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Articles

Photopolymerization of Epoxides. A New Type of Photopolymerization with Photodecomposable Silyl Ether as Coinitiator

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ABSTRACT: A new type of photoinitiation catalyst for epoxides was found. Catalysts that have been reported before release strong inorganic acids; however, this new catalyst does not. The catalyst consists of an aluminum compound and *o*-nitrobenzyl triphenylsilyl ether that was newly synthesized. The reaction mechanism is proposed as follows: The *o*-nitrobenzyl triphenylsilyl ether photodecomposes to form triphenylsilanol. The photogeneration of the silanol was also newly found. The catalyst, which consists of an aluminum compound and the triphenylsilanol, initiates the polymerization of epoxides. Epoxides do not polymerize at all in the absence of UV light. Quantum yield of the photogeneration is 0.20 (at 365 nm). The photogeneration of the silanol was influenced by the wavelength and the structure of triarylsilyl ether; however, the photogeneration was independent of temperature. Photopolymerization was also influenced by the above conditions and the structure of the aluminum compound. The catalyst that consists of tris(ethyl-3-oxobutanoato)aluminum and 4-chloro-2-nitrobenzyl triphenylsilyl ether was the most active.

Introduction

Some photoinitiation catalysts for epoxide polymerizations are known.[1-3] For example, diazonium salts of Lewis acids are well-known.[1a-f] Recently, Crivello reported other new photoinitiation catalysts,[2a-g] namely, sulfonium salts and iodonium salts of BF$_4^-$, AsF$_6^-$, PF$_6^-$ and SbF$_6^-$. Photoinitiation mechanisms of these catalysts were also reported.[2h,i] These catalysts photodecompose to form strong inorganic acids that polymerize epoxides cationically. In this report, we call these catalysts "strong acid type catalyst". There was no report on "nonstrong acid type catalyst" except for Irie and Hayashi's work. Hayashi reports a unique photopolymerization without using catalysts that photogenerate strong inorganic acid.[3] Cyclohexene oxide was photopolymerized by pyromellitic acid anhydride at −78 °C. The polymerization was explained in terms of the donor–acceptor mechanism.[3] We found a new photoinitiation catalyst that initiates polymerization cationically; however, it belongs neither to the above strong inorganic acid catalysts nor to the donor–acceptor type catalysts. In this paper, the profile of the new catalyst, the photodecomposition and photopolymerization characteristics, and the mechanism are reported.

Experimental Section

Materials. Cyclohexene oxide, styrene oxide, cyclododecene oxide, cyclopentene oxide, butyl glycidyl ether, and phenyl glycidyl ether were used as the epoxy monomer. These compounds were dried over CaH$_2$, distilled, and stored in a nitrogen atmosphere. Tris(acetylacetonato)aluminum (Al(acac)$_3$), tris(ethyl 3-oxobutanoato)aluminum (Al(etaa)$_3$), tris(salicylaldehydato)aluminum (Al(sa)$_3$), and other aluminum compounds listed in Table II were synthesized by reacting triisopropoxyaluminum with each ligand.[4] *o*–Nitrobenzyl triphenylsilyl ether was newly synthesized as follows: 0.2 mol of triphenylchlorosilane and 0.2 mol of *o*-nitrobenzyl alcohol were dissolved in 500 mL of tetrahydrofuran. Dry triethylamine (0.2 mol) in 50 mL of tetrahydrofuran was added to the solution dropwise. The solution was refluxed for 2 h, the precipitate was removed, and the filtrate was concentrated. The residue was chromatographed over silica gel with toluene and recrystallized from chloroform–cyclohexane (1:1). Other new silyl ethers were also synthesized in the same way. Characterization of these silyl ethers was as follows (refer to Table I on the notation of the silyl ether):

H: ^{1}H NMR (CDCl$_3$) δ 5.30 (2 H, s, CH$_2$) 7.36–8.10 (19 H, aromatic proton); IR 3060, 2920, 1520, 1340, 1125 cm^{-1}; UV (CH$_3$CN) 221 (ϵ 29 000), 254 (5300), 257 (5700), 260 (6100), 265 (6200), 270 (5500), 306 nm (1700). Analysis: Found: C, 73.07; H, 5.22; N, 3.40. Calcd for C$_{25}$H$_{21}$NO$_3$Si: C, 72.97; H, 5.14; N, 3.47.

