

Synthesis and Ultraviolet-Curing Behaviors of Vinyl Ether Functionalized Polyurethane Oligomers

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ABSTRACT: The vinyl ether functionalized oligomer is one of the most basic components of vinyl ether functionalized materials for cationic UV-curable coatings. In this study, three types of vinyl ether functionalized polyurethane oligomers (i.e., polyether, polyester, and polydimethylsiloxane) were synthesized with diisocyanate, diol, and hydroxyethyl vinyl ether. These oligomers were characterized by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy. The effect of the raw material ratio on the oligomer, UV-curing behaviors, and thermal properties of these oligomers were investigated. The UV-curing behavior was analyzed by real-time Fourier transform infrared spectroscopy. The vinyl ether terminated polyester urethane oligomer exhibited better UV curing, with a higher final conversion and maximum UV-curing rates. In addition, the light intensity was enhanced for oligomers with better UV-curing properties. Research on these vinyl ether functionalized oligomers is essential to the development and applications of cationic vinyl ethers systems. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40501.

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INTRODUCTION

As alternatives to traditional thermally cured and solvent-based resins, UV-curable systems are green chemical materials because of their high efficiency, environmental friendliness, lower energy consumption, high-quality coatings, and fast curing response.^{1–4} The applications of the UV-curing technique have increasingly been used for the development of coatings, adhesives, inks, microelectronics, and biological materials.^{5–7}

According to the UV-curing mechanism, UV-curing technology can be divided into free-radical, cationic, and radical-cationic hybrid curing processes. Currently, most UV-curable resins are primarily based on the free-radical polymerization of high reactive (meth)acrylate monomers.^{8–12} Although (meth)acrylates exhibit good chemical resistance and rapid curing, they also exhibit certain inevitable disadvantages, including health hazards, detrimental coating shrinkage, and inhibition by oxygen.^{10–15} There are also several disadvantages associated with the free-radical photopolymerization process, including (1) it is severely inhibited by oxygen, which normally causes unsatisfactory surface curing, and (2) it leads to a contraction in the reaction volume. In contrast to free-radical UV-curing, cationic UV curing has several advantages, including no obvious coating shrinkage and the absence of oxygen inhibition, and the cationic

UV-curable compounds have low volatile organic compounds (VOC).^{15,16} In recent years, cationic UV-curable systems have been widely used in various industries. Currently, epoxies and vinyl ethers appear to be the most promising cationic UV-curable systems. However, the applications of epoxies are greatly limited because of their disadvantages, such as their slow curing speed, high viscosity, and poor flowability, which lead to inconvenient operation. Vinyl ethers appear to be more attractive alternatives to epoxies and (meth)acrylates, and the curing rates of vinyl ethers have been reported to be at least as fast as the curing rates of (meth)acrylate resins.^{17,18} In addition to their fast curing rates, additional positive features of vinyl ethers include their low odor and low shrinkage.

The vinyl ether system is based on oligomers (or prepolymers) with the addition of vinyl ether monomers, cationic protonic acids, and other additives. The research focus on vinyl ether monomers has led to several advances, and certain vinyl ether monomers, such as monofunctional or difunctional vinyl ether monomers (e.g., cyclohexyl vinyl ether (CHVE), 2-ethylhexyl vinyl ether (EHVE), butanediol divinyl ether (BDDVE), diethyleneglycol divinyl ether (DVE-2), and triethyleneglycol divinyl ether (DVE-3)) manufactured by BASF, are commercially available. In addition, Hiroshi et al.¹⁹ developed silicon-containing vinyl ethers that were suitable for nano-imprint photoresists. To

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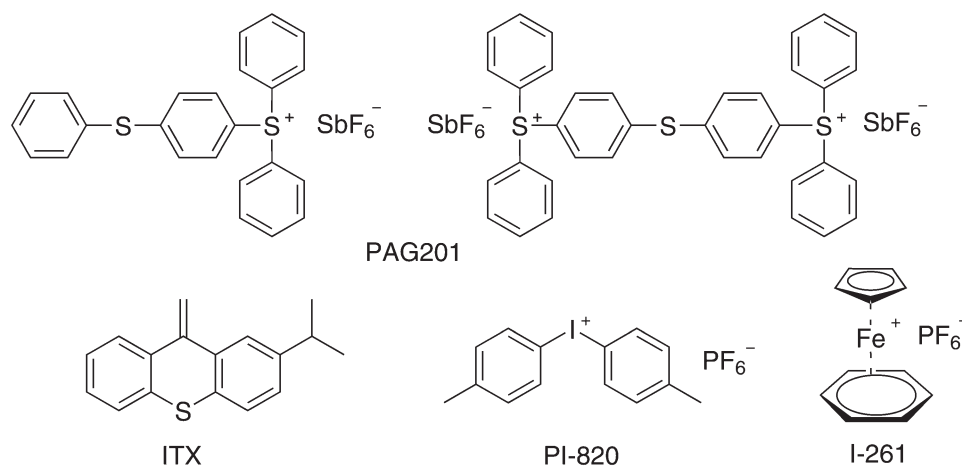


Figure 1. Structures of the photoinitiators used in this study.

overcome the difficulty in formulating coatings based on only monomers and to promote the development of the vinyl ether cationic UV-curing system, some vinyl ether functionalized oligomers have been developed. Lapin¹³ reported vinyl ether oligomers synthesized with triethylene glycol monovinyl ether and toluene diisocyanate (TDI). The results from this study indicate that coatings with excellent physical and mechanical properties were obtained upon UV irradiation. Kayaman-Apohan et al.¹ synthesized a variety of vinyl ether oligomers and studied their cationic curing properties. The photopolymerization processes were strongly affected by the hydrophilicity of the oligomers.²⁰

Our laboratory has been studying vinyl ethers for several years, and we have reported a series of vinyl ether functionalized compounds.^{8,9,21–24} In the presence of the PAG201 photoinitiator, fluorine-containing and silicon-containing vinyl ether monomers exhibit rapid curing rates and a low surface free energy that enable them to perform better in applications.^{8,9,24} On the basis of these results, three types of vinyl ether polyurethane oligomers were synthesized. These oligomers combine the advantages of vinyl ethers and polyurethane, and polyurethane exhibits excellent physical and mechanical properties, such as substrate adhesion,²⁵ flexibility, and impact strength. The effects of the raw material ratio on the performance of the products, photopolymerization kinetics, and thermal decomposition of these oligomers were investigated.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) and TDI were purchased from J&K Chemical (Beijing, China). Hydroxyl-terminated polydimethylsiloxane (PDMS), poly(propylene glycol) 400 (PPG400), and hydroxyethyl vinyl ether (HEVE) were provided by Alfa Aesar (Tianjin, China). Poly(ethylene glycol) 400 (PEG400) was provided by the Guangfu Fine Chemical Research Institute (Tianjin, China). Dibutyltin dilaurate (DBTDL) was supplied by Beijing Stable Chemical Co., Ltd. (Beijing, China). Tetrahydrofuran was supplied by the Sinopharm Group Chemical Reagent Co., Ltd.

