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Photopolymerization of Cyclohexene Oxide by the Use of Photodecomposable Silyl Peroxide. Aluminum Complex/Arylsilyl Peroxide Catalyst

Shuzi Hayase,* Yasunobu Onishi, Shuichi Suzuki, and Moriyasu Wada

Chemical Laboratory, Toshiba Corporation, Research and Development Center, Komukai Toshiba Cho, Saiwai Ku, Kawasaki 210, Japan.

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ABSTRACT: A new photoinitiating catalyst for epoxides was found. Catalysts that have been reported so far release strong inorganic acids, which this new catalyst does not produce. This new catalyst consists of an aluminum compound and triarylsilyl peroxide, some of which were newly synthesized. The reaction mechanism of this catalyst is proposed as follows: The arylsilyl peroxide was photodecomposed to form aryl silanol. Then the arylsilanol interacted with the aluminum compound and formed a cationic catalyst, which had been reported by the present authors. This composite catalyst initiated the polymerization of epoxides cationically. Epoxides did not polymerize in the absence of UV light. The arylsilyl peroxide was stable thermally below 150 °C. Quantum yields of the photodecomposition of various silyl peroxides were measured. The photogeneration of the arylsilanol was influenced by the wavelength, structure of arylsilyl peroxide, temperature, and solvent used. Photodecomposition products were analyzed, and the photodecomposition mechanism was proposed. The relationship between the structure of the silyl peroxide and the catalyst activity was also investigated. The catalyst having the highest activity was tris(ethyl 3-oxobutanoato)aluminum and tri-2-naphthylsilyl *tert*-butyl peroxide.

Introduction

Some photoinitiation catalysts for epoxide polymerization are known.[1-15] For example, diazonium salts of Lewis acids are well-known.[1-6] Recently, Crivello reported other new photoinitiation catalysts,[7-12] namely, sulfonium salts and iodonium salts of HBF_4, $HAsF_6$, HPF_6, and $HSbF_6$. Photoinitiation mechanisms of these catalysts and synthesis of sensitive sulfonium salts were also reported.[16-18] These catalysts photodecompose to form strong inorganic acids that polymerize epoxides cationically. Therefore, in this report, we call these catalysts "strong-acid catalyst".

The present authors already reported a new catalyst,[19] which is a "non-strong-acid catalyst". The catalyst consists of an aluminum compound and the photodecomposable organosilane, *o*-nitrobenzyl triarylsilyl ether (ONBSi). The photopolymerization mechanism has two steps. The first step was the photogeneration of silanol from the ONBSi. The second step was the polymerization of epoxides by the resultant catalyst, which consists of an aluminum compound and arylsilanol. The quantum yield when the silanol was photogenerated from the ONBSi was 0.21 using UV light (365 nm). In this type of catalyst, any organosilane can be used if the organosilane is photodecomposed to form organosilanol; however, it is necessary for the photodecomposable organosilane to be very stable at room temperature and be photodecomposed swiftly to form arylsilanol at a high ratio. We investigated the photodecomposition of silane in order to find a more photosensitive catalyst than ONBSi and discovered that "arylsilyl peroxide" photogenerated silanol more effectively and could be used for the coinitiators in the photopolymerization catalyst. In order to clarify the characteristics of the catalyst, several new arylsilyl peroxides were prepared, and the relation between the catalyst structure and the activity was examined.

In this paper, the profile of the new catalyst, the mechanism of photodecomposition, and the photopolymerization characteristics and mechanism are reported.

Experimental Section

Cyclohexene oxide was dried over CaH_2 and then distilled and stored under a nitrogen atmosphere. Tris(ethyl 3-oxobutanoato)aluminum ($Al(etaa)_3$) was synthesized by reacting triisopropoxyaluminum with ethyl acetoacetate.[20] Triphenylsilyl *tert*-butyl peroxide (3Ph-Bu), diphenylbis(*tert*-butylperoxy)silane (2Ph-2Bu) and triphenylsilyl cumyl peroxide (3Ph-Cu) were prepared by the method described in the literature.[21,22] 1-naphthyldiphenylsilyl *tert*-butyl peroxide (ANa2Ph-Bu), tris(4-chlorophenyl)silyl *tert*-butyl peroxide (3ClPh-Bu), tri-2-naphthylsilyl *tert*-butyl peroxide (3BNa-Bu), (2-methylphenyl)diphenylsilyl *tert*-butyl peroxide (MePh2Ph-Bu), and di-1-naphthylbis(*tert*-butylperoxy)silane (2ANa-2Bu) were newly prepared.

ANa2Ph-Bu was prepared as follows. All materials were distilled under N_2, and all experiments were carried out in N_2.