5-CH$_3$: ^{1}H NMR (CDCl$_3$) δ 2.41 (3 H, s, CH$_3$), 5.28 (2 H, s, CH$_2$), 7.22–8.02 (18 H, aromatic proton); IR 3050, 2850, 1540, 1435, 1120; UV (CH$_3$CN) 218 (ϵ 27 000), 253 (4400), 258 (5500), 264 (6500), 270 (6700), 278 nm (6200). 4-Cl: ^{1}H NMR (CDCl$_3$) δ 5.25 (2 H, s, CH$_2$), 7.32–8.08 (18 H, aromatic proton): IR 3060, 1535, 1434, 1120 cm^{-1}; UV (CH$_3$CN) 218 (ϵ 34 700), 252 (3600), 258 (4900), 263 (4700), 271 (3600), 306 nm (1500). Analysis: Found: C, 67.62; H, 4.31; N, 3.06; Cl, 7.88. Calcd for C$_{25}$H$_{20}$ClNO$_3$Si: C, 67.33; H, 4.52; N, 3.14; Cl, 7.95.

4,5-OCH$_3$: ^{1}H NMR (CDCl$_3$) δ 3.84 (3 H, s, OCH$_3$), 3.93 (3 H, s, OCH$_3$), 5.34 (2 H, s, CH$_2$), 7.36–7.69 (17 H, aromatic proton);

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IR 3050, 1510, 1320, 1280, 1085 cm^{-1}; UV (CH_3CN) 214 (ϵ 32 800), 221 (32 400), 242 (10 600), 265 (2300), 271 (2400), 297 (4300), 346 nm (6300). Analysis: Found: C, 68.45; H, 5.08. Calcd for $C_{27}H_{25}NO_5Si$: C, 68.77; H, 5.34.

Photolysis. The photolysis was carried out with a 400-W high-pressure mercury lamp (UVL 400H, Riko Kagaku Sangyo) or some low-pressure mercury lamps (UVL 10JA, UVL 30JA, and UVL 60JA). The lamp was surrounded by a water-cooled quartz photolysis well. Samples were placed in a "merry-go-round" holder that rotated about the lamp to provide even illumination during photolysis. The entire apparatus was immersed in a thermostated water bath at the specified temperature. The decomposition was measured by liquid chromatography with an ODS silica column. Methanol was used as solvent. The silica was pretreated with octadecylsilane. An apparatus that radiates a parallel UV light (collimated beam) (USHI-UI 501) was also used with a 400-W high-pressure mercury lamp. A UVD-36A filter was used for transmitting the light of 365 nm in all cases. The emission wavelength of UV light when the high-pressure mercury lamp and UVD 36A filter were used was almost entirely 365 nm with a small component of 313 nm. The ratio of intensity between 365 and 313-nm bands was 100:3. The intensity of UV light was changed in the following two ways: In Figure 1, photodecomposition was carried out by an apparatus that radiates a parallel UV light. The apparatus has a small hole in the path of the UV light in order to adjust the intensity of the light by changing the magnitude of the hole. There are four holes. I_0 means the relative UV intensity when the second hold from the smallest hole was used. In the experiment in Figure 4, a merry-go-round type UV radiation apparatus was used, and the UV intensity was varied by changing the low-pressure lamp, namely, 10-W (UVL 10JA), 30-W (UVL 30JA), or 60-W lamp (UVL 60JA).

Photopolymerization. The catalyst was dissolved in cyclohexene oxide in a nitrogen atmosphere in a quartz tube with a glass stopper. The UV radiation was carried out in the same manner as in the photolysis. After polymerization, a small amount of aniline was added into the polymerization system, followed by the removal of the unreacted monomer from the polymerization system under reduced pressure; the polymer was then washed with acetone and dried. The catalytic activity was measured by the polymer weight.

Analysis and Identification of Triphenylsilanol in the Photodecomposition Product. Two grams of *o*-nitrobenzyl triphenylsilyl ether in 10 mL of acetonitrile was irradiated by use of a merry-go-round type UV radiation apparatus with a 400-W high-pressure mercury lamp. After the photodecomposition of the silyl ether was completed, the triphenylsilanol was analyzed by gas chromatography. INIPOT-KS (Gasukuro Kogyo, Inc.) coated with silicone OV-17 was packed in a 2 m × 3 mm o.d. column. The column temperature was 290 °C.

The molecular weight distribution of the polymer in Table II was determined with a Toyo Soda Model 801 gel permeation chromatograph at 40 °C. The four columns were connected in series, each packed with G-2000H_8 × 3 and G 4000H_8 (Toyo Soda polystyrene gel), respectively. Tetrahydrofuran was used as solvent, and the instrument was calibrated to a first approximation with polystyrene standard of known molecular weights.

