Synthesis and Cationic Photopolymerization of Novel Monomers Based on Dicyclopentadiene

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A series of novel epoxide monomers and oligomers based on dicyclopentadiene (DCPD) were prepared using straightforward synthetic methodology. The differentiated reactivity of the two double bonds in DCPD makes it possible to conduct the addition of alcohols and silanes preferentially at the norbornenyl double bond. Epoxidation of these adducts afforded mono- and difunctional monomers bearing epoxycyclopentyl groups. These epoxide monomers display excellent reactivity in the photoinitiated cationic ring-opening polymerizations using diaryliodonium salt and other onium salt photoinitiators. The high reactivity of these novel DCPD monomers can be attributed to the high ring strain present in the epoxycyclopentyl ring system. Also prepared during the course of this work were two inorganic/organic hybrid systems in which epoxy DCPD moieties are placed as pendant groups onto a siloxane backbone. Photopolymerization of these oligomers also takes place very rapidly under UV irradiation conditions to yield glassy resin matrixes with very good thermal oxidative resistance.

Introduction

In a recent publication, we have described the synthesis, characterization, and photoinitiated cationic polymerization of a number of novel monomers that incorporate the dicyclopentadiene (DCPD) core.[1] Our motivation for this work was to determine whether cationically polymerizable dicyclopentadiene-based monomers bearing epoxy, vinyl ether, or both types of polymerizable functional groups would exhibit high reactivity in photoinitiated cationic polymerizations. We were able to definitively demonstrate that these monomers exhibit excellent photoresponse when irradiated with UV light in the presence of typical onium salt cationic photoinitiators such as diaryliodonium and triarylsulfonium salts. As a result of these studies, we became convinced that monomers based on DCPD possess reactivity compatible with their potential use in many thin, high-speed film applications such as photopolymerizable protective and decorative coatings, printing inks, and adhesives. Among the many advantages of photopolymerizations in these specific applications is their ability to produce fully polymerized, i.e., cured, network polymers very rapidly and without the use of polluting solvents by a brief, low-energy exposure to UV irradiation.

Especially attractive are the simple, facile, and high-yield methods that can be employed for the syntheses of cationically polymerizable epoxy DCPD monomers.[2,3] Some typical examples will be presented later in this paper. Last, the presence of the rigid, tetracyclic epoxy DCPD core in these monomers suggests that the resulting polymers will possess excellent rigidity, mechanical strength, and a high glass transition temperature. In addition, since the epoxy DCPD core has no absorption in the UV region, good mechanical properties may be obtained without the loss of photoresponse due to competitive absorption between the monomer and the onium salt photoinitiator.

Organic−inorganic hybrid monomers have received much attention in recent years and have been the subject of numerous papers and review articles.[4−6] In this laboratory, we have reported the preparation of a new class of highly reactive cationically photopolymerizable oligomers based on the hydrolysis of trialkoxysilane monomers bearing epoxycyclohexyl groups.[7,8] On the basis of our previous results and the above considerations, we have elected to continue our studies of the synthesis and reactivity of novel cationically photopolymerizable monomers and oligomers based on DCPD. This paper describes the preparation and results of kinetic study of cationic photopolymerization studies of several organic−inorganic hybrid monomers and oligomers containing the DCPD core.

Experimental Section

General Methods. Dicyclopentadiene, allyl alcohol, 3-chloroperoxybenzoic acid (*m*-CPBA), 1 bromopropane, benzyl alcohol, Amberlite IRA 400, and chlorotris(triphenylphos-

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* To whom correspondence should be addressed.

(1) Crivello, J. V.; Song, S. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3427.

(2) Gill, G. B. *Pericyclic Reactions*, Chapman and Hall: London, 1974; p 104.

(3) Bartlett, P. D.; Schneider, A. *J. Am. Chem. Soc.* **1946**, *68*, 6.

(4) Brinker C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: New York, 1990.

(5) Wenzel, J. *J. Non-Cryst. Solids* **1985**, *73*, 693.

(6) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.

(7) Crivello, J. V.; Mao, Z. *Chem. Mater.* **1997**, *9* (7), 1554.

(8) Crivello, J. V.; Mao, Z. *Chem. Mater.* **1997**, *9* (7), 1562.