Method 1. 1-Naphthyldiphenylsilyl Chloride (ANa2Ph-Cl). 1-Naphthyl bromide (20.7 g) in 100 mL of dried tetrahydrofuran (THF) was added dropwise to 100 mL of dried THF in which 2.4 g of Magnesium was dispersed. After the addition was completed, the reaction mixture was stirred for 1 h at 50 °C. The reaction mixture was added to a solution of 25.3 g of diphenyldichlorosilane in 100 mL of THF and stirred for 2 h at 50 °C. Then, half the volume of THF was removed by boiling, and 300 mL of dibutyl ether was added in order to precipitate the salt. The mixture was heated gradually to 100 °C in order to remove THF completely. After the precipitate was removed off, the filtrate was concentrated. The residue was dissolved in toluene, insoluble matter was filtered off, and the filtrate was distilled under reduced pressure to obtain the fraction (bp 220–240 °C (0.5 mmHg)) in 30% yield. The synthesis of silyl peroxide from ANa2Ph-Cl was carried out by the same method previously reported.[22]

Method 2. 1-Naphthyldiphenylsilane (ANa2Ph-H). 1-Naphthylmagnesium bromide, which was prepared from 2.4 g of Mg and 20.7 g of 1-naphthyl bromide in 200 mL of THF, was added dropwise to 21.9 g of diphenylchlorohydrosilane in 200 mL of THF and stirred for 2 h at 50 °C. After the THF was removed, the residue was extracted with ether. The ether-soluble matter was distilled under reduced pressure to obtain the product in 73% yield.

1-Naphthyldiphenylbromosilane (ANa2Ph-Br). ANa2Ph-H (5.5 g) and *N*-bromosuccinimide (8.9 g) in 100 mL of CCl_4 was refluxed for 3 h. After insoluble matter was filtered off, the reaction product was concentrated to obtain the product in 85% yield. ANa2Ph-Br was reacted with *tert*-butyl hydroperoxide in the same way. The crude ANa2Ph-Bu was chromatographed over silica (Merck) with petroleum ether–dichloromethane (1:1): ^1H NMR($CDCl_3$) δ 1.18 (9 H, s, CH_3), 7.28–8.31 (17 H, aromatic proton); IR 3065, 2980, 1590, 1509, 1431, 1366, 1195, 1121 cm^{-1}; UV (CH_3CN) 205 (49300), 267 (5290), 275 (7280), 286 (8660), 296 nm (6150). Anal. Calcd for $C_{26}H_{26}O_2Si$: C, 78.35; H, 6.58. Found: C, 79.10; H, 6.71.

MePh2Ph-Bu was prepared in the same way as ANa2Ph-Bu: ^1H NMR($CDCl_3$) δ 1.17 (9 H, s, CH_3), 2.34 (3 H, s, CH_3), 7.14–7.71 (14 H, aromatic proton); IR 3050, 2980, 1590, 1430, 1365, 1195, 1130, 1119, 1110 cm^{-1}. Anal. Calcd for $C_{23}H_{26}O_2Si$: C, 76.20; H, 7.23; Si, 7.75. Found: C, 76.51; H, 7.36; Si, 7.08.

Preparation of 3BNa-Bu. Tri-2-naphthylsilane, which was synthesized from 2-naphthyl bromide and $HSiCl_3$, was brominated by the use of NBS and reacted with *t*-BuOOH in the same way as ANa2Ph-Bu. The 3BNa-Bu was chromatographed over silica with CH_2Cl_2–petroleum benzin (2:1): ^1H NMR (acetone-d_6) δ 1.22 (9 H, s, CH_3), 7.48–8.32 (21 H, aromatic proton); IR 3040, 2980, 1590, 1515, 1365, 1329, 1191, 1090 cm^{-1}; UV (CH_3CN) 269.5 (16100), 277.5 (15800), 308 (1700), 315 (1400), 323 nm (1658). Anal. Calcd for $C_{34}H_{30}O_2Si$: C, 81.93; H, 6.02; Si, 5.64. Found: C, 82.32; H, 6.59; Si, 5.22.

Preparation of 3ClPh-Bu. Tris(4-chlorophenyl)silane, which was formed from 4-chlorophenylmagnesium bromide and $HSiCl_3$, was brominated by NBS and then reacted with *t*-BuOOH. The crude 3ClPh-Bu was chromatographed over silica with petroleum benzin–$CHCl_3$(1:1): yield 75%; ^1H NMR (acetone-d_6) δ 1.12 (9 H, s, CH_3), 7.44–7.71 (12 H, aromatic proton); IR 2980, 1580, 1486, 1020 cm^{-1}; UV (CH_3CN) 259 (10200), 265.5 (11500), 270 nm (8790). Anal. Calcd for $C_{22}H_{21}Cl_3O_2Si$: C, 58.48; H, 4.68; Cl, 23.54. Found: C, 58.67; H, 5.00; Cl, 23.44.