Quantum yields were measured with the method described in the literature.[5a–c] A merry-go-round type UV radiation apparatus was used. Silyl ether (1.20×10^{-2} mol) in acetonitrile was photodecomposed in a 10-mm quartz tube. The 365-nm light was transmitted through the UVD 36A filter by a high-pressure mercury lamp, as described under photolysis. The 254-nm light was transmitted by a low-pressure mercury lamp. Decomposition of silyl ether was measured by liquid chromatography, and photogeneration of silanol was measured by gas chromatography.

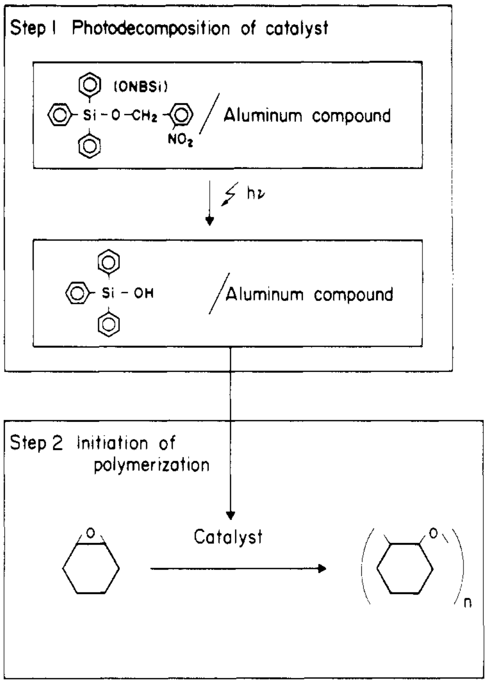
NMR spectra were measured by use of FX 90Q (JEOL).

Results and Discussion

Profile of the New Catalyst. The catalyst is a composite system. It consists of an aluminum compound and *o*-nitrobenzyl triphenylsilyl ether (ONBSi) that was newly synthesized.

The photopolymerization mechanism can be divided into two parts (Scheme I).

Scheme I
Mechanism of Photopolymerization

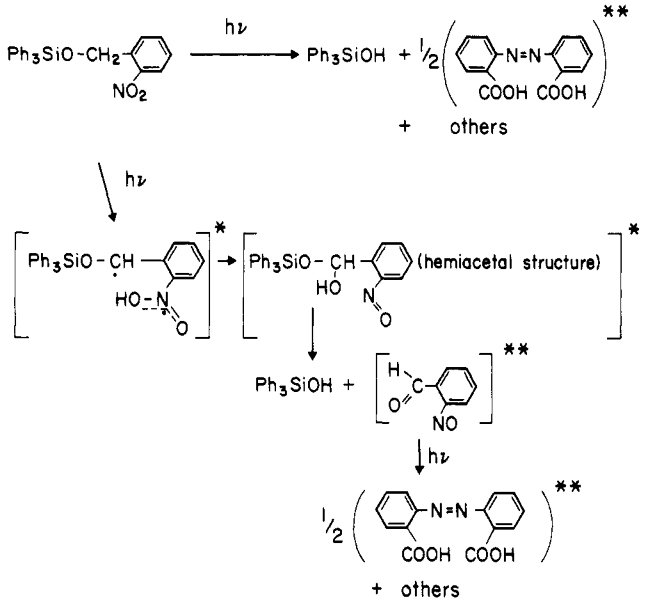


The first step is the photogeneration of silanol from the ONBSi. The second step is the polymerization of epoxides by the photogenerated catalyst. The second step proceeds even without UV light. The total reaction mechanism is as follows: The aluminum compound is stable under UV radiation; however, the ONBSi photodecomposes to form triphenylsilanol. The catalyst (AS catalyst), which consists of the aluminum complex and the triphenylsilanol produced by photodecomposition of ONBSi, initiated the polymerization of epoxides cationically. We have already reported that the AS catalyst polymerized epoxide cationically.[6a–c] The mechanism of the polymerization is proposed as follows.[6c] In the case of Al(etaa)$_3$/triphenylsilanol catalyst, at first part of Al(etaa)$_3$ reacts with a part of triphenylsilanol to form the compounds containing a Al–O–Si linkage. The reaction is a kind of ligand exchange. Here, the mole concentration of Al(etaa)$_3$ used is the same as that of the triphenylsilanol. Then, unreacted triphenylsilanol interacts with the compound containing Al–O–Si linkage. The O of SiOH, which is a kind of donor, coordinates with the Al of the Al–O–Si linkage, which is a kind of acceptor. The catalyst activity increased with an increase in the strength of the interaction. Because of the coordination, the H of the SiOH is polarized to form H^+, which polymerizes epoxides cationically.[6c] Therefore, the polymerization is greatly retarded by amines. The epoxides did not polymerize in the absence of either the aluminum compound or the ONBSi even if irradiated with UV light. The polymerization did not proceed at all in the absence of UV light even if both the aluminum compound and the ONBSi were present.

