC.
[c] Refers to the reaction mixture that gelled.

TABLE II
Viscosity of Different Oligomers

Oligomer name	Molecular weight	Viscosity, mPa · s
EBECRYL Resin 600	500[a]	3000(H, 60°C)[a]
EBECRYL Resin 605	450[b]	7500(H, 25°C)[a]
EBECRYL Resin 210	1500[a]	3900(H, 60°C)[a]
EBECRYL Resin 270	1500[a]	3000(H, 60°C)[a]
EBECRYL Resin 285	1200[a]	23000(H, 25°C)[a] 47000(25°C)[c]
DAO	1244[c]	5100(25°C)[c]
75%DAO added 25%TPGDA	1008[b]	2200(25°C)[c]

[a] Data come from product introduction of UCB Chemicals (Belgium). H refers to Höppler viscosity.
[b] Mean molecular weight calculated according to mass percent of two component.
[c] Dada obtained from experiments.

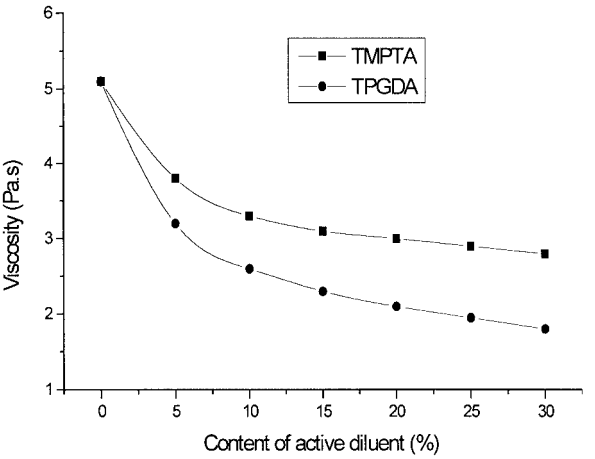

Figure 5 Viscosity of DAO systems with different active diluents (25°C).

cules of their products compete and each product has its optimum reaction time, which is 6 h for DAO.

Viscosity of DAO

Dendritic oligomers have unique rheological behavior, one of which is that the viscosity is lower than that of linear oligomers with similar molecule weight, as shown in Table II. For example, the viscosity of DAO is 10.85% of that of EBECRYL Resin 285, that is, 75%EBECRYL Resin 270 with added 25% TPGDA, while the viscosity of 75%DAO with added 25%TPGDA is only 4.68% of that of EBECRYL Resin 285.

Furthermore, the effects of temperature and active diluents on viscosity of DAO have been studied. The results are exhibited in Figures 4 and 5. From Figures 4 and 5, it can be seen that the viscosity of DAO drops evenly when temperature and amount of active diluents rises. This phenomenon is decided by the dendritic structure of DAO and different from that of linear oligomers.

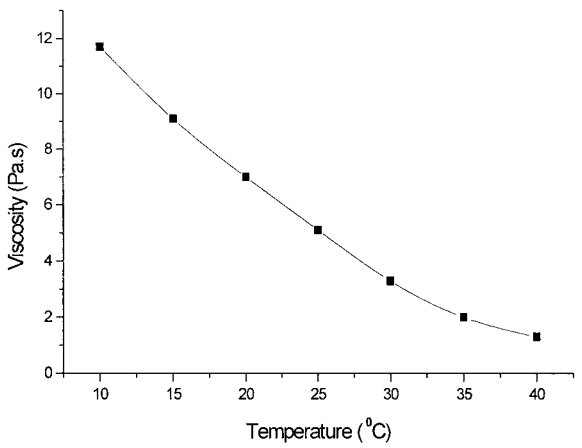

Figure 4 Viscosity of DAO at different temperatures.

UV curable properties

Curing speed

In the presence of photoinitiator and exposed to the UV lamp, the dendritic acrylate oligomer (DAO) can be both rapidly cured without or with reactive diluent. To compare curing speed of different oligomers, the samples were exposed to the UV lamp (80 W) until the cured film become dry to the touch. The results are shown in Table III.

From Table III, it can be seen that time for dry to the touch of the systems with DAO is remarkably less than that of the systems with EBECRYL Resin 600 and EBECRYL Resin 270, no matter if they are with or without active diluent TPGDA. The curing speed of the DAO system is, respectively, 7.5 and 10.3 times higher than that of the EBECRYL Resin 600 and EBECRYL Resin 270 system at the same conditions. The curing speed of the DAO system is higher without TPGDA.