Preparation of 2ANa-Bu. Di-1-naphthyldichlorosilane, which was prepared from 1-naphthylmagnesium bromide and $SiCl_4$, was distilled under reduced pressure and the fraction (bp 200–215 °C (0.5 mmHg)) was collected. The distillate was washed with petroleum ether. The di-1-naphthyldichlorosilane was reacted with *t*-BuOOH in the same way as ANa2Ph-Bu to obtain the product in 5% total yield. The crude 2ANa-2Bu was chromatographed over silica with petroleum benzin–CH_2Cl_2 (1:1): ^1H NMR (acetone-d_6) δ 1.22 (18 H, s, CH_3), 7.36–8.56 (14 H, aromatic proton); IR 3060, 2980, 2930, 1592, 1508, 1364, 1192 cm^{-1}, UV (CH_3CN) 277 (13800), 296 (13000), 300 (10400), 310 (24200), 314 (17100), 318 nm (10800). Anal. Calcd for $C_{28}H_{32}O_4Si$: C, 72.99; H, 7.02; Si, 6.10. Found: C, 71.92; H, 6.58; Si, 6.31.

Preparation of 3Ph-Cu. 3Ph-Cu was prepared from triphenylsilyl chloride and cumyl hydroperoxide in the same way as the case of 3Ph-Bu: ^1H NMR (acetone-d_6) δ 1.49 (6 H, s, CH_3), 7.31–7.70 (20 H, aromatic proton).

These silyl peroxides except for 3Ph-Cu had no shock sensitivity. 3Ph-Cu was somewhat shock sensitive. However, 3Ph-Cu was stable in solution.

Thermal Properties of Silyl Peroxide. Melting points and decomposition temperatures were measured by a Perkin-Elmer DSC-2C. The melting point listed here is the temperature during which an endotherm was detected when heat was given at the rate of 5 °C/min in N_2. Because of the rapid rise in temperature, the range of melting point was a little wider: 3 Ph-Bu, mp 56–62 °C and T_d (decomposition temperature) = 192 °C; 3Ph-Cu, mp 81 °C and T_d = 184 °C; 3ClPh-Bu, mp 87–88 °C and T_d = 194 °C; ANa2Ph-Bu, mp 88–92 °C, T_d = 180 °C; 2ANa-2Bu, mp 77–78 °C and T_d = 165 °C; 3BNa-Bu mp 97–115 °C and T_d = 215 °C; MePh2Ph-Bu, mp 42–56 °C and T_d = 180 °C; 2Ph-2Bu, liquid, T_d = 170 °C.

Preparation of Silanol. Silanols were prepared by reacting the arylsilyl bromides or chlorides with H_2O in the presence of aniline. A representative reaction condition was as follows: 9.9 g of tris(4-chlorophenyl)silyl bromide in 30 mL ether and 2.1 g of aniline in 30 mL ether were added dropwise to 0.4 g of H_2O in 100 mL ether at −10 °C. After the reaction mixture was stirred for 1 h at room temperature, the precipitate was removed and the filtrate was concentrated under reduced pressure. The crude tris(4-chlorophenyl)silanol(3ClPh-OH) was chromatographed over silica with CH_2Cl_2–petroleum ether (2:1): 3ClPh-OH, ^1H NMR($CDCl_3$) δ 1.42 (OH, s, 1 H), 7.24–7.55 (12 H, aromatic proton); IR 3200, 3030, 1555, 1468, 1387, 1133 cm^{-1}. Tri-1-naphthylsilanol (3ANa-OH): ^1H NMR($CDCl_3$) δ 3.20 (1 H, s, SiOH), 7.23–8.33 (21 H, aromatic proton); IR 3600, 3040, 1585, 1504, 1478, 1320 cm^{-1}. Di-1-naphthylsilanediol (2ANa-2OH): ^1H NMR(CD_2Cl_2–$CDCl_3$ = 1:1) δ 3.39 (2 H, s, SiOH), 7.28–8.26 (14 H, aromatic proton); IR 3560, 3140, 3040, 1585, 1428, 1322, 1218, 1148 cm^{-1}. 2-Naphthyldiphenylsilanol (ANa2Ph-OH): ^1H NMR($CDCl_3$) δ 2.70 (1 H, s, SiOH), 7.23–8.18 (17 H, aromatic proton); IR: 3300, 3030, 1586, 1505, 1428, 1112 cm^{-1}. *o*-Methylphenyldiphenylsilanol (MePh2Ph-OH): ^1H NMR($CDCl_3$) δ 2.49 (1 H, s, SiOH), 7.15–7.56 (14 H, aromatic proton), 2.32 (3 H, s, CH_3); IR 3280, 3040, 2980, 1587, 1426, 1116 cm^{-1}. Tri-2-naphthylsilanol: ^1H NMR($CDCl_3$) δ 1.72 (1 H, s, SiOH), 8.51–6.93 (21 H, aromatic proton); IR 3260, 3025, 1623, 1588, 1499, 1327, 1272, 1087 cm^{-1}.

Photolyses. The photolysis was carried out by use of a low-pressure mercury lamp (UVL 60JA). The lamp was surrounded by an air-cooled quartz photolysis wall. 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 using liquid chromatography with an ODS silica column. CH_3OH–H_2O (5:1) (v/v) was used as solvent. The silica was pretreated with octadecylsilane. An apparatus that emits collimated UV light (USHI-UI 501) was also used with a 400-W high-pressure mercury lamp.