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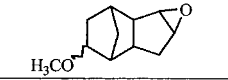
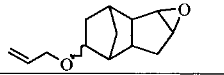
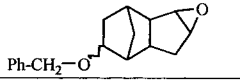
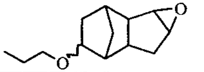
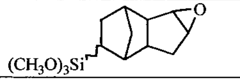
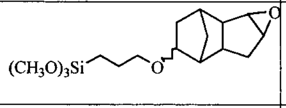
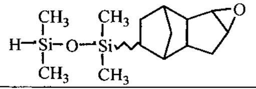
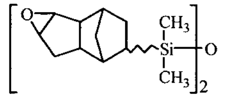
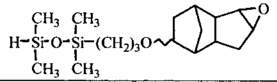
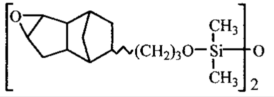
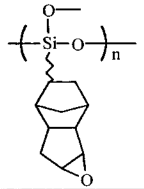
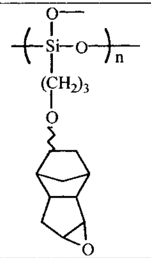
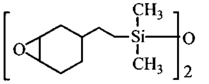
Table 1. Structures and Characteristics of DCPD Monomers and Oligomers

Notation	Structure	Yield (%)	Mp/Bp (°C/mm)	Elemental Analysis Calculated %C	%H	Found %C	%H
IIIa		53.5	90/ 07mm	73.30	8.95	73.40	8.79
IIIb		51.5	117/ 1.6mm	75.69	8.80	75.40	8.69
IIIc		66.7	161/ 0.45mm	79.65	7.86	79.48	7.85
IIId		71.3	120/ 1.9mm	74.96	9.68	73.86	9.60
V		33.2	132/ 0.4mm	57.74	8.20	57.84	8.10
VI		20.2	165/ 0.38mm	58.50	8.59	58.59	8.50
IX		25.8	119/ 0.30mm	59.52	9.28	59.72	9.25
X		52.8	75	66.92	8.89	66.69	8.86
XI		35.8	-	59.77	9.74	58.81	9.38
XII		28.3	-	65.89	9.22	64.64	9.10
XIII		-	-	57.32	6.21	57.52	7.94
XIV		-	-	58.45	7.12	61.95	8.13
XV		95	-	62.83	9.95	62.64	9.72

phine)rhodium(I) chloride were purchased from the Aldrich Chemical Co (St. Louis, MO). All the silanes employed in this investigation were purchased from the Gelest Co. (Tullytown, PA). 8-Hydroxytricyclo[5.2.1.$0^{2,6}$]dec-3-ene (hydroxy DCPD epoxide) was obtained as a sample from the Elf-Atochem Company (Blooming Prairie, MN). PC-1000 (1,3-bis[2-((3,4-epoxycyclohexyl)ethyl)]-1,1,3,3-tetramethyldisiloxane, **XV**) was received as a gift from the Polyset Co. (Mechanicville, NY). Photoinitiators (4-(*n*-undecyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC11**) and (4-(*n*-octyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC8**)[9] were prepared as described previously. Other reagents and solvents were used as received. Routine infrared spectra were obtained using a Midac-M1300 Fourier transform infrared spectrometer. Gas chromatographic (GC) analyses were preformed using a Hewlett-Packard 5890 gas chromatograph equipped with a 10 m 5% OV-17 phenylsilicone capillary column and a flame ionization detector. ^{1}H NMR experiments were carried out using either a Varian XL-200 (200 MHz) or an Inova-300 spectrometer at room temperature using $CDCl_3$ as the solvent and employing tetramethylsilane (TMS) as an internal standard. Thermal gravimetric analyses were carried out in air at a heating rate of 40 °C/min using a Perkin-Elmer (Stamford, CN) thermal analyzer equipped with a TGA-7 module. Gel permeation chromatography (GPC) was carried out with the

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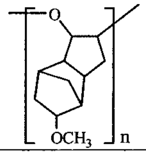
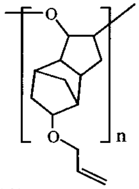
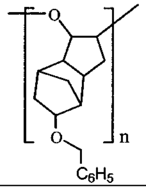
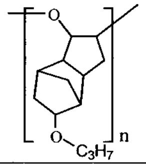
[9] Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3951.

