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# Photopolymerization kinetics of dendritic poly(ether–amide)s

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## Abstract

The UV-curable dendritic poly(ether–amide)s (DPEA) with different chemical structures of end-groups were synthesized and their photopolymerization kinetics were studied by Photo-DSC. The effects of chemical structures of end-groups, photoinitiator concentration, and co-monomer content on the UV curing rate and the final unsaturation conversion of these dendritic poly(ether–amide)s were investigated. The pendulum hardness and thermal stability of the UV-cured films were also studied. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Dendritic poly(ether–amide); UV curing; Kinetics

## 1. Introduction

A research area, which has obtained increasing interest during the last decade concerns improvement of macromolecular properties by changing the macromolecular architecture. One group of these materials is dendritic polymer, which was made from a core molecule in layers called generations or repeated reactions of multifunctional monomers, e.g. $AB_2$, giving backbone structures with numerous branching points [1,2]. These polymers are also characterized by a large number of end-groups, which greatly affect their properties. Several intriguing properties, such as low viscosity as melt and in solution and high solubility, and reactivity in comparison to linear counterparts, have been described for these polymers [3,4].

One potential application for these polymers is as UV-curable oligomers used in coating and adhesive systems. Although significant progress has been made in the research of dendritic polymers for various applications [5–8], there is still not much information on their use in UV curable coating and adhesive systems [9–13].

This study deals with the synthesis of (meth)acrylate-modified dendritic poly(ether–amide)s (DPEA-MA) and their UV curing kinetics, as well as the properties of UV-cured films.

## 2. Experimental

### 2.1. Materials

Dendritic poly(ether–amide) (DPEA-OH) with hydroxyl end-groups was synthesized by a three-step procedure with a divergent route starting from pentaerythritol [14]. Palmitoyl chloride was supplied from Fluka AG, Switzerland. Glycidyl methacrylate (GMA) was supplied from Hengguang Chemical Company, Luoyang, China. Acryloyl chloride was synthesized in our lab by the reaction of acrylic acid with benzyl chloride. Epoxy acrylate E20-A with molar mass of around 1080 as a traditional linear oligomer was synthesized by modifying the epoxy resin E20 (supplied from Shanghai Third Reagent Company) with acrylic acid. Trimethylolpropane triacrylate (TMPTA) as a co-monomer was supplied from Sartomer Company (USA). Benzoyl-1-hydroxyl-cyclohexanol (Irgacure-184) from Ciba-Geigy, Switzerland was used as a photo-fragmenting initiator. Other chemicals were supplied from Shanghai Third Reagent Company.

### 2.2. Synthesis

#### 2.2.1. Preparation of methacrylated dendritic poly(ether-amide) (DPEA-MA)

DPEA 8.36 g (0.01 mol, theoretically 0.12 mol OH), stannic chloride 0.025 g (0.071 mmol), and *p*-hydroxyanisole 0.05 g (0.143 mmol) were added into a three-necked flask equipped with a cooling tube, a dropping funnel, and a

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mechanical stirrer. The flask was placed in an oil bath previously heated to 100°C. Then GMA 17.95 g (0.126 mol) was slowly dropped into the above reaction vessel, and left stirring for 8 h. Residual GMA was removed in vacuum affording light yellowish viscous liquid.

FT-IR: 1637, 815 $\mathrm{cm^{-1}}$ (methacrylate unsaturation), 1719 $\mathrm{cm^{-1}}$ (ester carbonyl)

$^1$H NMR ($CDCl_3$, ppm): 1.95 (–**C**$\mathbf{H_3}$, methacrylate), 2.62 (–$CH_2$**C**$\mathbf{H_2}$CONH), 2.99 (–**OH**), 4.23–4.41 and 3.51–3.74 (broad peaks, all kinds of –**C**$\mathbf{H_2}$ and **CH**), 5.6 (–C=**C**$\mathbf{H_2}$, *trans* to methyl), 6.14 (–C=**C**$\mathbf{H_2}$, *cis* to methyl)