Photopolymerizations. The catalyst was dissolved in cyclohexene oxide under a nitrogen atmosphere in a quartz tube with a glass stopper. The UV irradiation was carried out in the same way as 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, and the polymer was then washed with acetone and dried. The catalytic activity was measured by the polymer weight. Polymerization in the dark was carried out in the same way as the case of photopolymerization, except that the irradiation was omitted. Quantum yields were measured by the method described in the literature.[24-26] An apparatus which emits collimated UV light (USHIO-UI 501) was used through a KL25 filter (Toshiba Glass) that transmits 254-nm light. NMR spectra were measured by a JEOL FX 90Q spectrometer.

Photodecomposition Products. Silyl peroxide (2.0 g) in 100 mL of dry benzene was irradiated by using a 400-W high-pressure mercury lamp (UVL 400H). The lamp was surrounded by a water-cooled quartz photolysis wall. The lamp system was immersed in a reaction vessel that has a condenser and an N_2 inlet. The reaction vessel is a closed system, and silyl peroxide solution was introduced into the reaction vessel and then stirred magnetically while UV irradiation was carried out. The decomposition product was separated by use of 20 mm (diameter) × 250 mm (length) column packed with Nucleosil 5C18 (ODS silica). The eluent was methanol. H_2O was gradually mixed with the methanol up to CH_3OH–H_2O = 5:1. These fractions were analyzed by use of ^1H NMR and IR spectroscopies (FTS-20C) (Digilab) and gas chromatography–mass spectrometry (JMX-DX-300) (JEOL).

Relative Acidity of Various Silanols. Silanol (0.7×10^{-4} mol) was dissolved in 1 mL of $CDCl_3$ or acetone-d_6. The relative acidity was assumed from subtraction of chemical shift between SiOH in polar solvent and that in nonpolar solvent, namely,

Table I
Photodecomposition of Various Silyl Peroxides

abbrev	solvent	concn, M	temp, °C	quantum yield,[a] %	% silanol formed	% decompn peroxide
3Ph-Bu[c]	Bu_2O	1.6×10^{-2}	40	0.71[d]	80[b]	
3ClPh-Bu[c]	Bu_2O	1.6×10^{-2}	40	0.58[d]	61[b]	
ANa2Ph-Bu[c]	Bu_2O	1.6×10^{-2}	40	0.72[d]	78[b]	
3BNa-Bu[c]	Bu_2O	1.6×10^{-2}	40	0.83[d]	85[b]	
3Ph-Bu[c]	CH_3CN	1.2×10^{-2}	25		61[b]	
3Ph-Bu[c]	CH_3CN	1.2×10^{-2}	70		75[b]	
3Ph-Bu[e]	CHO[f]	1.2×10^{-2}	15			39
3Ph-Bu[e]	CHO[f]	1.2×10^{-2}	43			42
3Ph-Bu[e]	CHO[f]	1.2×10^{-2}	60			48
3Ph-Cu[e]	CHO[f]	1.2×10^{-2}	25			38
3Ph-Cu[e]	CHO[f]	1.2×10^{-2}	60			45
3Ph-Bu[g]	CHO[f]	1.1	40		100[h]	
3Ph-Bu[g]	acetone	1.1	40		100[h]	
3Ph-Bu[g]	toluene	1.1	40		93[h]	
3Ph-Bu[g]	xylene	1.1	40		99[h]	
3Ph-Bu[g]	CH_3CN	1.1	40		63[h]	
3Ph-Bu[g]	benzene	1.1	40		54[h]	
3Ph-Cu[g]	toluene	1.1	40		100[h]	
3Ph-Cu[g]	CH_3CN	1.1	40		61[h]	
2Ph-2Bu[i]	Bu_2O	1.5×10^{-2}	40			52
2ANa-2Bu[i]	Bu_2O	1.5×10^{-2}	40			28
3Ph-Bu	CH_3CN	1.2×10^{-2}	40			1.20%/min[j]
3Ph-Bu	CH_3CN	1.2×10^{-2}	40			1.29%/min[k]
3Ph-Bu	CH_3CN	1.2×10^{-2}	40			3.03%/min[l]

[a] Photogeneration of silanol. [b] Amount of silanol photogenerated/amount of silyl peroxide photodecomposed. [c] Collimated beam, KL 25 filter (254 nm). [d] Irradiation time, 120 min; conversion about 50%. [e] Merry-go-round type. [f] Cyclohexene oxide. [g] Merry-go-round type, (400-W high-pressure mercury lamp). [h] Rate of silanol from silyl peroxide when silyl peroxide was photodecomposed completely. [i] Irradiation time, 80 min. 2Ph-2Bu and 2ANa-2Bu were mixed in Bu_2O, and the mixture was photodecomposed in order to compare their photodecomposition rate relatively. [j] Relative intensity at 254 nm was 1.00. UVL 10JA low-pressure mercury lamp was used. [k] Relative intensity at 254 nm was 1.37. UVL 30JA low-pressure mercury lamp was used. [l] Relative intensity at 254 nm was 2.60. UVL 60JA low-pressure mercury lamp was used.