Table 2. Molecular Weights of Linear Polymers Prepared by Photopolymerization

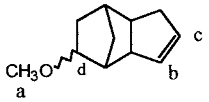
Structure	n	M_w	M_N	M_w/M_N
	30	5320	2400	2.2
	31	6440	2610	2.5
	15	3790	1970	1.93
	35	7480	2470	3.0

aid of a Hewlett-Packard gel permeation chromatograph equipped with a refractive index detector and a μ-styragel column (particle size 5 μm, mixed 24−34 Å pores). THF was used as the eluent at a flow rate of 1.0 mL/min. Elemental analyses (EA) were performed by Atlantic Microlabs, Norcross, GA.

Synthesis of Monomers and Model Compounds. Table 1 gives the structures, melting points or boiling points, and the results of the elemental analyses of the key model compounds, monomers, and oligomers prepared during the course of this investigation. Representative experimental procedures are given for compounds **IIa** and **IIIa**. Details of the synthesis of all the other compounds together with their characterization are given as Supporting Information to this article. Due to the presence of multiple isomers in all cases and the consequent complexity of the ^{1}H NMR spectra, only the chemical shifts of key functional groups are reported. Coupling constants for the resonances were not reported. The molecular weights of oligomeric compounds (Table 2) were determined by GPC and are reported relative to polystyrene standards. Because of the IUPAC names of the compounds being very complex (for example, **IIa** is 8-*exo*-methoxytricyclo-[5.2.1.0^{2,6}]dec-3-ene) and due to the presence in all cases of isomers, we have elected to use shortened names in the text.

Preparation of DCPD Methyl Ether (8-exo-Methoxytricyclo-[5.2.1.0^{2,6}]dec-3-ene) (IIa).[10]To 24.3 mL (0.6 mol) of methanol cooled in an ice-bath was added 2.2 mL (0.04 mol) of 96.2% sulfuric acid dropwise while the reaction mixture was stirred and maintained at a temperature between 5 and 20 °C. After addition was complete, dicyclopentadiene (DCPD), **I** (14.1 mL, 0.1 mol), was added gradually, and when this addition was complete, the mixture was heated and stirred in an oil bath, under reflux for 24 h. The reaction mixture was poured into 50 mL of 5% aqueous $NaHCO_3$, and the resulting oil was taken up in 60 mL of toluene. After separation of the organic layer, it was washed with 50 mL of water and then dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure, and the resulting oil subjected to further purification by vacuum distillation. Pure **IIa** was obtained as a colorless oil having a strong floral odor and a boiling point of 95°/13 mmHg. The yield was 11.97 g (72.9%) based on DCPD.

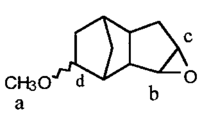
^{1}H NMR ($CDCl_3$, 200 MHz,δ (ppm)): 5.70−5.61 (m, 1H, H_c); 5.50−5.37 (m, 1H, H_b); 3.27 (s, 3H, H_a), 3.39−3.10 (m, 1H, H_d); 2.63−1.09 m, 10H).



Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.22; H, 9.75.

Synthesis of DCPD Methyl Ether Epoxide (9-exo-Methoxy-11-oxatetracyclo[6.2.1.0^{2,7}0.^{4,6}]undecane) (IIIa). Into a 250 mL round-bottom flask equipped with a magnetic stirrer, addition funnel, and thermometer was placed 17.5 g (0.073 mol) of 3-chloroperoxybenzoic acid (*m*-CPBA) dissolved in 166 mL of dichloromethane. The mixture was cooled in an ice bath, and 10.8 g (0.066 mol) of **II** in 76 mL of dichloromethane was added dropwise maintaining the temperature between 0 and 5 °C. After addition was complete, the reaction mixture was allowed to warm to room temperature and stirring continued for 24 h. The reaction mixture was filtered to remove the precipitated 3-chlorobenzoic acid and then poured into 60 mL of saturated aqueous $NaHCO_3$. The organic layer was separated, washed with distilled water, and dried over anhydrous Na_2SO_4, and then the solvent was removed using a rotary evaporator. DCPD methyl ether epoxide **VII** was isolated in 73.4% yield (8.74 g) as a colorless oil with a boiling point of 90 °C/0.7 mmHg.

^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 3.50−3.46 (m, 1H, H_c); 3.28 (s, 3H, H_a); 3.26−3.20 (m, 2H, H_b and H_d); 2.33−1.41 (m, 10H).



Anal. Calcd for $C_{13}H_{18}O_2$: C, 73.30; H, 8.95. Found: C, 73.40; H, 8.79.