### 2.2.2. Methacrylated dendritic poly(ether–amide) with acrylate end-groups (DPEA-MA-A)

25.46 g (0.01 mol) DPEA-MA obtained from the above preparation was mixed with 30 ml of dichloromethane and 20 ml of triethylamine (0.012 mol). Then the mixture was slowly dropped into the ice-cooled reaction vessel which already contained 11.7 ml (0.144 mol) of acryloyl chloride, and left stirring at ambient temperature until the disappearance of the hydroxyl peak (3400–3100 $\mathrm{cm^{-1}}$) in FT-IR spectrum. The obtained solution was stepwise extracted with 1 M HCl, 10 wt% $NaHCO_3$, and distilled water, then dried over anhydrous $MgSO_4$ and filtered. Finally, dichloromethane was evaporated from the solution giving a yellowish viscous liquid.

FT-IR: 1726 $\mathrm{cm^{-1}}$ (ester carbonyl), 1635, 809 $\mathrm{cm^{-1}}$ (acrylate unsaturation)

$^1$H NMR ($CDCl_3$, ppm): 1.94 (–**C**$\mathbf{H_3}$, methacrylate), 2.62 (–$CH_2$**C**$\mathbf{H_2}$CONH), 5.88, 6.12, 6.42 (–C=**C**$\mathbf{H_2}$ and –**CH**=**C**$\mathbf{H_2}$)

### 2.2.3. Methacrylated dendritic poly(ether–amide) with acetate end-groups (DPEA-MA-AC)

25.46 g (0.01 mol) DPEA-MA obtained from the above preparation was mixed with 30 ml of dichloromethane and 14.42 ml (0.144 mol) of acetic anhydride. The mixture was firstly left stirring at ambient temperature for 1 h, then at 50°C for 12 h. Finally the solution was treated as the above procedure, and dichloromethane was evaporated giving a yellowish viscous liquid.

FT-IR: 811 $\mathrm{cm^{-1}}$ (methacrylate unsaturation), 1732 $\mathrm{cm^{-1}}$ (ester carbonyl)

$^1$H NMR ($CDCl_3$, ppm): 1.88(–**C**$\mathbf{H_3}$, methacrylate), 2.09 (–**C**$\mathbf{H_3}$, acetate), 2.55(–$CH_2$**C**$\mathbf{H_2}$CONH), 5.55(–C=**C**$\mathbf{H_2}$, *trans* to methyl), 6.07(–C=**C**$\mathbf{H_2}$, *cis* to methyl)

### 2.2.4. Methacrylated dendritic poly(ether–amide) with palmitic end-groups (DPEA-MA-P)

25.46 g (0.01 mol) DPEA-MA obtained from the above preparation was mixed with 30 ml of dichloromethane and 20 ml of triethylamine (0.012 mol), then 39.58 g (0.144 mol) palmitoyl chloride was slowly added into the above mixture. The reaction mixture was left stirring at 50°C until the disappearance of the hydroxyl peak (3400–3100 $\mathrm{cm^{-1}}$) in FT-IR spectrum. The solution was then treated as the above procedure. Finally, dichloromethane was evaporated giving a white waxy solid.

FT-IR: 1738 $\mathrm{cm^{-1}}$ (ester carbonyl), 1644, 812 $\mathrm{cm^{-1}}$ (methacrylate unsaturation), 716 $\mathrm{cm^{-1}}$ (long carbon chain)

$^1$H NMR ($CDCl_3$, ppm): 0.81(–**C**$\mathbf{H_3}$, long chain), 2.09 (–**C**$\mathbf{H_3}$, methacrylate), 2.6(–$CH_2$**C**$\mathbf{H_2}$CONH), 1.23(–**C**$\mathbf{H_2}$, long chain), 2.26(–**C**$\mathbf{H_2}$COO, long chain), 5.53(–C=**C**$\mathbf{H_2}$, *trans* to methyl), 6.2(–C=**C**$\mathbf{H_2}$, *cis* to methyl)

## 2.3. UV curing

Three DPEA-MA (DPEA-MA-A/AC/P) samples were mixed with Irgacure 184 (3 wt%) and drawn on glass plates with a 75 μm applicator, respectively, then exposed to an UV lamp (1 kW, 80 w $\mathrm{cm^{-1}}$, made by Lantian Company, Beijing) at variable conveyor speeds in air.