(Beijing, China) and was purified by distillation in the presence of sodium metal. The photo-initiators cationic photoinitiator salt which is the mixed triaryl sulfonium hexafluoroantimonate salts (PAG201), Photo-initiator Iodonium bis(4-methylphenyl)hexafluorophosphate (PI820), Irgacure 261 (i-261), and Isopropylthioxanthone (ITX) were provided by Shenzhen Rongda Electronic Material Co., Ltd. (Shenzhen, China), and the structures of the photoinitiators are listed in Figure 1.

Measurements

The IR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corp., Waltham, MA). The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance PRX400 spectrometer (Bruker, Germany). The number-average molecular mass of the samples were calculated on the basis of end-group analysis with a titration method to determine the —NCO content of prepolymers. The Fourier transform infrared (FTIR) data were obtained with an Avatar 380 FTIR spectrometer (Nicolet). The photopolymerization rates (R_p 's⁻¹) and conversion rates of vinyl ether functionalized polyurethane were monitored with FTIR spectroscopy. The thermogravimetric analysis (TGA) of the polymers was performed with a Mettler Toledo TGA/DSC 1/1100 instrument. The samples were run from 30 to 600°C with a heating rate of 10°C/min under nitrogen. The dynamic viscosities of the samples were performed with a rotational viscometer NDJ-1 (Brookfield) at room temperature.

Synthesis of Vinyl Ether Functionalized Polyurethanes

The synthesis of vinyl ether functionalized polyurethane oligomers were performed in two steps. A 250-mL, three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and pressure-equalized dropping funnel was charged with diisocyanate. Then, polyol was added from a dropping funnel to the vigorously stirred diisocyanate. The reaction was conducted at a specific temperature until the theoretical isocyanate value was obtained. A standard di-*n*-butylamine back-titration method was used to determine the NCO content of the prepolymer.²⁶ In the second step, HEVE was added dropwise to the reaction medium. After the mixture was stirred for 1 h, 0.05 wt % DBTDL was added to the reaction as a catalyst. When the NCO content reached zero, which was

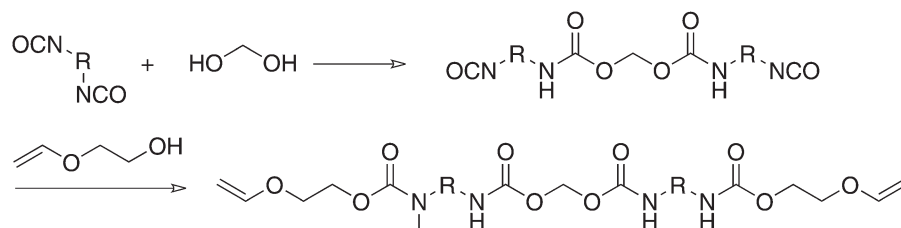


Figure 2. Synthetic procedures for the vinyl ether functionalized polyurethane oligomers.

determined on the basis of the disappearance of the characteristic NCO peak at 2275 cm^{-1} in the IR spectrum, the reaction was completed. The reaction schemes are shown in Figure 2.

Different oligomeric structures were obtained when different materials were chosen, and their performance also varied. IPDI or TDI was chosen as the reactant because the —NCO activity was higher. According to the types of diols (i.e., polyether diol, polyester diol, and hydroxyl-terminated PDMS), the synthesized products were named polyether polyurethane, polyester polyurethane, and polydimethylsiloxane polyurethane, respectively, and were named the oligomer synthesized with IPDI(I), PPG400(PPG) and HEVE(E) (IPPGE), the oligomer synthesized with TDI(T), PPG400(PPG) and HEVE(E) (TPPGE), the oligomer synthesized with IPDI(I), PEG400(PEG) and HEVE(E) (IPEGE), the oligomer synthesized with TDI(T), PCDL and HEVE(E) (TPCDLE), and the oligomer synthesized with IPDI(I), PDMS and HEVE(E) (IPDMSE). In addition, the structural formulas are shown later in Figure 3 and Table I.

Synthesis of Vinyl Ether Functionalized Polyether Polyurethanes

A 250-mL, four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and pressure-equalized dropping funnel was charged with IPDI (4.45 g, 0.02 mol). PPG400 (4.00 g, 0.01 mol) containing 0.02 wt % DBTDL as a catalyst was added from a dropping funnel to the vigorously stirred IPDI for 20 min, and the reaction proceeded at room temperature until the theoretical isocyanate value was reached. In the second step, HEVE (1.84 g, 0.02 mol) was added dropwise to the reaction medium at 60°C , and the reaction was continued until the NCO content reached zero. This was determined on the basis of the disappearance of the IR peak of —NCO . The product was a white viscous liquid and was referred to as IPPGE.