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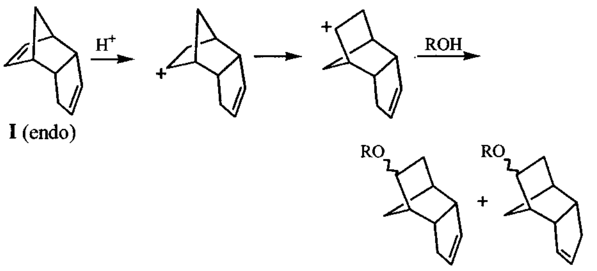
[10] Bruson, H. A.; Riener, T. W. *J. Am. Chem. Soc.* **1946**, *68*, 8.

Photopolymerization Studies Using Real-Time Infrared Spectroscopy (RTIR). Photopolymerizations of all the monomers and oligomers in this work were monitored using real-time infrared spectroscopy (RTIR). The method and apparatus employed in this analytical technique have been described in detail previously.[1] During this work, the decrease in the absorbance band due to the epoxycyclopentane groups at 837.2 cm^{-1} of the respective monomers and oligomers was monitored.

Results and Discussion

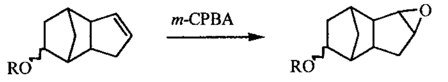
Design and Synthesis of Hybrid Monomers. The synthetic methods we have employed in this investigation for the preparation of monomers bearing the DCPD core take advantage of the fact that there is large difference in reactivity between the norbornene and cyclopentene double bonds present in DCPD. The greater reactivity of the norbornene double bond permits the regioselective functionalization of this site without involvement of the markedly less reactive cyclopentene double bond. This differentiated reactivity allows for the facile synthesis of monomers bearing two different functional groups. For example, the acid-catalyzed addition of alcohols to *endo*-DCPD occurs primarily at the more reactive norbornene double bond.[8] As shown in eq 1, the addition of alcohols to the commercially available *endo*-DCPD (**I**) takes place readily in the presence of sulfuric acid as a catalyst to give the *d,l-exo*-DCPD alkyl ethers, **IIa**−**d**.



(1)

IIa (R = CH_3)
IIb (R = allyl)
IIc (R = benzyl)
IId (R = propyl)

The ^1H NMR spectra of **IIa**−**d** show that these compounds consist of a mixture of all four possible diastereoisomeric *exo* isomers resulting from addition to both carbon atoms of the norbornene double bond. Due to the Wagner−Meerwein rearrangement shown in eq 1, the corresponding *endo*-DCPD isomers are probably absent in **IIa**−**d**. Yields of **IIa**−**d** are typically 80−90%. Direct epoxidation of **IIa**−**d** with 3-chloroperoxybenzoic acid give the epoxide model compounds and precursors **IIIa**−**d** in good yields.

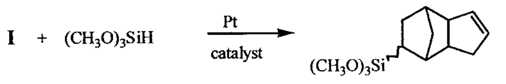


IIIa-d

(2)

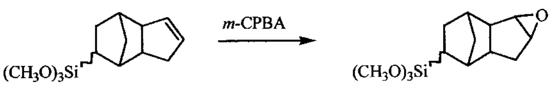
The epoxidation of these latter compounds introduces an additional chiral element that increases the number of possible isomers. There are 64 possible isomers of compounds **IIIa**−**d**. Due to the complexity of these mixtures and similarity of their boiling points, no attempt was made to isolate and purify any given isomer. Rather, in this paper the entire isolated isomeric mixture is represented by a single structural formula and this mixture employed directly in the subsequent cationic photopolymerizations and kinetic studies.

Similarly, the platinum-catalyzed regioselective addition of trimethoxysilane to DCPD affords **IV** in high yield (eq 3). Subsequent epoxidation (eq 4) of **IV** with *m*-CPBA yields the desired monomer precursor. **V** bearing both epoxide and trimethoxysilane groups. This latter reaction takes place without appreciable hydrolysis of the trialkoxysilane group.



IV

(3)



V

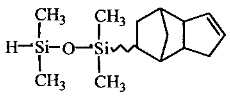
(4)

An analogous reaction sequence shown in eq 5 was carried out for the preparation of **VI**.

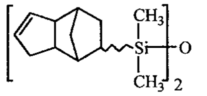
VI

(5)

The hydrosilation of **I** with 1,1,3,3-tetramethyldisiloxane (TMDS) was carried out in a regioselective manner in the presence of Wilkinson's catalyst [$(C_6H_5)_3P)_3Rh(I)Cl$] to afford the monosubstituted derivative **VII** in high yield.[11] Alternatively, the reaction was run to give the disubstituted compound **VIII**.