## 2.4. Measurements

### 2.4.1. FT-IR spectra

Infrared spectra were recorded on a MAGNA-IR 750 (Nicolet Instrument Corporation, USA).

### 2.4.2. $^1$H NMR measurement

Nuclear magnetic resonance (NMR) spectra were recorded on a DMX-500 (Brucker Company, Switzerland) using $CDCl_3$ as a solvent and using its signal as a reference.

### 2.4.3. VPO measurement

Vapor phase osmometer (VPO) was performed on a QX-08 apparatus at 35°C, and acetone was used as a solvent.

### 2.4.4. Photopolymerization kinetics

The photopolymerization kinetics was monitored by a modified CDR-1 DSC (made by Shanghai Balance Instrument Company). The digitized data based on the trace on a strip chart recorder were analyzed by the software Origin 5.0 on a personal computer. The initiator, Irgacure 184 was applied in the concentration of 4 wt%. Polymerization was carried out in an inert atmosphere. An UV spotcure system BHG-250 (Mejiro Precision Company, Japan) was used for the irradiation of the samples. The incident light intensity at the sample pan was measured to be 2.04 mW $\mathrm{cm^{-2}}$.

The unsaturation conversion ($P$) was calculated by the following formula: $P = H_t/H_\infty$, where $H_t$ is the heat effect within $t$ second, $H_\infty$ is the heat effect of 100% conversion of double bonds. DSC curves were adjusted by the weight of sample ($g$). The polymerization rate was defined by $\mathrm{mmol_{C=C}\,g^{-1}\,s^{-1}}$, namely, variation of the double bonds concentration (mmol $\mathrm{g^{-1}}$) per second [15]. For calculating the polymerization rate and $H_\infty$, the values for the heat of polymerization $\Delta H_0 = 70\ \mathrm{J\,mmol^{-1}}$ [11] (per methacrylic double bonds) and $\Delta H_0 = 86\ \mathrm{J\,mmol^{-1}}$ [16] (per acrylic double bonds) were taken, respectively. The concentration of double bonds was calculated from $^1$H NMR measurement.

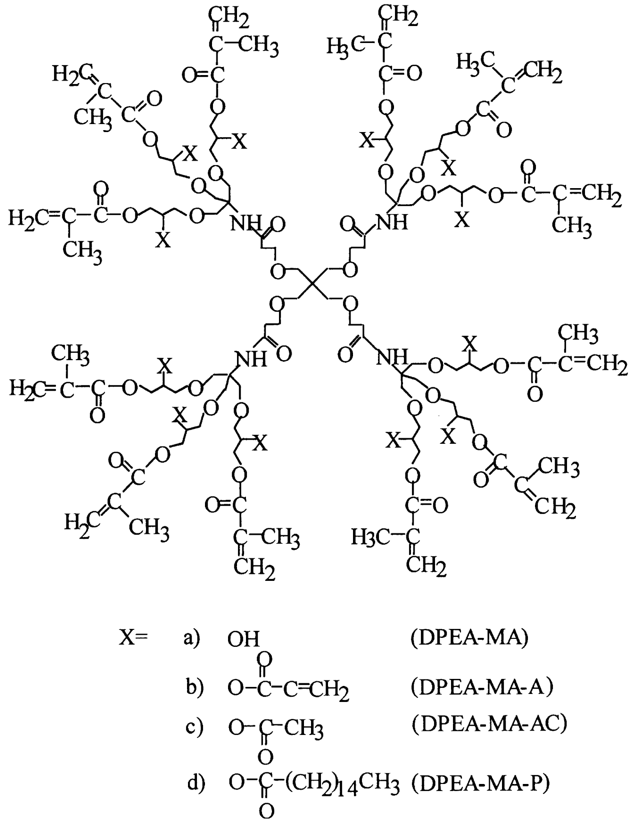

Fig. 1. Idealized formulae of DPEA-MA, DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P.