By changing the ratio of IPDI and PPG400, we produced a series of vinyl ether functional polyurethanes oligomers, which were numbered IPPGE-1, IPPGE-2, IPPGE-3, IPPGE-4, IPPGE-5, and

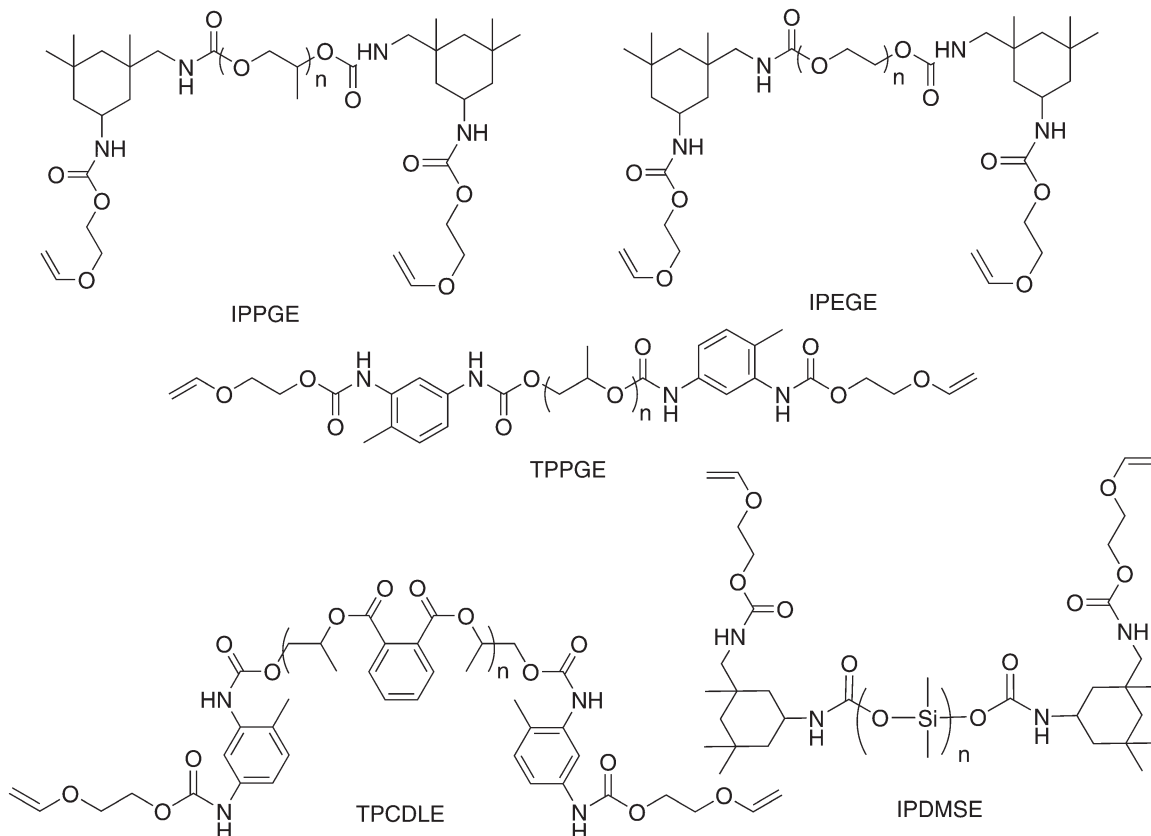


Figure 3. Structures of the vinyl ether functional polyurethane oligomers.

Table I. Formulations Used for the Synthesis of UV-Curable Vinyl Ether Functional Polyurethane Oligomers

Sample	Raw material			Feed ratio	Double-bond density (%)	M_n
	Diisocyanate	Diol	Hydroxyl vinyl ether			
IPPGE	IPDI	PPG400	HEVE	2:1:2	7.71	1115
TPPGE	TDI	PPG400	HEVE	2:1:2	10.49	820
IPEGE	IPDI	PEG400	HEVE	2:1:2	7.64	1126
TPCDLE	TDI	PCDL	HEVE	2:1:2	13.23	650
IPDMSE	IPDI	PDMS	HEVE	2:1:2	1.80	4792

M_n , number-average molecular weight.

IPPGE-6, where the average molecular mass of the oligomers increased, and the content of carbon-carbon double bonds was decreased. All of the oligomers were synthesized with the procedure described previously. The structural formulas of IPPGE are shown in the Supporting Information in Scheme S1. Their feed ratio and average molecular mass are shown in Table II.

The IR spectra of these oligomers were similar; this indicated that they possessed the same functional groups, such as C=C-O, N-H, and C=O.

IPPGE-1. IR (KBr, cm^{-1}): 3330 (N-H), 3120 (=C-H), 1700 (C=O), 1610 (C=C).

The characteristic -NCO band at 2270 cm^{-1} was no longer detectable.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 6.36–6.43 (dd, 2H, C=CH-O-), 4.00–4.20 (m, 15H, $\text{CH}_2=\text{C}-\text{O}$, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 0.95–1.05 (s, 18H, -C- CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ): 160.1 (C=O), 151.2, 85.0 (C=C-O), 32.5 (CH_3).

TPPGE. IR (KBr, cm^{-1}): 3338 (N-H), 3115 (=C-H), 1715 (C=O), 1617 (C=C), 1600–1450 (C=C benzene). $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3 , δ): 7.95 (m, 2H, benzene), 7.20–7.50 (m, 4H, benzene), 6.46–6.51 (dd, 2H, C=CH-O-), 4.00–4.20 (m, 15H, $\text{CH}_2=\text{C}-\text{O}$, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 0.95–1.05 (s, 18H, -C- CH_3). $^{13}\text{C-NMR}$ spectrum (100 MHz, CDCl_3 , δ): 158.0 (C=O), 152.5, 85.1 (C=C-O), 135.1, 133.8, 130.5, 128.4, 118.0, 114.1 (benzene).

IPEGE. IR (KBr, cm^{-1}): 3332 (N-H), 3124 (=C-H), 1720 (C=O), 1618 (C=C). $^1\text{H-NMR}$ spectrum (400 MHz, CDCl_3 , δ):

6.47–6.50 (dd, 2H, C=CH-O-), 4.00–4.20 (m, 18H, $\text{CH}_2=\text{C}-\text{O}$, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$), 0.95–1.05 (s, 18H, -C- CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ): 156.8.1 (C=O), 152.0, 85.3 (C=C-O), 32.5, 28.2 (CH_3).