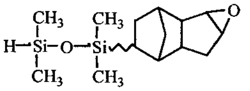


VII

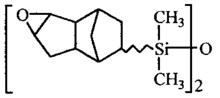


VIII

Subsequent epoxidation of these compounds yields respectively mono- and diepoxides **IX** and **X**.

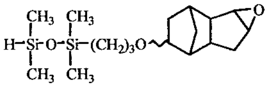


IX

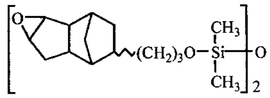


X

In a similar manner, compounds **XI** and **XII** were prepared by the rhodium-catalyzed condensation of TMDS with **IIb** followed by epoxidation.



XI



XII

Last, the straightforward ion exchange resin catalyzed hydrolysis of monomers **V** and **VI** gave epoxy pendant functional oligomers **XIII** and **XIV**.[7]

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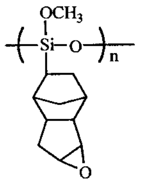
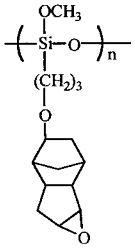
(11) Crivello, J. V.; Bi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31* (11), 2729.



XIII



XIV

It should be noted that the structures of the inorganic–organic hybrid oligomers shown above and in Table 1 are "idealized" and that the actual materials are highly complex mixtures that incorporate both linear as well as highly condensed ring containing repeat units. Although nominally the trialoxysilane groups in the starting materials are trifunctional, hydrolysis/condensation proceeds to give colorless, viscous, soluble oligomers.

Cationic Photopolymerization Studies. Since the photoinitiated cationic polymerizations of the monomers investigated in this study were found to be very rapid, we have elected to monitor the course of these polymerizations using real-time infrared spectroscopy (RTIR). RTIR was pioneered by Decker and Moussa,[12,13] and we[14,15] have reported the use of this technique for the determination of the rates of very rapid cationic photopolymerizations that are completed on a time scale of a few seconds. RTIR involves following in real-time the disappearance of specific infrared bands characteristic of the functional groups undergoing polymerization. The photopolymerization studies reported in this communication were conducted using the cationic photoinitiators (4-(*n*-undecyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC11**) and (4-(*n*-octyloxy)phenyl)-phenyliodonium hexafluoroantimonate (**IOC8**) at concentrations of 0.01–1.0 mol % per epoxy functional group present. Both of these photoinitiators were soluble in all the monomers studied and have high quantum yields ($\Phi = 0.5-0.7$).[16] The monomers and oligomers were coated onto a thin polypropylene film, covered with another film, and irradiated with UV light at room temperature. Simultaneously, the conversions of the epoxide functional groups to polymer were monitored by following the decrease in the intensity of the 837–839 cm^{-1} (epoxycyclopentyl) infrared absorption bands upon UV exposure as a function of time. Since many of these substrates were found to be highly reactive, it was found necessary to adjust the light intensity (420–1500 $\text{mJ/(cm}^2\cdot\text{min)}$) to slow the polymerization sufficiently to allow data collection and to facilitate direct comparison of the rates between various monomers.

To provide a baseline for a comparison of the various DCPD monomers prepared during the course of this investigation, the cationic epoxide ring-opening photopolymerizations of the four DCPD model compounds **IIIa–d** were conducted using **IOC11** as the photoinitiator. The results are shown in Figure 1. As may be gauged from inspection of the initial slopes of the four curves in this figure, these monomers display excellent reactivity. This reactivity can be ascribed to the presence of the strained epoxycyclopentyl ring in these monomers. Previously, we had shown that monomers containing epoxycyclopentyl groups exhibit approximately the same reactivity in photoinitiated cationic epoxide ring-opening polymerization as those with epoxycyclohexyl groups.[17] Among the monomers shown in Figure 1, the rates of polymerization as given by the slopes of the initial portion of the conversion versus time curves occurs in the order **IIIc** > **IIIb** > **IIId** > **IIIa**. Table 2 gives the molecular weights of the solid, linear polymers obtained by cationic photopolymerization of these epoxy functional DCPD monomers. The molecular weights were determined by GPC and are based on polystyrene standards. In all cases, bulk photopolymerization of these monomers takes place to give low molecular weight polymers. One reviewer has suggested and we concur that this is probably due to the presence of chain transfer. This would also account for the high conversions reached in the polymers derived from these monomers.