### 2.4.5. Pendulum hardness

The pendulum hardness of the cured films was determined using a QBY pendulum apparatus (made by Tianjin Instrument Company, China). The films were applied on glass plates with a 75 μm applicator.

### 2.4.6. Thermogravimetric analysis

The thermal degradation temperature of the cured samples was taken as the temperature at which 5% weight loss measured on a Shimadzu TG-50 at a heating rate of 10 K min$^{-1}$ from 25 to 700°C.

Table 1
Data on DPEA-MA, DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P

| Samples | $D_s$ (%)[a] | $M_{\mathrm{NMR}}$[b] | $M_{\mathrm{E}}$[c] | $C_{\mathrm{D}}$ (mmol/g)[d] |
|---|---|---|---|---|
| DPEA-MA | 61 | 1879 | 1560 | 3.9 |
| DPEA-MA-A | 58 | 2253 | 2130 | 6.34 |
| DPEA-MA-AC | 92 | 2341 | 2210 | 3.13 |
| DPEA-MA-P | 44 | 3149 | 2980 | 2.1 |

[a] Degree of substitution from $^1$H NMR measurement.

[b] Molar mass from $^1$H NMR measurement.

[c] Molar mass from VPO measurement.

[d] Double bonds concentration from $^1$H NMR measurement.

## 3. Results and discussions

The idealized formulae of DPEA-MA, DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P were shown in Fig. 1.

The $^1$H NMR integral of methylene next to amide bond was used as an internal standard. The $^1$H NMR integral of the terminal methacrylic and acrylic double bonds and the $^1$H NMR integral of terminal methyl groups of methacrylate, acetate and palmitoyl chloride long alkyl chain were used to determine the degree of substitution, molar mass and the concentration of double bond of DPEA-MA, DPEA-MA-A, DPEA-MA-AC, and DPEA-MA-P. The results were shown in Table 1.

From $^1$H NMR measurement, the substitution degree of DPEA-MA was 61%. DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P were synthesized by modifying DPEA-MA with acryloyl chloride, acetic anhydride and palmitoyl chloride, respectively. Their corresponding substitution degrees were 58, 92 and 44% measured by $^1$H NMR.

### 3.1. Photopolymeriation kinetics

The most important parameters characterizing the photopolymerization of multifunctional oligomers are the rate at peak maximum ($R_{\mathrm{P}}^{\max}$) and the final degree of double bond conversion after given irradiation time ($P^{\mathrm{f}}$) [16]. The discussion of the results in this sector was based mainly on the values of these parameters obtained from the polymerization of the individual formulation.

### 3.1.1. The influence of the chemical structures of end-groups

As shown in Fig. 1, DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P are the three kinds of UV curable dendritic oligomers that have the same backbone structure but different chemical structures of end-groups. Their UV curing kinetics was shown in Figs. 2 and 3. It has been found that the $R_{\mathrm{P}}^{\max}$ of DPEA-MA-A is the highest, which due to its higher reactivity of acrylic functional group and higher double bond concentration. The $R_{\mathrm{P}}^{\max}$ of DEPA-MA-P is the lowest. DPEA-MA-AC has higher $R_{\mathrm{P}}^{\max}$ than DPEA-MA-P because of the higher double bond concentration of the former. From Fig. 3, it has been also found that although dendritic oligomers have much higher molar mass and a large amount of double bonds, they all have higher $P^{\mathrm{f}}$ than that of E20-A after given UV irradiation time. It indicates that their functional end-groups are highly accessible for polymerization. However, the dendritic systems need longer irradiation time reaching $R_{\mathrm{P}}^{\max}$ and have broader rate peak. Moreover, E20-A has higher rate than the dendritic systems in the initial slope of rate peak. As a result, the different trends are observed in the initial slope of conversion curve that the dendritic systems need longer irradiation time for leveling off the unsaturation conversion curves than E20-A.