Synthesis of Vinyl Ether Functionalized Polyester Polyurethanes

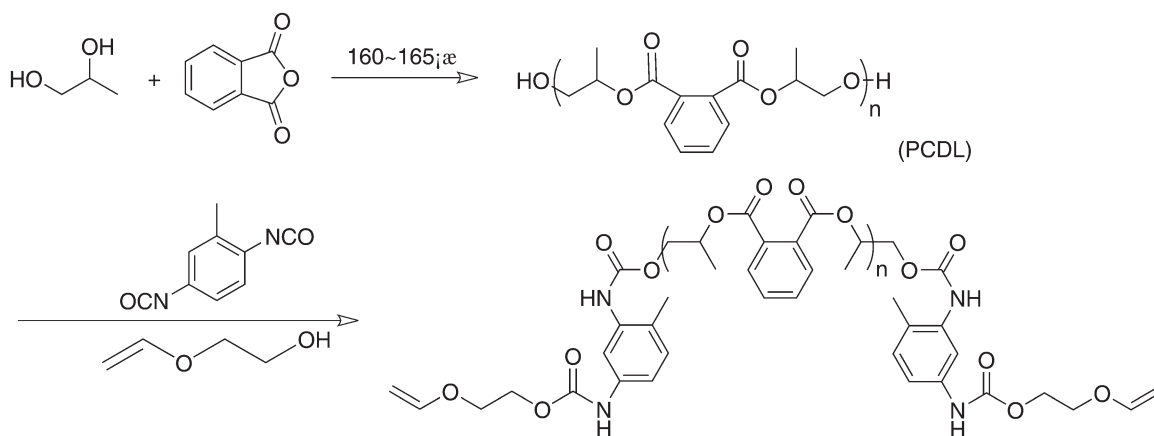
To a 250-mL, four-necked flask equipped with a mechanical stirrer and a nitrogen inlet, a water knockout trap was charged with phthalic anhydride (0.05 mol), propylene glycol (0.01 mol), and distilled toluene (50 mL). The reaction refluxed to 140°C . When the phthalic anhydride was completely dissolved, the reaction was maintained at 165°C for 2 h followed by slow warming to 200°C . The reaction was complete when the water knockout trap contained no drops. Next, the product dried to obtain a polyester diol [poly(carbonate diol) (PCDL)]. The following step was performed as stated previously, except that PCDL was used instead of PPG400. The product was a yellow viscous liquid and referred to as TPCDL. The procedure for this reaction is shown later in Scheme 1.

IR (KBr, cm^{-1}): 3334 (N-H), 1724 (C=O), 1617 (C=C), 1600–1450 (C=C benzene), 841 (=C-H). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 8.20 (m, 2H, benzene), 8.01 (m, 2H, benzene CH=C-NH), 7.60 (m, 2H, benzene), 7.20–7.30 (m, 4H, benzene), 6.45–6.50 (dd, 2H, C=CH-O-), 4.20–4.50 (m, 18H, $\text{CH}_2=\text{C}-\text{O}$, $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ): 154.2 (C=O), 151.2, 85.3 (C=C-O), 134.8, 132.5, 128.0, 118.0, 114.1 (benzene), 66.9, 63.2 (C-C), 20.4 (- CH_3).

Table II. Effect of the Feed Ratio of IPDI and PPG400 on Vinyl Ether Functional Polyether Polyurethane

Sample	Feed ratio (molar ratio)			Double-bond density (%)	Dynamic viscosity (cp)	Degree of polymerization	M_n
	IPDI	PPG400	HEVE				
IPPGE-1	2	1	2	7.72	1,020	1	1115
IPPGE-2	3	2	2	5.20	5,637	2	1653
IPPGE-3	4	3	2	3.34	19,515	3	2579
IPPGE-4	5	4	2	3.06	15,277	4	2812
IPPGE-5	6	5	2	2.32	47,820	5	3714
IPPGE-6	11	10	2	1.65	49,260	10	5198

M_n , number-average molecular weight.



Scheme 1. Synthetic procedures for the vinyl ether functionalized polyester polyurethane oligomers.

Synthesis of Vinyl Ether Functionalized PDMS Polyurethanes

The procedure was the same as the one mentioned previously. The product was a white solid. The reaction scheme is shown later in Scheme 2.

IR (KBr, cm^{-1}): 3311 (N—H), 1712 (C=O), 1616 (C=C), 1536 (N—H), 1100–1050 (Si—O—Si), 841 (C—H), 800 (Si—CH₃). ¹H-NMR (400 MHz, CDCl₃, δ): 6.45–6.50 (dd, 2H, C=CH—O—), 4.00–4.20 (m, 12H, CH₂=C—O, O—CH₂—CH₂—O), 0.95–1.05 (s, 18H, —C—CH₃), 0.15 (s, 300H, Si—CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ): 166.8 (C=O), 157.0, 87.8 (C=C—O), 34.5, 25.7 (CH₃), 0.00 (Si—CH₃).

Testing of Photocuring Behavior

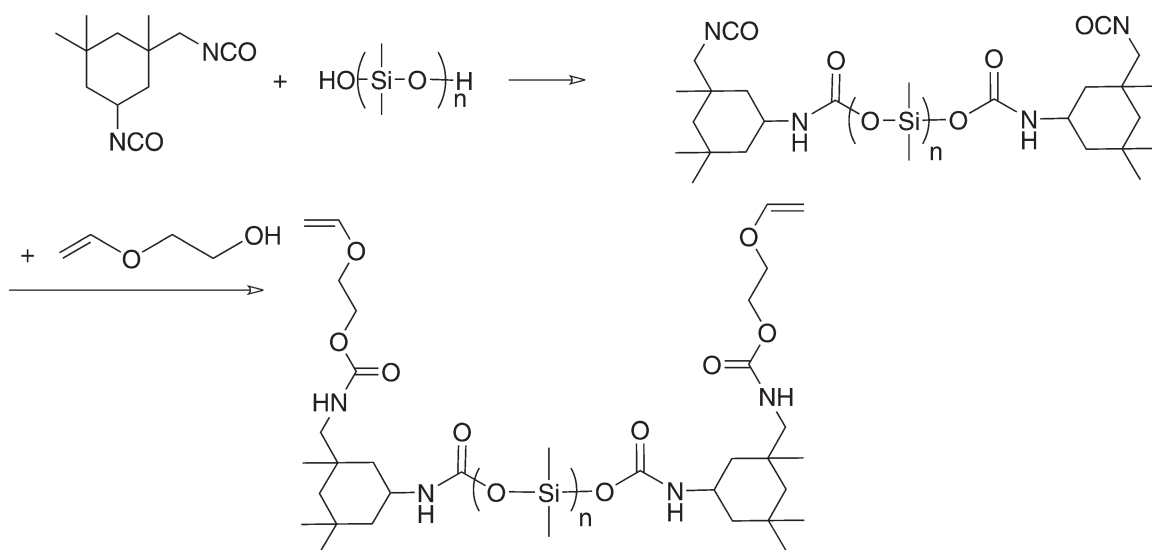
The photosensitive system was prepared by the mixture of the oligomer, initiator, and solvent. The mixture was dissolved to obtain a clear photosensitive solution with ultrasonic waves. The photosensitive solutions were coated onto KBr plates. The effects of the UV light intensity, initiator type, initiator concentration, and structure of the samples on the UV-curing behavior were investigated.