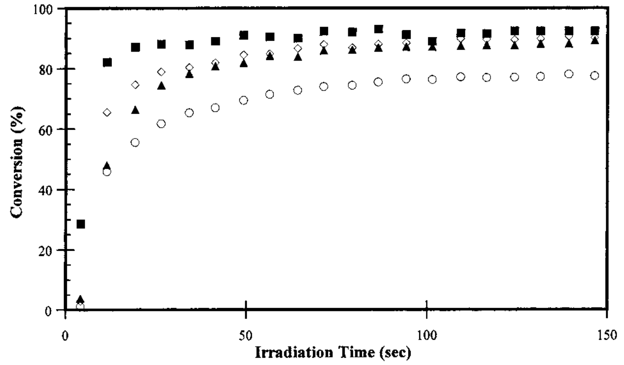


Figure 1. RTIR study of the cationic of ring-opening epoxide photopolymerization of **IIIa** (○), **IIIb** (◇), **IIIc** (■), and **IIId** (▲). Light intensity: 411 $\text{mJ/(cm}^2\text{ min)}$; 0.01% IOC10.

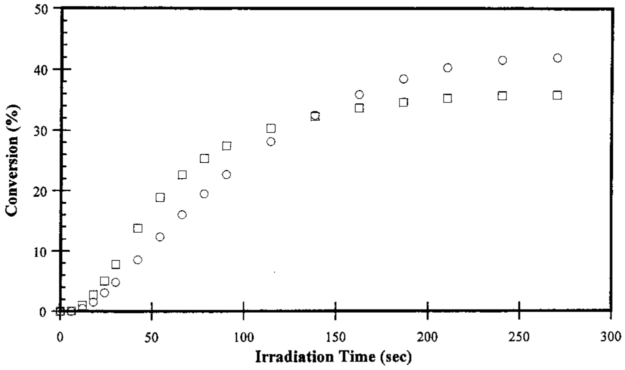


Figure 2. Comparison between the photopolymerizations of **IX** (□) and **XI** (○). Light intensity: 1500 $\text{mJ/(cm}^2\text{ min)}$; 1.0% IOC8.

Figure 2 gives a comparison of the polymerizations of related monomers **IX** and **XI** that contain both an epoxy DCPD group and a silicon–hydrogen bond conducted over a 5-min period of continuous irradiation. The behavior of these two monomers is very similar

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[12] Decker, C.; Moussa, K. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3429.

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[15] Crivello, J. V.; Löhden, G. *Chem. Mater.* **1996**, *8* (1), 209.

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[17] Crivello J. V.; Linzer, V. *Polimery* **1998**, *68* (11/12), 661.

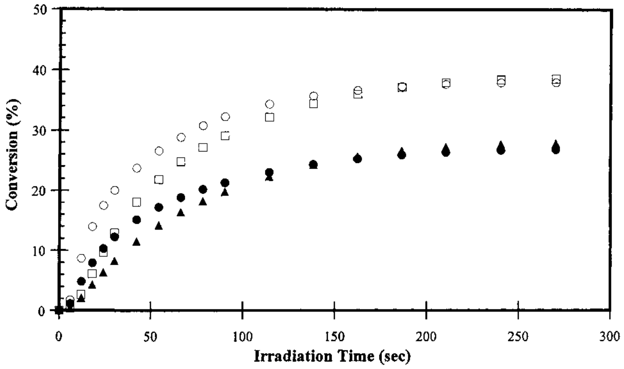

Figure 3. RTIR study of the cationic of ring-opening epoxide photopolymerization monomers **IX** (□), **X** (●), **XII** (▲), and **XV** (○). Light intensity: 1500 mJ/(cm^2 min); 1.0% IOC11.

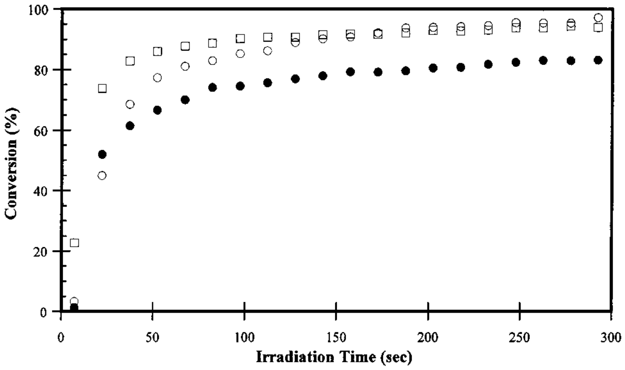

Figure 4. Comparative study of the photoinitiated cationic ring-opening polymerizations of **IIIa** (●), **V** (□), and **VI** (○). Light intensity: 421 mJ/(cm^2 min); 1.0% IOC11.