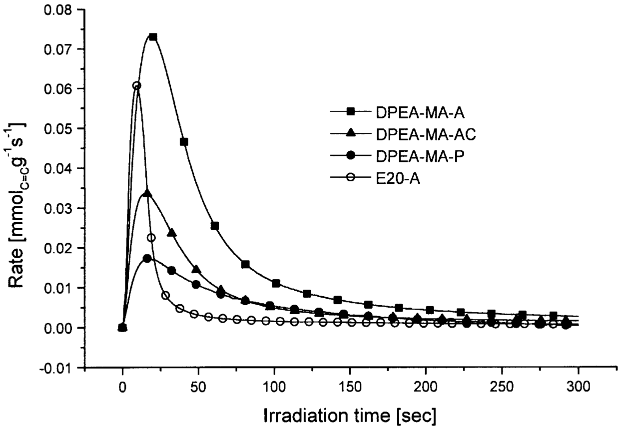

Fig. 2. Polymerization rate comparison of DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P with E20-A using 4 wt% Irgacure 184 as a photoinitiator.

### 3.1.2. The influence of the photoinitiator concentration

The influence of the photoinitiator content on photopolymerization of DPEA-MA-A was shown in Figs. 4 and 5. It has been shown that the formulation containing 4 wt% of Irgacure 184 has a higher $R_P^{max}$ and a lower $P^f$, also takes less time to reach $R_P^{max}$ in comparison to the formulation containing 2 wt% of Irgacure 184. Moreover, the rate peak of the former formulation is narrower than the later one. These phenomena attribute to the larger number of photoinitiator radicals produced in initiation stage of the former formulation, resulting in improvement of chain propagating rate. At the same time, the rate of chain termination reaction is also improved. Consequently, the later formulation gives a higher conversion than the former one.

### 3.1.3. The influence of co-monomer content

From Figs. 6 and 7, it can be seen that both $R_P^{max}$ and $P^f$ of DPEA-MA-A are promoted with 20 wt% TMPTA addition. The $R_P^{max}$ goes from 0.0735 up to 0.0996 mmol$_{C=C}$ g$^{-1}$ s$^{-1}$, this is mainly because the mobility of molecule goes up due

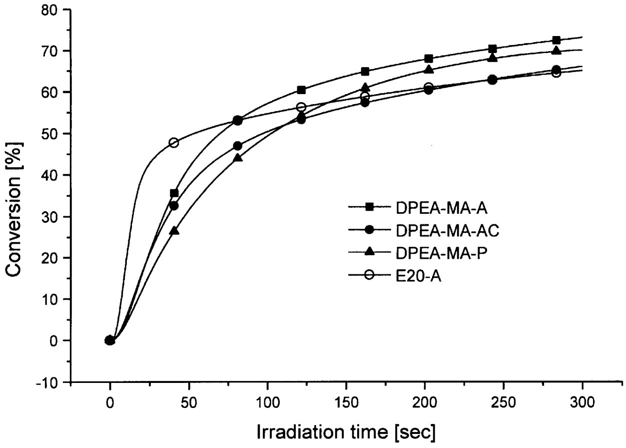

Fig. 3. Unsaturation conversion comparison of DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P with E20-A using 4 wt% Irgacure 184 as a photoinitiator.

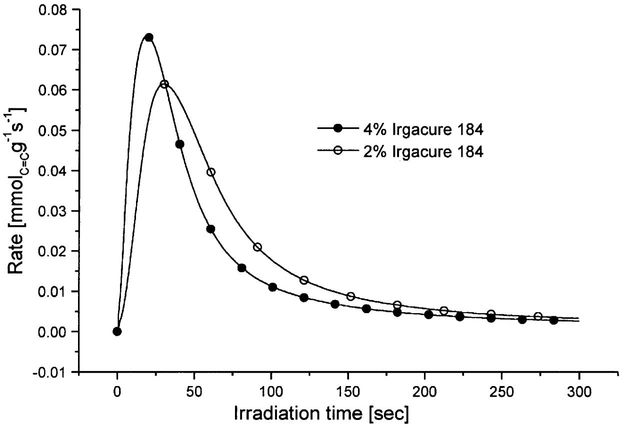

Fig. 4. Polymerization rate comparison of DPEA-MA-A with different photoinitiator contents.