RESULTS AND DISCUSSION

Thermal Properties Determined by TGA

The thermal properties of oligomers play an important role in determining their applications. The thermal properties were determined by TGA at temperatures ranging from 30 to 600°C under nitrogen. The results indicate that the vinyl ether terminated polyurethanes oligomers exhibit good stability and were maintained below 100°C. Figure S1 in the Supporting Information shows the weight loss curves of the vinyl ether terminated polyurethanes. Table III lists the characteristic thermal decomposition temperatures of the oligomers, including the weight loss content at 100°C, the temperature of the initial 5% weight loss ($T_{5\%}$), the temperature of 50% weight loss ($T_{50\%}$), and the residue at 600°C. The weight loss at 100°C was probably due to moisture and/or solvent in the samples. The thermal stabilities of the polyether polyurethanes were better than those of polyester and PDMS polyurethanes (IPPGE-1, TPPGE, IPEGE > IPCDL > IPDMSE).

The thermal degradation mechanism of polyether polyurethanes involves one stages. The stage (175–400°C) involved the



Scheme 2. Synthetic procedures for the vinyl ether functionalized PDMS polyurethane oligomers.

Table III. Characteristic Thermal Decomposition Data for the Oligomers

Sample	Weight loss			Residual weight content (%)
	Weight loss at 100°C (%)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	
IPPGE-1	1.74	176	308	6.27
TPPGE	1.67	147	303	4.50
IPEGE	0.18	196	337	4.35
IPCDLE	1.96	118	266	8.01
IPDMSE	3.70	110	316	0.92

decomposition of the carbamic ester²⁷ (hard segment) and ether (soft segment). The polyester polyurethanes exhibited three stages. The initial stage (100–190°C) may have been due to solvent evaporation or reactant degradation. The second decomposition at 200–350°C was attributed to the degradation of urethane hard segments, which may have generated primary amines, CO₂, and polyhydric alcohols. The final decomposition at 350–470°C corresponded to ester soft segment. The dimethylsiloxane polyurethanes exhibited four stages. The first stages (100–175°C) may have been due to solvent or reactant evaporation. The second stages (175–280°C) involved the decomposition of the urethane hard segments. The third stage (280–370°C) involved the decomposition of the silicon-containing soft segment. The final stage (370–500°C) corresponded to intermolecular or intramolecular rearrangements, with the formation of low-molecular-weight silicon-containing cyclic organic products, which were volatile at high temperatures.²⁸

The effect of the chain length of polyurethanes on the oligomer stability was examined. Figure S2 in the Supporting Information indicates that the molecular chain length had no significant effect on the polyurethane degradation but contributed to the weight loss rate of the oligomers. When the chain was shorter, the weight loss rate was faster.

UV-Curing Kinetics Determined by FTIR Spectroscopy

The cationic polymerization of the vinyl ether functionalized polyurethanes was followed via real-time IR spectroscopy through the monitoring of the decrease of the peak at 1620 cm⁻¹; this corresponded to the vinyl ether double bonds (C=C stretching) upon UV exposure. By measuring the major absorbance peaks, we characterized the degree of polymerization. The double-bond conversion (DC) and speed of polymerization was calculated with eqs. (1) and (2):²⁹

$$DC(\%) = (A_0 - A_t) / A_0 \times 100 \quad (1)$$

where A_0 is the area of the characteristic absorbance peaks before excitation and A_t is the area of the characteristic absorbance peaks after excitation for time t :

$$\frac{R_p}{[M]_0} = \frac{d(DC)}{dt} \quad (2)$$

where R_p is the photopolymerization rate of the double bonds and $[M]_0$ is the original concentration of the oligomer.

The most important parameters characterizing the photopolymerization behavior of a multifunctional oligomer are the rate at peak maximum (R^{max}) and the final degree of DC after a given irradiation time.

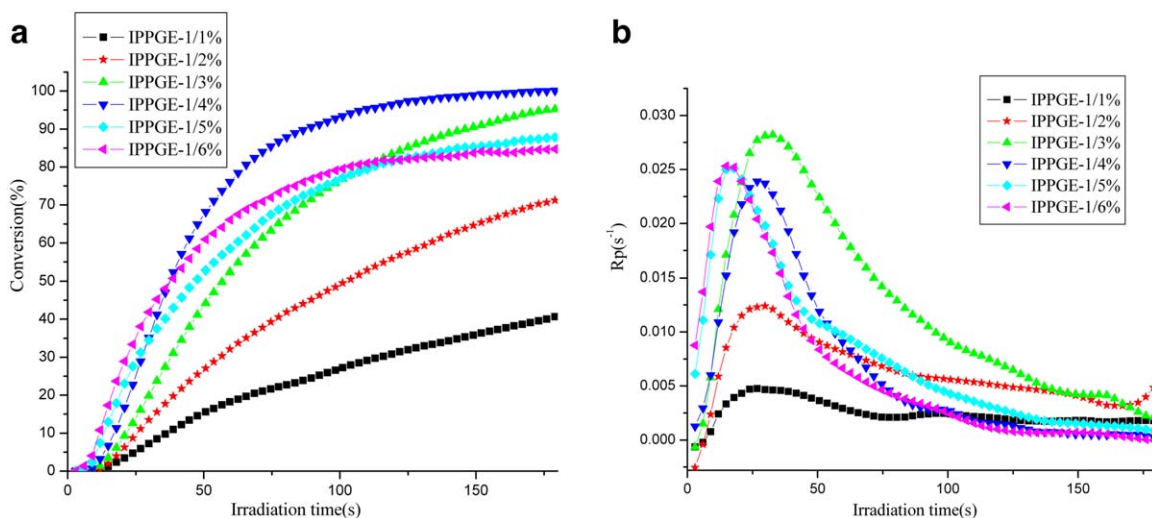


Figure 4. Effect of the initiator concentration on the vinyl ether polymerization for the oligomer IPPGE-1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