The photoinitiation consists of two reactions that were newly found by us. One of them is the photogeneration of triphenylsilanol from *o*-nitrobenzyl triphenylsilyl ether in step 1. The other is the polymerization of epoxide catalyzed by aluminum compound/organosilanol in step 2.[6a–c]

Photogeneration of Triphenylsilanol. Photogeneration of alcohol from *o*-nitrobenzyl ether has been used as a protection for hydroxy groups for peptide synthesis.[7b] However, photogeneration of silanol from *o*-nitrobenzyl

Scheme II
Proposed Reaction Mechanism of ONBSi Photodecomposition[a]



[a] Asterisk: intermediate inferred from ref 7g,i. Double asterisk: inferred from ref 7e.

silyl ether has not been reported.

The o-nitrobenzyl triphenylsilyl ether was newly synthesized by the reaction of triphenylchlorosilane with o-nitrobenzyl alcohol in the presence of triethylamine. The conversion of triphenylsilanol from ONBSi was 99.8%, as analyzed by gas chromatography after the complete photodecomposition of the ONBSi. Scheme II shows the possible reaction mechanism that was inferred from the report on photolysis of o-nitrobenzyl ether and oxidation of alkylbenzene by nitrobenzene.[7a-h] In this scheme, we identified only the triphenylsilanol, and the other species (intermediates or products) were inferred from the literature.[7e,g,h] The first step is the oxidation of the CH_2 group by a nitro group. To begin with, the o-nitrobenzyl group is excited by UV irradiation. According to the literature, the excited state may be $^{3}(\pi\text{–}P^{*})$[7h] or $^{3}(n\text{–}\pi^{*})$.[7g] An electron of the CH_2 group shifts to the nitro group to form a radical ion pair,[7g,i] and then the proton shifts from the CH_2 group to the nitro group. The nitro group is changed to -N(O)OH. The OH group shifts from N(O)OH to -CH-, which is converted to -CHOH-. This product has a hemiacetal structure. The hemiacetal smoothly decomposes to form triphenylsilanol. Nitrosobenzaldehyde is believed to be converted to azobenzene derivatives by UV radiation.[7b]

The quantum yield of the photolysis was 0.41 when the 254-nm light was radiated and 0.20 when a high-pressure mercury lamp with a UVD 36A filter that transmits light of 365 nm was used (see Experimental Section). As the conversion of triphenylsilanol from ONBSi was 99.8%, the photogeneration of triphenylsilanol was measured by the decrease of ONBSi. These values were almost the same as those reported in the case of other o-nitrobenzyl ether photodecomposition.[7f] Figure 1 shows the relation between the photogeneration rate and the intensity of the UV light. I_0 means relative intensity of the UV light. The photogeneration rate increased linearly with the increase in the intensity of the UV light. The photogeneration rate was unaffected by temperatures from 25 to 65 °C.

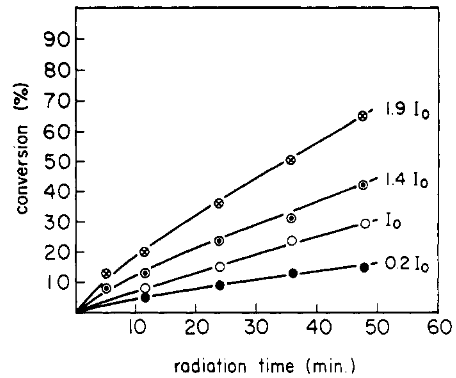


Figure 1. Photodecomposition of ONBSi at various intensities. ONBSi, 0.022 M in CH_3CN; 365 nm, I_0, relative UV intensity (see Experimental Section).

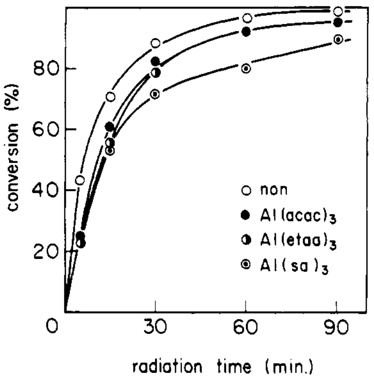


Figure 2. Photodecomposition of ONBSi in the presence of aluminum complex. ONBSi, 0.0258 M; aluminum complex, 0.012 M in acetonitrile; 400-W high-pressure mercury lamp.