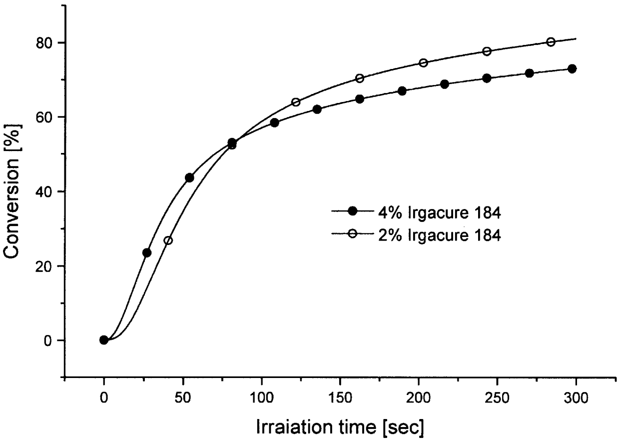

Fig. 5. Unsaturation conversion comparison of DPEA-MA-A with different photoinitiator contents.

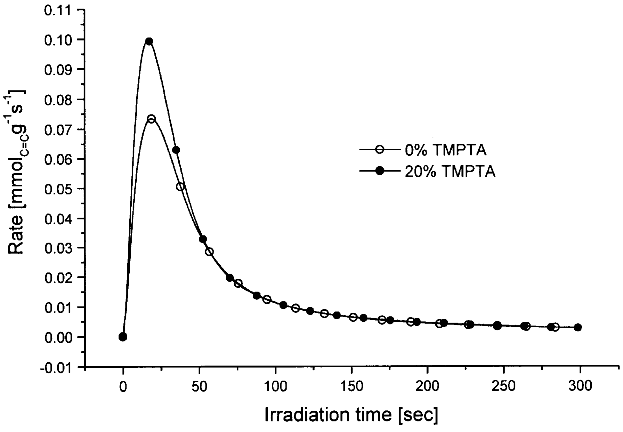

Fig. 6. Polymerization rate comparison of DPEA-MA-A with different co-monomer contents using 4 wt% Irgacure 184 as a photoinitiator.

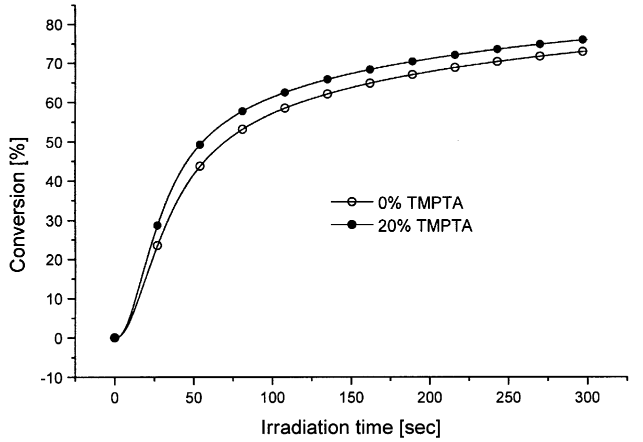

Fig. 7. Unsaturation conversion comparison of DPEA-MA-A with different co-monomer contents using 4 wt% Irgacure 184 as a photoinitiator.

to reducing the viscosity of the system when TMPTA is added. Moreover, it is worth to note that $P^f$ also goes from 73 up to 76%. It can be supposed that TMPTA molecules disperse DPEA-MA-A molecules and react to form a polymer network with DPEA-MA-A molecules. The photopolymerization happens mainly between TMPTA and DPEA-MA-A molecules, not only between DPEA-MA-A molecules. As a result, the mobility of the polymer network goes up. Some double bonds of DPEA-MA-A, which are trapped in the case of absence of co-monomer, are released upon the addition of the co-monomer and take part in the polymerization.