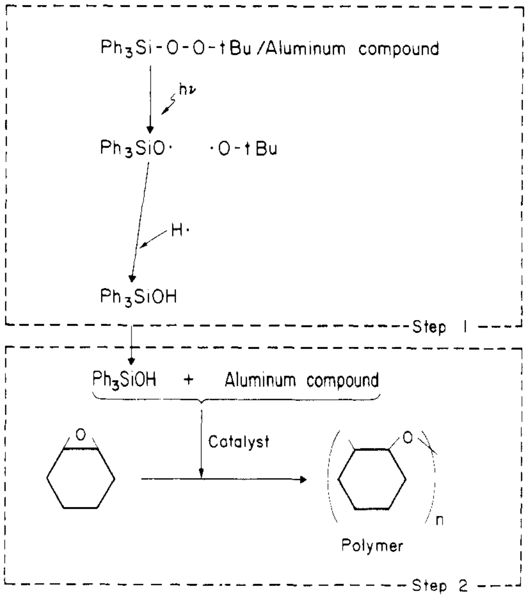
between chemical shift of SiOH in acetone-d_6 and that in $CDCl_3$.

Results and Discussion

Profile of the Catalyst. The catalyst is a composite system consisting of an aluminum compound and arylsilyl peroxide. Some of the arylsilyl peroxides described here were prepred for the first time. The photopolymerization mechanism can be divided into two steps.

The first step is the photogeneration of silanol from the silyl peroxide. The second step is the polymerization of epoxides by the photogenerated catalyst. The second step proceeds even in the absence of UV light. The total reaction mechanism is as follows: The aluminum compound is stable under UV radiation; however, the silyl peroxide photodecomposes to form the aryl silanol. The catalyst (AS catalyst), which consists of the aluminum complex and the arylsilanol produced by photodecomposition of silyl peroxide, initiates the polymerization of epoxides cationically. We have already reported that the AS catalyst polymerized epoxide cationically.[26-28] The mechanism of the polymerization is proposed as follows.[28] In the case of $Al(etaa)_3$/triphenylsilanol catalyst, first, a part of $Al(etaa)_3$ reacts with a part of triphenylsilanol to form the compounds containing Al–O–Si linkage. The reaction is a kind of ligand exchange. Here, the molar concentration of $Al(etaa)_3$ used is the same as that of arylsilanol. Then, unreacted arylsilanol interacts with the compound containing Al–O–Si linkage. The oxygen of SiOH, which is a kind of donor, coordinates with 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 hydrogen of the SiOH is polarized to form H^+, which polymerizes epoxides cationically.[26-28] Therefore, the polymerization is greatly retarded by amines. The epoxides were not polymerized in the absence of either the aluminum compound or the silyl peroxide, even irradiated with UV light. The polymerization did not proceed at all in the absence of UV light, even when both the aluminum compound and the silyl peroxide were present.

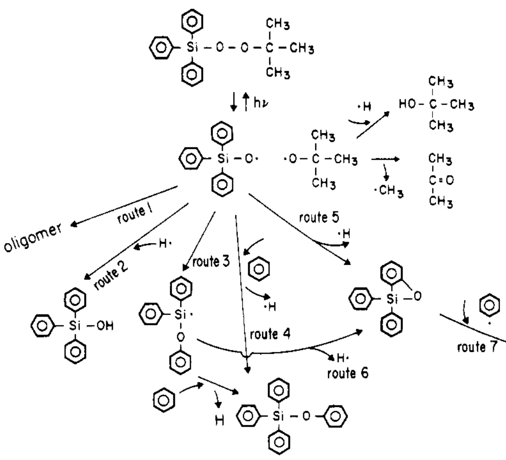
Scheme I
Reaction Mechanism



Arylsilyl *tert*-butyl peroxides were stable against heat and impact and had no explosive property. All arylsilyl *tert*-butyl peroxides were not decomposed up to about 160 °C, as described in Experimental Section.

Photogeneration of Arylsilanol. Triphenylsilyl hydroperoxide has been reported to thermally decompose to form triphenylsilanol, diphenylphenoxysilanol, and diphenylsiloxane oligomer.[29] The paper also reported that

Scheme II
Photodecomposition of 3Ph-Bu



triphenylsilyl hydroperoxide photodecomposed; however, there was no report about the photodecomposition product.

The authors found that arylsilyl peroxide photodecomposed to form arylsilanol more effectively than arysilyl peroxide thermally decomposed. The percentage of triphenylsilanol generated when 3Ph-Bu was completely photodecomposed varied depending on the solvent. These values are shown in Table I. When the photodecomposition was carried out in toluene, cyclohexene oxide, xylene, and acetone, the percentage of silanol formed was more than 90%. However, in the cases when benzene or acetonitrile was used, the value was very low. In the case of 3Ph-Cu, the percentage of silanol formed was also high when 3Ph-Cu was photodecomposed in toluene and low when photodecomposed in acetonitrile.