Photodecomposition of the silyl ether was examined in the presence of various aluminum complexes because both silyl ether and aluminum complex are contained in the polymerization system and the aluminum complex may affect the photodecomposition behavior. The results are shown in Figure 2. The decomposition rate of ONBSi decreased in the following order when various aluminum complexes were present with ONBSi (a high-pressure mercury lamp was used without filter): no aluminum complex present > $Al(acac)_3$ > $Al(etaa)_3$ > $Al(sa)_3$

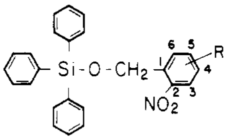
The decomposition rates of ONBSi under the 254-nm light and the 365-nm light in the presence of $Al(acac)_3$ were examined separately. The ratio of the photodecomposition rate in the presence of $Al(acac)_3$ to that in the absence of $Al(acac)_3$ was 34% under 254-nm light. In the case of 365-nm light, the ratio was 93%.

The reason the photodecomposition rate is affected by the structure of the aluminum complex and the wavelength of UV light could be explained by the fact that the absorption of the aluminum complex overlapped with that of ONBSi. The UV absorption of the $Al(sa)_3$ is greatest and that of $Al(acac)_3$ is weakest among them, and the overlap is larger at 254 nm than that at 365 nm.

The photodecomposition was also affected by the structure of the silyl ether. The results are shown in Table I. The introduction of methoxy groups to the benzene ring of the o-nitrobenzyl group decreased the quantum yield. In contrast, the introduction of a methyl or a chloro group to the benzene ring increased the quantum yield. The great decrease in the quantum yield when the methoxy group was introduced can be explained as follows: As mentioned before, the photodecomposition is considered to be initiated by an electron transfer from a benzyl CH_2 group to the nitro group.[7e] Therefore it is assumed that the difference of electron density between the CH_2 group and the nitro group in the excited state is important in order to explain the substitution effect. Namely, in the

Table I
Photodecomposition of Various Silyl Ethers

R	quantum yield1)	^{13}C-NMR chemical shift (ppm)2)		
		CH_2 [A]	$\dot{C}$-NO_2 [B]	[B]-[A]
H	0.20	62.87	146.69	83.82
5 Me	0.26	62.45	145.10	82.65
4 Cl	0.22	62.59	149.05	84.46
4,5 MeO	0.04	63.32	138.66	75.34



1) 365 nm, 2) $CDCl_3$

excited state, the higher the electron density of the methylene group and the lower the electron density of the nitro group is, the higher the photodecomposition rate is. Substituents introduced to the benzene ring of the *o*-nitrobenzyl group can affect the relative electron density of both the nitro group and the methylene group. Both variety of the substituent and the position of the substitution were presumed to be important. The relative electron density of the CH_2 group and the carbon bonded to the nitro group were assumed from ^{13}C NMR chemical shifts. The difference in the quantum yield should be explained in terms of the electronic character of the excited silyl ether. However, in this experiment, the difference in the quantum yield was explained in terms of the electronic character of the silyl compound in the ground state, namely, chemical shift values measured in the ground state, because it was presumed that the electron density of a compound in the excited state is also higher than that of others in the excited state if the electron density of the compound in the ground state is higher than that of others in the ground state. The presumption will be more probable when the electronic character of silyl ether in the ground state is greatly different from that of the others in the ground state. It was also reported that the electronic state of the ground state explained the increase in photoreduction rate when substituted alkylbenzenes were photoreduced by nitrobenzene.[7i-k] Introduction of a methoxy group to the benzene ring of alkylbenzene increased the photoreduction rate greatly. Table I shows chemical shift values of various silyl ethers. A remarkable change of the chemical shift was shown by introducing a methoxy group. The introduction of the methoxy group increased the chemical shift value of the CH_2 group and decreased the chemical shift value of the carbon bonded to the nitro group. This means that the electron density of the CH_2 group was decreased and that of the nitro group was increased by the introduction of a methoxy group, and the electron was difficult to shift from the CH_2 group to the NO_2 group. Because of this, the quantum yield could decrease in value.

Photopolymerization Characteristics. Table II shows the photopolymerization results. The catalyst activity of $\mathrm{Al(etaa)_3}$/ONBSi was varied greatly by the variation of epoxides used, as shown in Table II. Among them, the polymer conversion of cyclohexane oxide was excellent. Styrene oxide, cyclododecene oxide, and cyclopentene oxide polymerized more easily than butyl glycidyl ether and phenyl glycidyl ether.