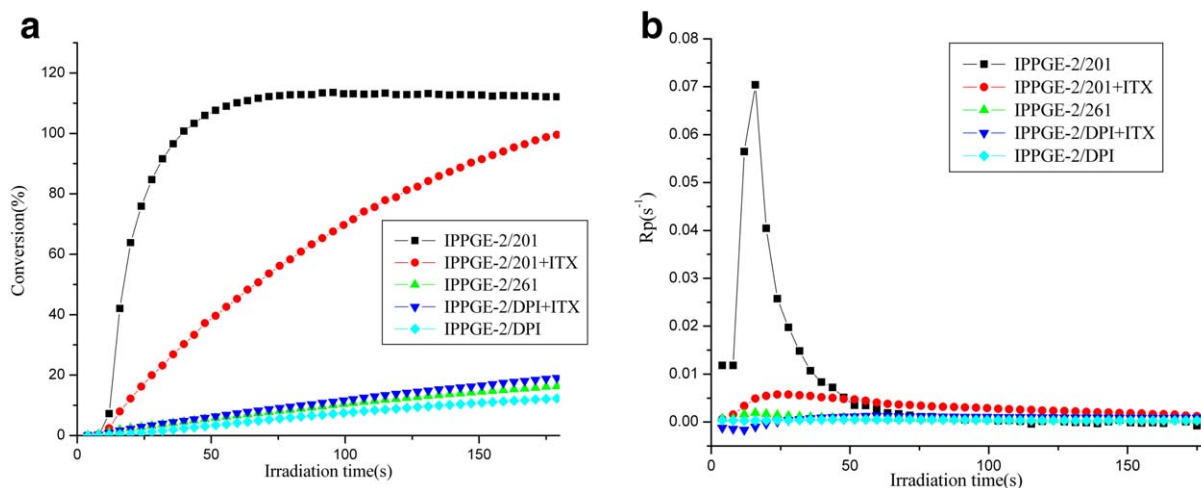


Figure 5. Effect of the initiator types on the vinyl ether functional polymerization for the oligomer IPPGE-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of the Photoinitiator Concentration on the Kinetics of the Polymerization of the Oligomers

The concentration of the photoinitiator is extremely important to the photopolymerization system. As the concentration of the photoinitiator increases, the speed of the polymerization process and the degree of final polymerization increases. When the concentration of the photoinitiator reaches a critical level, the speed of polymerization and the degree of final polymerization plateau. This concentration is defined as the optimal concentration of the initiator. With FTIR spectroscopy, the kinetic curves for the photopolymerization process of our synthesized vinyl ether functionalized polyurethane (IPPGE-1) were obtained with different concentrations of PAG201 (1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 wt %) as initiators at 30 mW/cm². When the concentration of the PAG201 initiator increased from 1.0 to 4.0 wt %, the speed of the polymerization process of the double bonds increased. As shown in Figure 4(a,b), the curing rate peak of IPPGE-1 appeared at 26.8 s, and the maximum curing rate was 2.82% s⁻¹; the final conversion also increased to nearly 100% when the concentration of the initiator was 4.0 wt %. When the concentration

of the initiator was between 4.0 and 6.0 wt %, the speed of polymerization and final conversion was less than 90%. On the basis of these data and with the cost and efficiency taken into consideration, the optimal concentration was 3.0–4.0 wt %.

Effect of the Initiator Type on Photopolymerization

The type of initiator is another important factor affecting the photopolymerization of oligomers. Figure 5 compares the photopolymerization of IPPGE-2 with three different cationic photoinitiators (i.e., PAG201, PAG201 containing 0.25 wt % ITX, PI820, PI820 containing 0.25 wt % ITX and i-261) under the same irradiation conditions (3.0 wt % and 100 mW/cm² UV light intensity, 300–500-nm light wavelength). The results show that i-261 and PI820 were poor initiators. The rate measured for PAG201 was about 70 times higher than i-261 and PI820 (Figure 5, the curing rate peak of IPPEG-2 with PAG201 as an initiator appeared at 15.9 s, and the maximum rate was 7.04% s⁻¹). Thus, in this group of investigated photoinitiators, the most efficient initiator for the cationic oligomers was PAG201. What is more, the photosensitizer (i.e., ITX) was also

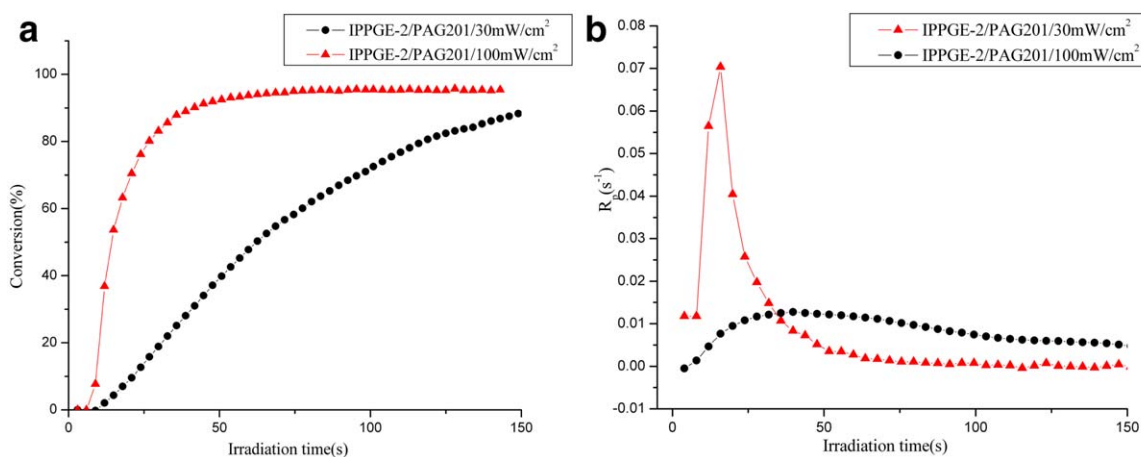


Figure 6. Effect of the light intensity on the vinyl ether functional polymerization of the oligomer IPPGE-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