These values suggested that the percentage of silanol formed in the solvent from which hydrogen abstraction was more facile was larger than those solvents in which it was not. In order to examine the reason for the low value when silanol was generated in benzene, photodecomposition products in benzene were analyzed. As shown in Scheme II, acetone, *tert*-butyl alcohol, triphenylsilanol, triphenylphenoxysilane, (*o*-hydroxyphenyl)triphenylsilane, cyclic ether, and silane oligomers having a phenyl group were detected.

Scheme II shows the possible reaction mechanism. 3Ph-Bu photodecomposes homolitically at the O–O linkage. The *tert*-butyl radical forms acetone and *tert*-butyl alcohol. The silyloxy radical abstracts hydrogen radical from the solvent and forms triphenylsilanol (route 2). There are two possible mechanisms for triphenylphenoxysilane formation. One route is attack of the triphenylsilyloxy radical on benzene (route 4). The other route contains rearrangement, which forms silyl radical as reported in the literature.[29] When the silyl radical attacks benzene, triphenylphenoxysilane forms (route 3). The attack of silyl radical on benzene was already reported.[30] In the same way, cyclic silyl ether is formed by the attack of silyloxy radical onto the adjacent phenyl group (route 5) or by the attack of silyl radical, which is formed by the rearrangement, on the phenoxy group (route 6). (*o*-Hydroxyphenyl)triphenylsilane is probably formed when phenyl radical attacks the cyclic silyl ether (route 7). We do not have any idea on the structure of the siloxane oligomer formed by route 1, except that the yellow oligomer contains phenyl groups and has a molecular weight of about 1400. The oligomer may be formed by the consecutive reaction between a phenyl group bonded to Si and a silyl radical or a silyloxy radical. In a solvent in which hydrogen radical abstraction is facile, the percentage of silanol formed was high because route 2 is predominant. However in benzene, because of route 1, route 3, route 4, and route 5, which relate to the reaction between benzene and silyl radical or silyloxy radical, are competitive; therefore, the formation of silanol was probably retarded in benzene.

Scheme III
Photodecomposition of 3ClPh-Bu

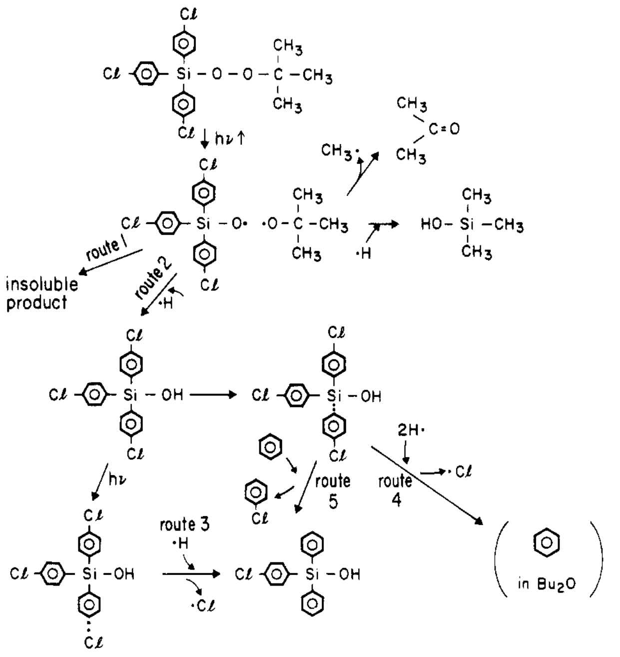


Table I gives the quantum yields of various silyl peroxides by photodecomposition to silanols. The quantum yield of 3BNa-Bu was highest and that of 3ClPh-Bu was lowest. 3Ph-Bu had almost the same value as ANa2Ph-Bu. 2ANa-2Bu and 2Ph-2Bu have two peroxide linkages in the molecule. 2ANa-2Bu, which has two 1-naphthyl groups, photodecomposed faster than 2Ph-2Bu. In this case, both monosilanol and silanediol were formed. The silanediol increased and the monosilanol decreased gradually in the course of photodecomposition.