The polymer yield of cyclohexene oxide increased with an increase in the amount of ONBSi; however, when the amount of the aluminum compound was varied, the yield showed a maximum value at the concentration of 0.02 mol % to cyclohexene oxide. This phenomenon can be explained in terms of the rate of the silanol photogeneration in the presence of the aluminum compound because the aluminum compound that absorbed UV light competes with silyl ether in the polymerization system. The amount of aluminum complex affected the rate of both steps 1 and 2 in Scheme I. The absence of the aluminum compound is best for effective photogeneration of the triphenylsilanol (step 1 in Scheme I); however, the aluminum compound is necessary for the initiation (step 2 in Scheme I). The concentration of aluminum compound when the catalyst system is most active can be obtained at the point of a good balance between the photogeneration rate of the silanol (step 1 in Scheme I) in the presence of aluminum com-

Table II
Photopolymerization of Epoxides with Aluminum Compound/Silyl Ether Catalyst

monomer	Al complex	mol %	ONBSi mol %	temperature (°C)	radiation time (min.)	yield (%)	M_w	M_n
CHO3)	$\mathrm{Al(etaa)_3}$	0.1	0.01	40	5	5	53000	28000
CHO3)	$\mathrm{Al(etaa)_3}$	0.1	0.02	40	5	9	53000	29000
CHO3)	$\mathrm{Al(etaa)_3}$	0.1	0.05	40	5	73	51000	28000
CHO3)	$\mathrm{Al(etaa)_3}$	0.5	0.02	40	50	10	43000	19000
CHO3)	$\mathrm{Al(etaa)_3}$	0.02	0.02	40	50	28	49000	28000
CHO3)	$\mathrm{Al(etaa)_3}$	0.005	0.02	40	50	25	54000	29000
CHO3)	$\mathrm{Al(etaa)_3}$	0.02	0.02	40	10	5	—	—
CHO3)	$\mathrm{Al(etaa)_3}$	0.02	0.02	51	10	39	—	—
CHO3)	$\mathrm{Al(etaa)_3}$	0.02	0.02	60	10	80	—	—
CHO3)	$\mathrm{Al(paa)_3}$1)	0.02	0.02	40	10	18	—	—
CHO3)	$\mathrm{Al(baa)_3}$2)	0.02	0.02	40	10	21	—	—
CPO4)	$\mathrm{Al(etaa)_3}$	0.1	0.5	65	100	53	—	—
CDO5)	$\mathrm{Al(etaa)_3}$	0.1	0.5	65	100	51	—	—
SO6)	$\mathrm{Al(etaa)_3}$	0.1	0.5	65	100	59	—	—
BGE7)	$\mathrm{Al(etaa)_3}$	0.1	0.5	65	100	23	—	—
PGE8)	$\mathrm{Al(etaa)_3}$	0.1	0.5	65	100	22	—	—
CHO3)	$\mathrm{Al(etaa)_3}$	0.1	0.5	65	10	98	—	—

400W high pressure mercury lamp. 1) $CH_3COCH_2COOCH_2CH_2CH_3$, 2) $CH_3COCH_2COOCH_2CH(CH_3)_2$, 3) cyclohexene oxide, 4) cyclopentene oxide, 5) cyclododecene oxide, 6) styrene oxide, 7) butyl glycidyl ether, 8) phenyl glycidyl ether.

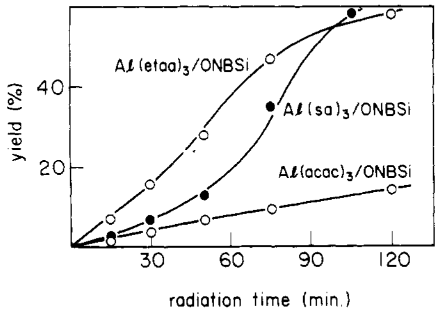


Figure 3. Photopolymerization of cyclohexene oxide with aluminum complex/ONBSi catalyst. 40 °C; aluminum complex, 0.02 mol %; ONBSi, 0.02 mol %; 400-W high-pressure mercury lamp.

pound and the rate of the initiation (step 2 in Scheme I).

Molecular weights of the polymer were all somewhat similar regardless of the irradiation time and the catalyst concentration. We have already reported that the molecular weight of poly(cyclohexene oxide) polymerized by tris(acetylacetonato)aluminum/diphenylsilanediol catalyst was almost independent of polymerization time.[6a] In the case of this photopolymerization, considerable chain-transfer reaction might also occur.