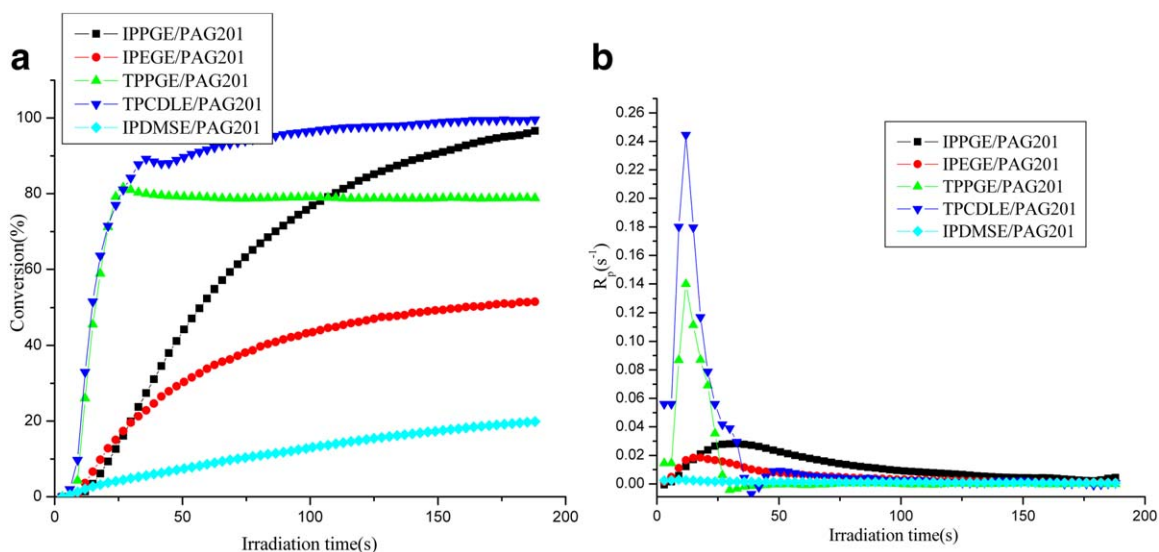


Figure 7. Effect of the oligomer structure on the photopolymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

studied. This showed that ITX affected the efficiency of the initiators. ITX decreased the efficiency of PAG201 (in Figure 8, the curing rate peak of IPPGE-2 with PAG201 mixed with ITX as an initiator appeared at 23.8 s, and the maximum curing rate was $0.57\% \text{ s}^{-1}$). Because PAG201 and ITX both absorbed at 300 nm, they would compete for photons. These results are in agreement with the previously reported initiating efficiency of initiators, and this depends mainly on the quantum yield.^{11,30}

Effect of the Light Intensity on the Photopolymerization of Oligomers

During the photopolymerization process, the appropriate light source is essential to UV curing. A simultaneous increase in the rate and the final conversion was achieved with an increase in the light intensity. Figure 6 shows the oligomer synthesized with IPDI(I), PPG400(PPG) and HEVE(E), with the feed ratio

of 3:2:2 (IPPEG-2) with PAG201 irradiated at different UV light intensities ranging from 30 to 100 mW/cm^2 . The polymerization started as soon as the UV light was switched on, and the R_p increased with an increase in the UV light intensity. The R_p increased by about six times with an increase in the UV light intensity from 30 to 100 mW/cm^2 [Figure 6(b)]. The R_p of photopolymerization depends on the UV light intensity.¹⁵ The final conversions were 90 and 95%, respectively, and this also increased with an increase in the UV light intensity [Figure 6(a)].

Effect of the Oligomer Structure on the Photopolymerization Kinetics

The use of different diisocyanates and diols will yield a series of polyurethanes with different structures; this can affect the photopolymerization. Peeters and Loutz³¹ studied the kinetics of photopolymerization; they suggested that R_p was directly

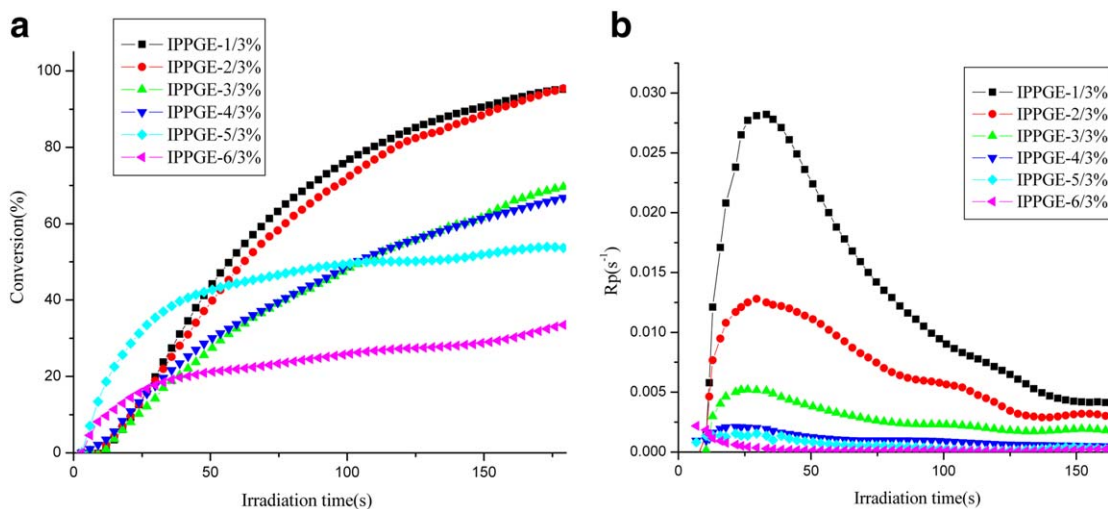


Figure 8. Effect of the chain length on the vinyl ether cationic photopolymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

proportional to the concentration of polymerization groups and could be affected by the polar group of the oligomers. From Figure 7, the final conversion followed the order TPCDLE > TPPGE > IPPGE-1 > IPEGE > IPDMSE. This order was consistent with the vinyl ether content (Table I). TPCDLE and TPPGE containing aromatic structures may increase the electron density on the vinyl ether double bond and promote them to undergo cationic polymerization. Figure 7 shows that the curing rate peak of TPCDLE appeared at 11.9 s, the maximum curing rate was 24.4% s⁻¹, and the final conversion also increased to nearly 100%, and the corresponding values of TPPGE were 11.9 s, 14.0% s⁻¹, and 80%, respectively. IPPGE had a higher final conversion compared with IPEGE because IPPGE contained a greater electron-releasing ability of methyl groups. Thus, IPPGE had a higher R_p and final conversion compared with IPEGE. IPDMSE was solid, and its chain was less flexible. In addition, it contained the lowest vinyl ether double-bond content; this may significantly reduce R_p and the final conversion.