In order to examine the lowest quantum yield of 3ClPh-Bu, the photodecomposition products were analyzed. When 3ClPh-Bu was photodecomposed in benzene, tris(4-chlorophenyl)silanol, bis(4-chlorophenyl)phenylsilanol, products which are insoluble in CH_3OH-H_2O (5:1) and nonvolatile up to 300 °C, acetone, and *tert*-butyl alcohol were produced. Possible reaction in benzene is shown in Scheme III. First, O–O bond cleaved homolitically. Tris(4-chlorophenyl)silanol was formed by the abstraction of hydrogen radical (route 2). Bis(4-chlorophenyl)phenylsilanol was formed by cleavage of the Cl–phenyl bond and abstraction of hydrogen radical (route 3). Bis(4-chlorophenyl)phenylsilanol might be formed by cleavage of the Si-phenyl bond, followed by reaction with benzene (route 5). When the photodecomposition was carried out in Bu_2O, benzene is formed. Benzene might be formed by cleavage of both the Si–phenyl bond and the Cl–phenyl bond (route 4). In the case of 3ClPh-Bu, there was a large amount of insoluble product compared with the case of 3Ph-Bu. Because of the Cl group, the reaction of 3ClPh-Bu is more complicated than that of 3Ph-Bu. That is the reason why the quantum yield of 3ClPh-Bu was lowest.

The photodecomposition rate increased with an increase in temperature, as shown in Table I, where, at these tem-

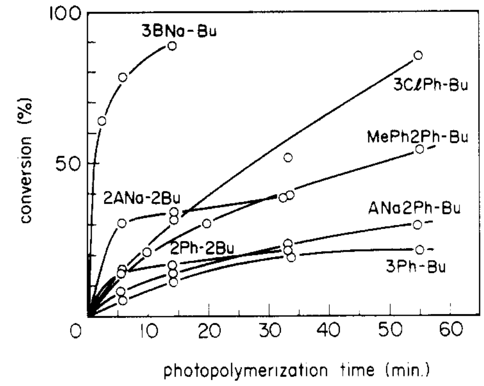


Figure 1. Photopolymerization of cyclohexene oxide with Al(etaa)$_3$/silyl peroxide. Photopolymerization conditions: 40 °C, 60-W low-pressure mercury lamp, merry-go-round type, 3.33 × 10^{-3} M Al(etaa)$_3$, 1.55 × 10^{-2} M peroxide, toluene–cyclohexene Oxide (10:35) (v/v).

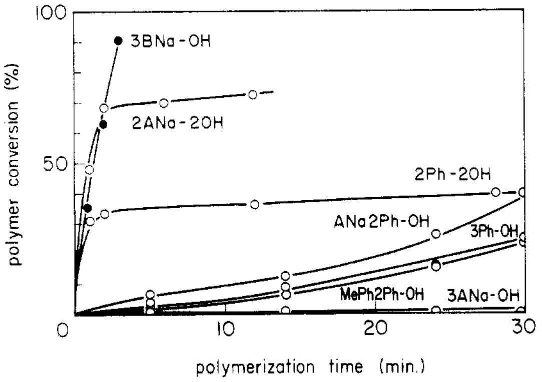


Figure 2. Polymerization of cyclohexene oxide with Al(etaa)$_3$/silanol in the dark. Polymerization conditions: 40 °C, 5.0 × 10^{-3} M silanol, 3.8 × 10^{-3} M Al(etaa)$_3$, toluene–cyclohexene oxide (1:3) (v/v).

peratures, any thermal decompositions were observed in the dark. It may be explained by a cage effect, namely, the O–O bond in 3Ph-Bu photodecomposes to form a silyloxy radical and recombines to form the O–O bond in a cage, and only the radical, which could escape from the cage, is involved in the next reaction. The rise of temperature may help the radical escape from the cage.

Table I also shows that the ratio of silanol photogeneration from silyl peroxide increased with an increase in temperature. The same trend was also observed on the photodecomposition of 3Ph-Cu, because abstraction of H radical (route 2) probably occurred more easily than other route at higher temperature.

Table I also shows the relation between the photogeneration rate and the intensity of the UV light. The photogeneration rate increased linearly with an increase in the intensity of the UV light.

Photopolymerization of Cyclohexene Oxide. Figure 1 shows the photopolymerization results of cyclohexene oxide when Al(etaa)$_3$/silyl peroxide catalyst was used. Figure 2 shows the polymerization results of cyclohexene oxide in the dark when Al(etaa)$_3$/silanol was used. The polymerization behavior in Figure 2 has a relation to the relative polymerization rate in Scheme II, step 2. The activity of Al(etaa)$_3$/3BNa-Bu was the best of all, because both quantum yield and the rate of step 2 in Scheme II were highest. It is also explained in the same reason that 2ANa-2Bu was more active than 2Ph-2Bu. The catalytic activity of 3Ph-Bu was almost the same as that of 3Ph-Cu. There was a large difference in polymer conversion between silyl peroxide with one peroxide unit and that with two peroxide units. In the case of the silyl peroxide with two peroxide units (2Ph-2Bu, 2ANa-2Bu), the polymerization almost stopped after fast polymerization, as shown in Figure 1. The same polymer conversion curve as that with Al(etaa)$_3$/2ANa-2Bu or Al(etaa)$_3$/2Ph-2Bu was seen when cyclohexene oxide was polymerized by Al(etaa)$_3$/2ANa-2OH or Al(etaa)$_3$/2Ph-2OH in the dark. Therefore, step 2 in Scheme II is responsible for the photopolymerization curve. According to our investigation on initiation mechanism, the proton in SiOH initiates polymerization, and SiO$^-$ is present as a counteranion in the cationic polymerization. In the case of silanediol, the silanolate anion adds easily to the cation site of the growing polymer chain and causes termination because bulkiness around Si is very small compared to the monosilanol.[26-28]