Figure 3 shows how the catalyst activity was varied by the structure of the aluminum compound. In the following explanation of Figure 3, polymerization before 30 min was called the "initial stage" and that after 60 min was called the "final stage". At the initial stage of the polymerization in Figure 3, the activity increased in the $Al(acac)_3 < Al(sa)_3 < Al(etaa)_3$. However, at the final stage, the activity was as follows: $Al(acac)_3 < Al(etaa)_3 < Al(sa)_3$.

The phenomena could also be explained in terms of (1) photodecomposition rate (step 1 in Scheme I) and (2) initiation rate (step 2 in Scheme I). The photodecomposition rate of ONBSi in the presence of the aluminum compound (step 1 in Scheme I) increased the $Al(sa)_3 < Al(etaa)_3 < Al(acac)_3$. However, the order of the initiation rate of cyclohexene oxide polymerization (step 2 in Scheme I) was as follows:[6c] $Al(acac)_3 < Al(etaa)_3 < Al(sa)_3$. The photopolymerization rate at the initial stage in Figure 3 will be affected by the photodecomposition rate of ONBSi mainly (step 1 in Scheme I), and the rate at the final stage in Figure 3 will be mainly affected by the initiation rate (step 2 in Scheme I).

In order to find a more active catalyst, the activity of some tris(alkyl 3-oxobutanoato)aluminums was examined. The results are shown in Table II. The introduction of an alkyl group into the alcohol group of the ester part increased the catalytic activity. Since the UV absorption of these aluminum complexes was the same as that of $Al(etaa)_3$, the increase in the catalytic activity can be explained in terms of the intiation rate. We have already reported that the catalyst activity of the aluminum compound/silanol catalyst is related to the interaction between the aluminum complex and silanol.[6c] We reported that the aluminum complex acts as a base and the silanol acts as an acid in this interaction. The introduction of an alkyl group increased the basicity of the aluminum complex slightly and thus increased the interaction strength. Because of this, the catalytic activity will be increased by the introduction of an alkyl group.

Figure 4 shows the polymerization characteristics when the UV intensity was varied. Polymer yield also increased with an increase in the strength of the UV light because the triphenylsilanol is photogenerated more rapidly: the higher the polymerization temperature, the faster the rate of the polymerization, as shown in Table II. Since the rate of the photogeneration (step 1 in Scheme I) is independent of temperature, the temperature dependence of the polymer yield can be explained by the fact that the polymerization rate (step 2 in Scheme I) is accelerated at higher temperature.

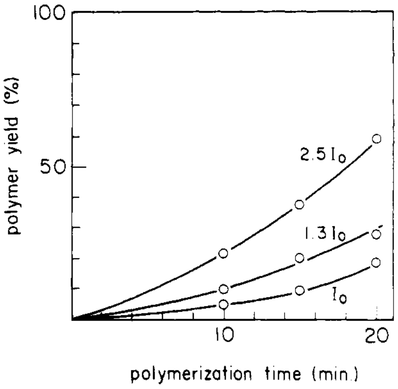


Figure 4. Dependence of polymer yield on UV intensity. Low-pressure mercury lamp; 40 °C; $Al(etaa)_3$, 0.02 mol %; ONBSi, 0.04 mol %; I_0, relative UV intensity.

Conclusion

A new, nonstrong acid type photoinitiation catalyst for epoxy compounds was found. The catalyst consists of an aluminum compound and *o*-nitrobenzyl triarylsilyl ether. The photodecomposition and photopolymerization were varied by the structures of the aluminum compound and silyl ether. The intensity and the wavelength of UV light also affected these reactions. The mechanism of the photoinitiation was also proposed.

Registry No. $Al(etaa)_3$, 15306-17-9; $Al(sa)_3$, 14325-56-5; $Al(paa)_3$, 15556-37-3; $Al(baa)_3$, 82847-33-4; *o*-nitrobenzyl triphenylsilyl ether, 88216-15-3; 5-methyl-2-nitrobenzyl triphenylsilyl ether, 97716-33-1; 4-chloro-2-nitrobenzyl triphenylsilyl ether, 98064-93-8; 4,5-dimethoxy-2-nitrobenzyl triphenylsilyl ether, 98064-94-9; poly(cyclodecene oxide), 98064-95-0; poly(cyclohexene oxide), 25702-20-9; poly(styrene oxide), 25189-69-9; poly(cyclopentene oxide), 26835-25-6; poly(butyl glycidyl ether), 25610-58-6; poly(glycidyl phenyl ether), 25265-27-4; tris(acetylacetonato)aluminum, 13963-57-0; triphenylchlorosilane, 76-86-8; *o*-nitrobenzyl alcohol, 612-25-9.