Influence of the photoinitiator on curing speed

The effect of photoinitiator on curing speed of DAO UV-curing system is exhibited in Figure 6. It can be seen that the systems with Irgacure 369 and CPT as the photoinitiator have a shorter time for the dry to the touch, even though their mass percent is lower, while the amount of Darocure 1173 has greater influence on time for dry to the touch. From 1.42 to 3.5%, the time for dry to the touch decreases quickly when the mass percent of Darocure 1173 increases; after 3.5%, it drops very slightly.

TABLE III
Time for Dry-to-Touch of Different UV-Curable Systems

Run	Oligomers, g (name)	TPGDA, %[a]	Darocur 1173, %[a]	Time for dry-to-touch, s
1	2 (DAO)	0	4.26	5
2	2 (DAO)	25	4.26	48
3	2 (DAO)	33.3	4.26	56.5
4[b]	2 (EBECRYL Resin 600)	33.3	4.26	480
5[b]	2 (EBECRYL Resin 270)	33.3	4.26	640

[a] Mass percent of oligomers.
[b] EBECRYL Resin 600 and EBECRYL Resin 270 with added 33.3%TPGDA are EBECRYL Resin 605 and EBECRYL Resin 285, respectively.

Influence of the active diluent on curing speed

Figure 7 shows influence of the active diluent on curing speed. Adding reactive diluent into DAO UV-curing system lowers its curing speed. The influence of TPGDA is greater than TMPTA. However, the time for dry to the touch is, respectively, 23 and 51 s, even if 30% TMPTA and 30% TPGDA are added, which are notably lower than that of the EBECRYL Resin 600 and EBECRYL Resin 270 system, as shown in Table III. That is to say, although it is not necessary, active diluents can be used in DAO UV-curing system to adjust properties of the cured system; at the same time, the UV-curing system can still keep higher curing speed.

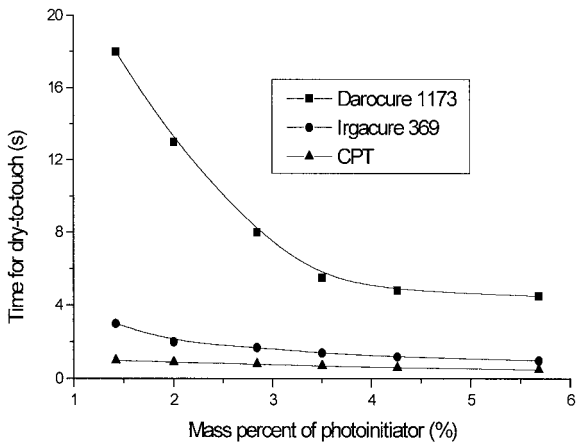

Figure 6 The curing speed vs. photoinitiator.

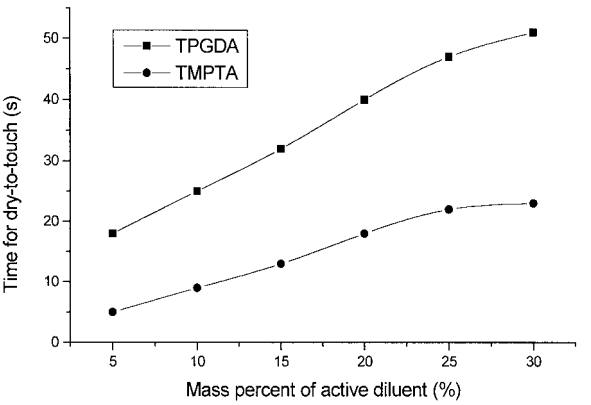

Figure 7 The curing speed vs. active diluent.

CONCLUSIONS

The dendritic acrylate oligomers (DAO) can be synthesized under mild conditions; that is, the mol ratio of TMPTA and EDA is 5.0 : 1.0, methanol as the catalyst and solvent, reaction time is 6 h, and reaction temperature is 30°C. DAO can be used in fast UV curing systems. DAO has low viscosity and high UV curing speed, compared with linear acrylic oligomers with similar molecule weights. Its curing speed is affected by photoinitiator and active diluent.

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