Effect of the Chain Length on Photopolymerization

All of these oligomers had the same number of vinyl ether end groups but different double bond contents. Their UV-curing kinetics are shown in Figure 8. The maximum R_p and DC values of these oligomers are listed in the Supporting Information in Table SI. IPPGE-1, which had the lowest molecular mass, had the highest R^{\max} (2.82% s⁻¹) and DC (95.5%) values among these oligomers under the same irradiation conditions. As the molecular mass increased, the maximum R_p and DC decreased because the molecular mass increased, the vinyl ether double-bond content decreased, and this also resulted in a longer chain where the vinyl ether end group more easily folded. This affected the photopolymerization behavior. In addition, the viscosity of the oligomers also improved, which also affected UV curing.

CONCLUSIONS

Three UV-curable vinyl ether functionalized polyurethane oligomers were synthesized with different double-bond densities and partial chain structures. This altered their cationic photopolymerization behaviors and thermal stability. The oligomers' photopolymerization kinetics, which are characterized by R^{\max} and the final conversion, were substantially affected by the vinyl ether double-bond content and aromatic structures. The highest R^{\max} and final conversion values were obtained for TPCDLE, which possessed the highest double-bond density and aromatic ring. The concentration and types of cationic photoinitiator and the light intensity were also investigated. The results indicate that the optimum concentration of the cationic initiator was 3.0–4.0 wt %. When the reaction was initiated by PAG201, the oligomers achieved a maximum degree of photopolymerization with less time, and the degree of polymerization was higher. On the basis of the TGA data, these oligomers were all stable under 100°C, and the polyether polyurethane oligomers were more stable. Therefore, vinyl ether polyurethane oligomers are promising oligomers for the application of cationic UV curing to coatings, inks, and adhesives.

REFERENCES

1. Kayaman-Apohan, N.; Amanoel, A.; Arsu, N.; Güngör, A. *Prog. Org. Coat.* **2004**, *49*, 23.
2. Kayaman-Apohan, N.; Demirci, R.; Cakir, M.; Gungor, A. *Radiat. Phys. Chem.* **2005**, *73*, 254.
3. Xie, C.; Shi, W. F. *Prog. Org. Coat.* **2010**, *69*, 252.
4. Li, C. G.; Cheng, J.; Yang, F.; Chang, W. K.; Nie, J. *Prog. Org. Coat.* **2013**, *76*, 471.
5. Castell, P.; Wouters, M. *J. Appl. Polym. Sci.* **2007**, *106*, 3348.
6. Lewis, L. N.; Katsamberis, D. *J. Appl. Polym. Sci.* **1991**, *42*, 1551.
7. Liow, S. S.; Lipik, V. T.; Widjaja, L. K.; Abadie, M. J. *J. Polym. Res.* **2012**, *19*, 1.
8. Fang, Y.; Zou, Y. Q. *Polym. Int.* **2013**, *62*, 1624.
9. Wang, S. Y.; Zou, Y. Q. *J. Appl. Polym. Sci.* **2013**, *129*, 3325.
10. Dolez, P.; Marek, M. *J. Appl. Polym. Sci.* **2001**, *8*, 546.
11. Yagci, Y.; Jockusch, S.; Turro, N. *J. Macromolecules* **2010**, *43*, 6245.
12. Cho, J. D.; Kim, E. O.; Kim, H. K.; Hong, J. W. *Polym. Test.* **2002**, *21*, 781.
13. Lapin, S. C. *Radiation Curing of Polymeric Materials*; American Chemical Society: Washington, DC, **1990**; Vol. 417, Chapter 26, p 363.
14. Decker, C.; Bendaikha, T. *Eur. Polym. J.* **1984**, *20*, 753.
15. Tripathy, R.; Crivello, J. V.; Faust, R. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 305.
16. Sangermano, M. *Pure Appl. Chem.* **2012**, *84*, 2089.
17. Crivello, J. V.; Lee, J. L.; Conlon, D. A. *Radiation Curing VI: Conference Proceedings*; Association for Finishing Processes: Chicago, **1982**; p 4.
18. Lapin, S. C. *Radcure'86: Conference Proceedings*; Association for Finishing Processes: Baltimore, MD, **1986**; p 15.
19. Hiroshi, I.; Frances, A. H.; Mark, W. H. *Proc. SPIE* **2006**, *6153*, 1A.
20. Putzien, S.; Louis, E.; Nuyken, O.; Crivello, J. V.; Kühn, F. Z. *J. Appl. Polym. Sci.* **2012**, *126*, 1188.
21. Diao, C.; Zou, Y. Q. *Proc. SPIE* **2011**, *7972*, 79721R.
22. Wang, J. G.; Zou, Y. Q. *J. Appl. Polym. Sci.* **2013**, *127*, 4850.
23. Fang, Y.; Zou, Y. Q. *Proc. SPIE* **2011**, *7972*, 79722B-1.
24. Xiao, S. Z.; Zou, Y. Q. *Chem. Res. Chin. Univ.* **2011**, *02*, 383.
25. Javni, I.; Petrovic, Z. S.; Guo, A.; Fuller, R. *J. Appl. Polym. Sci.* **2000**, *77*, 1723.
26. Asif, A.; Huang, C.; Shi, W. *Colloid Polym. Sci.* **2004**, *283*, 200.
27. Ni, B. L.; Yang, L. T.; Wang, C. S.; Wang, L. Y.; Finlow, D. E. *J. Therm. Anal. Calorim.* **2010**, *100*, 243.
28. Grant, D. H.; Grassie, N. *Polymer* **1960**, *1*, 445.
29. He, Y.; Xiao, M.; Nie, J. *Polym. Int.* **2007**, *56*, 1292.
30. Ivanov, V.; Decker, C. *Polym. Int.* **2001**, *50*, 113.
31. Peeters, S.; Loutz, J. M. *Proceedings of Radtech, Asia*; Malaysian Institute for Nuclear Technology, Kuala Lumpur, Malaysia, **1999**; p 13.