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Photoinitiated Interfacial Cationic Polymerization

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ABSTRACT: A new technique is reported for surface modification of polymers that is based upon photoinitiated cationic polymerization. The bulk, host sample is doped with a small amount of a cationic photoinitiator and exposed to radiation, thus creating a catalytic surface that, when exposed to an appropriate monomer, serves to initiate polymerization, thereby altering the surface properties of the bulk sample. The polymerization process is characterized by highly nonlinear growth kinetics. The effect of reaction variables on these kinetics has been explored and a molecular level model for the process is proposed.

In many applications of polymer materials, the chemical and physical properties of the surfaces are as important as the properties exhibited by the bulk material. This realization has stimulated several groups to develop methods for chemical modification of the surface of polymers.[1] The most common surface modification technique involves electron beam or γ irradiation of the sample followed by free radical initiated, graft polymerization.[2]

Surface modification via grafting reactions has been performed both in situ, by irradiation of the polymer surface in the presence of a reactive monomer, and by preirradiation followed by exposure to monomer in a subsequent step. The grafting reaction has, in turn, been carried out in two ways. Either the irradiated sample has been transferred in vacuo to a chamber in which the grafting reaction takes place[3] or it has been exposed to oxygen during or immediately after the irradiation. This latter process results in the formation of intermediate peroxides and hydroperoxides on the polymer surface which can be subsequently thermolyzed to form alkoxy radicals that function efficiently in the initiation of graft polymerization.[4]

Radiation-induced free radical graft polymerization has also been accomplished with UV light. Here, polymer samples were irradiated in a solution containing a vinyl monomer and a photosensitizer[5] or were irradiated after the surface of the sample was saturated with such a solution.[6] There are a few reports describing high-energy radiation-induced, ionic graft polymerization.[7,8] Evidence for an ionic mechanism is generally the successful grafting of a monomeric species, such as a vinyl ether, that is not prone to radical-initiated polymerization.

In the present work, we report a novel technique for surface modification of polymers that is neither grafting, in the usual sense, nor free radical in mechanism. We have studied a deposition technique that is based upon photoinitiated cationic polymerization. Here, the bulk sample is doped with a small amount of a soluble cationic photoinitiator. Exposure of the sample to UV light or high-energy radiation creates a strongly acidic surface due to radiolysis of the photoinitiator. After radiolysis, the sample is exposed to an appropriate monomer either in solution or in the gas phase. The photogenerated acid serves to initiate cationic polymerization of the monomer, thereby altering the surface properties of the bulk sample. An advantage of this technique is that the irradiated samples need not be handled in vacuo, UV exposures are routinely carried out in air and polymerization onto the surface from the gas phase has been successfully carried out hours after the exposure step.

The cationic photoinitiators that are most effective for this application are various onium salts. The existence of these onium salts has been known for nearly a century. The iodonium salts were first reported by Hartmann and Meyer in 1894[9] and the sulfonium salts first reported by von Halban in 1909.[10] Seventy years passed before the utility of these substances as cationic photoinitiators was realized. Now, a wide range of thermally stable photoinitiators based on diaryliodonium[11-13] and triarylsulfonium[14,15] salts of nonnucleophilic, complex metal halides have been prepared and tested. Irradiation of these compounds results in cleavage of a carbon-iodine[16] or carbon-sulfur[17] bond to generate a reactive radical cation. The radical cation abstracts hydrogen from its environment to ultimately form a stable, long-lived, strong Brønsted acid. The photogenerated acid can then be employed in the initiation of a variety of cationic polymerization processes. Although there are many monomer structures that undergo acid-catalyzed polymerization,[18] we have focused on simple vinyl ethers since these compounds are known to only undergo cationic or coordination polymerization and are inert to radical initiation.

The new surface modification technique is characterized by interesting and highly nonlinear polymer film growth kinetics. The film growth can be conveniently divided into three distinct phases. There is a short induction period, followed by rapid film growth, and finally a dramatic decrease or plateau in the polymerization rate. We have established a sensitive method for studying the kinetics of this process and have carried out experiments designed to provide insight into the factors that control the three stages of the reaction, i.e., the induction, the rapid growth region, and the plateau phenomenon.

Experimental Section

Materials. 2-Methoxypropene and *p*-methoxystyrene were purchased from Aldrich Chemical Co.; *p*-methoxystyrene was freed from inhibitor on a neutral aluminum oxide column before use, while 2-methoxypropene was used as received. Vinyl methyl ether, obtained from Matheson Inc., was also used as received. Poly(*p*-methoxystyrene) was prepared by free radical polymerization, purified by precipitation, and has $M_n = 68000$ and $M_w/M_n = 1.6$.

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