### 3.2. Pendulum hardness

Taking into account for some applications pendulum hardness is one of the important properties of an UV-cured film. The pendulum hardness of DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P films versus UV irradiation time is shown in Fig. 8. It can be seen that the films with different pendulum hardness are obtained by changing chemical structures of DPEA-MA end-groups. The film of DPEA-MA-A has the highest pendulum hardness due to the highest crosslink density resulting from the higher double bond concentration and $P^f$, while the film of DPEA-MA-P has the lowest hardness due to introducing the long alkyl chain of 16 carbons.

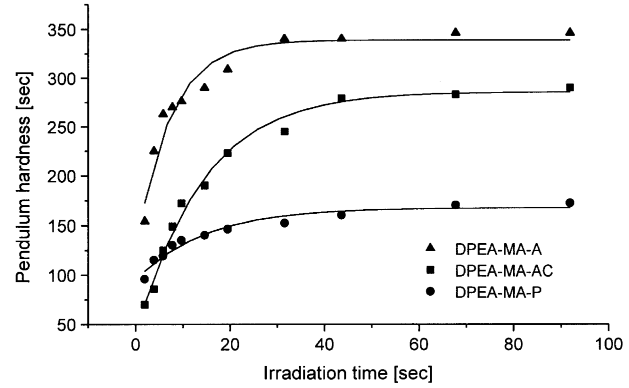

Fig. 8. Pendulum hardness of UV-cured films of DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P as a function of irradiation time with 3 wt% Irgacure 184 as a photoinitiator.

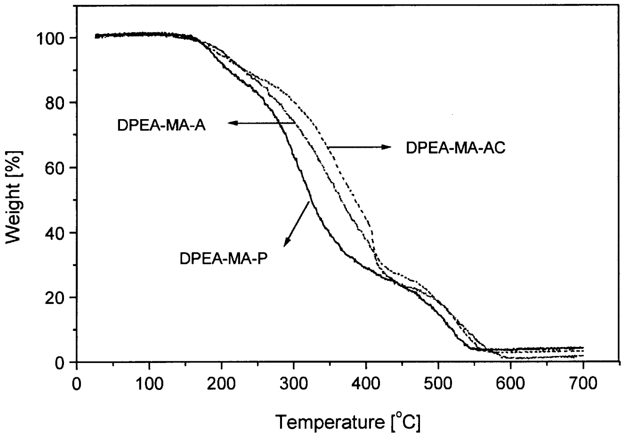

Fig. 9. TGA thermogram of UV-cured films of DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P.

### 3.3. Thermal stability

The thermal stability of UV-cured films of DPEA-MA-A, DPEA-MA-AC and DPEA-MA-P is shown in Fig. 9. It can be seen that these films all have acceptable thermal stability, the temperature of thermal degradation is 204°C for DPEA-MA-A, 195°C for DPEA-MA-AC and 188°C for DPEA-MA-P, respectively.

## 4. Conclusions

Three kinds of UV curable dendritic poly(ether–amide)s are synthesized. Their UV curing kinetics characterized by $P^f$ and $R_P^{max}$ is intensively affected by the chemical structures of end-groups, photoinitiator content, and co-monomer content. These dendritic oligomers all have higher $P^f$ than that of E20-A after given UV irradiation time but dendritic systems need longer irradiation time for leveling off the unsaturation conversion curves than E20-A. The formulation containing DPEA-MA-A and 4 wt% of Irgacure 184 has higher $R_P^{max}$, lower $P^f$ in comparison to the formulation containing DPEA-MA-A and 2 wt% of Irgacure 184. The addition of 20 wt% TMPTA as a co-monomer promotes both $R_P^{max}$ and $P^f$ simultaneously. Films with different pendulum hardness are obtained by changing chemical structures of DPEA-MA end-groups. The UV-cured films of these dendritic systems all have acceptable thermal stability with thermal degradation temperature over 185°C.

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