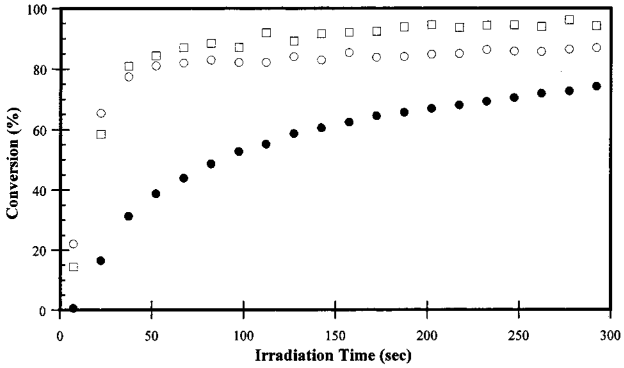

Figure 5. RTIR kinetic study of the cationic of ring-opening epoxide photopolymerizations of **V** (□), **XIII** (○), and **XIV** (●). Light intensity: 409 mJ/(cm^2 min); 2.0 wt % IOC11.

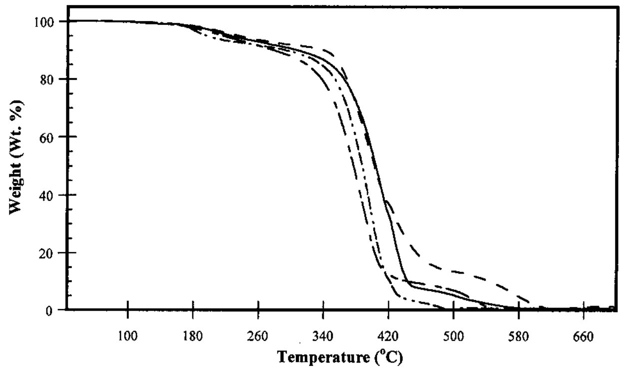

Figure 6. TGA analysis of polymers obtained from epoxy DCPD monomers **IIIa** (—), **IIIb** (— — —), **IIIc** (– – –), and **IIId** (– - - –) conducted at 40 °C/min in air.

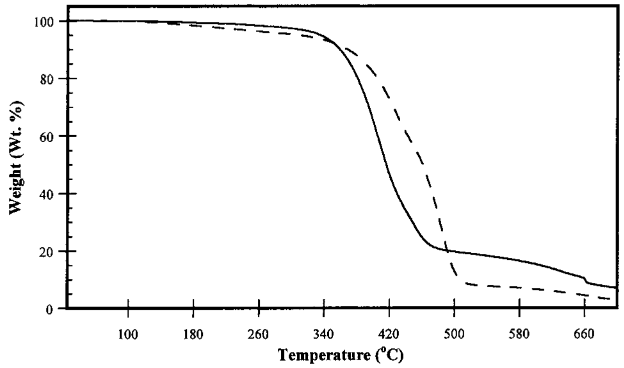

Figure 7. Comparisonof the thermal behavior of polymers derived from difunctional epoxy monomers **XV** (—) and **XII** (— — —) conducted at 40 °C/min in air.

even though **XI** contains an ether group that could serve as a competitive site for protonation.

In Figure 3 are compared the kinetic curves for monofunctional monomer **IX** and difunctional monomers **X** and **XII**. Also included in this figure is the corresponding conversion versus time curve for difunctional epoxycyclohexyl monomer, **XV**. All the monomers exhibit similar reactivity. In this series, monomer **XV** displays slightly greater reactivity than its difunctional DCPD epoxide counterparts. This is not surprising in light of the previous observations[18] that epoxynorbornane monomers are less reactive than their epoxycyclohexane counterparts due to the greater steric hindrance of the former compounds. Here, attack on the epoxycyclopentane ring during polymerization is also hindered due to steric influence of the bridge carbon of the neighboring norbornane ring.

Similar reactivity was observed for methoxy-substituted DCPD epoxide **IIIa** as for trimethoxysilyl-substituted analogues **V** and **VI** as is shown in Figure 4. The kinetic curves shown in this figure only depict the cationic polymerization of the epoxide groups. At the same time, the acid-catalyzed hydrolysis and condensation polymerization of the trimethoxysilyl groups also takes place in the presence of atmospheric moisture. The resulting polysiloxane—polyether polymers are insoluble due to cross-linking that occurs via this latter reaction. Another approach to the same types of inorganic—organic hybrid polymers consists of, first, hydrolyzing and condensing the trimethoxysilyl substituted monomers **V** and **VI** to give oligomers **XIII** and **XIV** and then carrying out the cationic ring-opening photopolymerization of the resulting epoxy-functional DCPD oligomers. The results of a RTIR study of the photopolymerization of **XIII** and **XIV** are shown in Figure 5. The photopolymerization of oligomer **XIII** takes place at nearly the same rate as its trimethoxysilyl precursor monomer, **V**. In comparison, the photopolymerization of oligomer **XIV** takes place at a somewhat slower rate. The reasons for the slower polymerization rate in this latter case are not understood at this time.

Thermal Stability of DCPD epoxide Polymers. Figures 6—8 show the results of a brief investigation of the thermal stability of polymers prepared by the photopolymerization of various monomers and oligomers prepared during the course of this work. All thermo-

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(18) Narayan, R.; Crivello, J. V. *Macromolecules*, **1996**, *29* (1), 433.

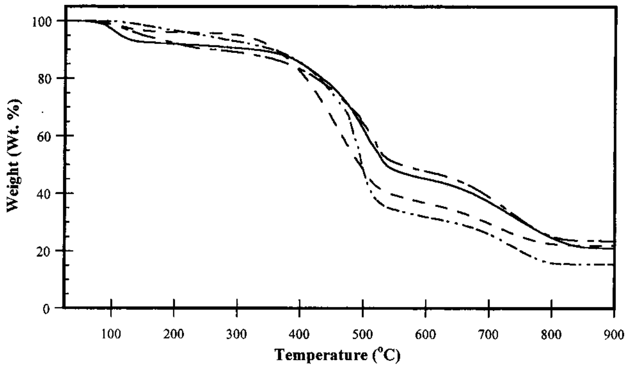

Figure 8. TGA analysis of polymers derived from trimethoxysilyl epoxy monomers **V** (—) and **VI** (— — —) with those derived from oligomers **XIII** (– - –) and **XIV** (– - - –). Analysis was carried out at 40 °C/min in air.

gravimetric analyses were carried out in ambient air at a heating rate of 40 °C/min. Monomers **IIIa–d** (Figure 6) display very similar thermal behavior under these conditions. There is a minor weight loss that occurs at approximately 200 °C. This is followed by rapid thermal decomposition at 400 °C.

Comparison between difunctional epoxy monomers **XII** and **XV** in Figure 7 shows that the thermal behavior of these two monomers is highly analogous. This was somewhat unexpected since the DCPD-derived epoxy monomer possesses several potential sites for facile oxidation including the linking ether group and the readily abstractable tertiary protons of the DCPD nucleus. Figure 8 shows the results of the thermal analysis of the polymers derived from the combined ring-opening and hydroysis-condensation polymerization of trimethoxysilyl-substituted monomers **V** and **VI**. Included for comparison are the curves for epoxy pendant oligomers **XIII** and **XIV**. Virtually the same behavior is noted for both types of materials. Apparently, efficient cross-linking present in these polymers provides excellent thermal stability and results in the formation of significant char formation at high temperatures.

Conclusions

Dicyclopentadiene is a convenient, inexpensive, and versatile substrate from which new monomers and oligomers for photoinitiated cationic polymerization can be constructed. This article reports the synthesis of several novel and potentially interesting high-reactivity epoxide monomers and oligomers that can be prepared from DCPD by the simple, straightforward synthetic methods outlined in this paper. Study of the photoinitiated cationic polymerizations of these materials revealed that epoxycyclopentane groups of these monomers undergo ring-opening polymerization at high rates and are comparable to those of analogous monomers containing the epoxycyclohexyl group. Thermal gravimetric analysis of the polymers derived from photopolymerization of the monomers and oligomers revealed that they display excellent stability when heated in air. We anticipate that these novel monomers may find considerable use in a variety of photocurable applications that require rapid photopolymerization rates.

Supporting Information Available: Text providing details of the syntheses of all compounds not already given in the Experimental Section together with their characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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