Table II
Relative Acidity of Silanols

silanol	SiOH chemical shift (ppm) CDCl$_3$ [A]	SiOH chemical shift (ppm) in acetone-d_6 [B]	[B] - [A]
ANa2Ph-OH	2.70	6.17	3.47
3Ph-OH	2.53	5.95	3.42
MePh2Ph-OH	2.49	5.87	3.38
3BNa-OH	1.72	6.32	4.60

The reason why the catalytic activity of Al(etaa)$_3$/3BNa-OH in the dark was highest was explained in terms of silanol acidity and bulkyness around Si. The relative acidity of silanol is summarized in Table II. The relative acidity was presumed from ^{1}H NMR chemical shift value, namely, the difference between the value measured in CDCl$_3$ and that measured in acetone. At larger differences of the chemical shift value, the acidity of the silanol was greater. ANa2Ph-OH had almost the same acidity as 3Ph-OH. The acidity of MePh2Ph-OH was slightly lower than that of 3Ph-OH because the electron-donating group, the CH$_3$ group, was bonded. 3BNa-OH showed the highest acidity because the naphthyl group had a much more electron-withdrawing character than a phenyl group and the 2-naphthyl group had almost the same bulkiness around SiOH as a phenyl group. On the contrary, 1-naphthyl group had more bulkiness because H in the 8 position is near the OH group; therefore, 3ANa-OH has no catalytic activity.

The photopolymerization rate when using MePh2Ph-Bu was higher than that when using 3Ph-Bu, although the corresponding silanols had almost the same initiation rate in dark. The methyl group that attached to the ortho position on the phenyl ring may improve the ratio of silanol photogeneration or photodecomposition rate because H of the methyl group is more easily abstracted and the ortho position is a suitable possition for an H shift from methyl group to silyloxy radical.

Conclusions

A new photopolymerization catalyst for epoxide was discovered. The catalyst consists of an aluminum compound and an arylsilyl peroxide. Arylsilyl peroxide photodecomposes to form arylsilanol in high conversion in solvents from which a hydrogen radical was easily removed; however, in solvents from which hydrogen radical was abstracted with difficulty, many byproducts were formed. From the reaction products, a photodecomposition mechanism was proposed. The photodecomposition rate and the initiation rate of polymerization were measured separately. Quantum yield was 0.58–0.83, which was higher than that of ONBSi. The order of catalyst concerning initiation catalytic activity was examined and explained by the structure of silanol, namely, bulkiness around SiOH and SiOH acidity. Tris-2-naphthylsilyl *tert*-butyl peroxide had the best photodecomposition rate and initiation rate.

Registry No. ANaCH-Cl, 65787-77-1; ANa2Ph-H, 100447-84-5; ANa2Ph-Br, 100447-85-6; ANa2Ph-Bu, 100447-86-7; MePh2Ph-Bu, 100447-87-8; 3BNa-Bu, 100447-88-9; 3ClPh-Bu, 94780-15-1; 2ANa-Bu, 100447-89-0; 3Ph-Cu, 31731-51-8; 3ClPh-OH, 18373-61-0; 3ANa-OH, 18919-22-7; 2ANa-2OH, 18676-77-2; ANa2Ph-OH, 100447-90-3; MePh2Ph-OH, 736-71-0; 3Ph-Bu, 18751-58-1; 2Ph-2-Bu, 15188-08-6; 3Ph-OH, 791-31-1; Al(etaa)$_3$, 15306-17-9; 2Ph-2OH, 947-42-2; HSiCl$_3$, 10025-78-2; *t*-BuOOH, 75-91-2; SiCl$_4$, 10026-04-7; 1-naphthyl bromide, 90-11-9; diphenyldichlorosilane, 80-10-4; diphenylchlorohydrosilane, 1631-83-0; 1-naphthylmagnesium bromide, 703-55-9; *N*-bromosuccinimide, 128-08-5; tri-2-naphthylsilane, 100447-91-4; 2-naphthyl bromide, 580-13-2; tris(4-chlorophenyl)silane, 6485-82-1; (4-chlorophenyl)magnesium bromide, 873-77-8; di-1-naphthyldichlorosilane, 18676-65-8; triphenylsilyl chloride, 76-86-8; cumyl hydroperoxide, 80-15-9; tris(4-chlorophenyl)silyl bromide, 18557-72-7; tri-2-naphthylsilanol, 100447-92-5; cyclohexene oxide, 286-20-4; cyclohexene oxide (homopolymer), 25702-20-9.

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Compatibility of Substituted Phenol Condensation Resins with Poly(methyl methacrylate)

John R. Pennacchia, Eli M. Pearce,* T. K. Kwei, Bernard J. Bulkin, and Jong-Pyng Chen

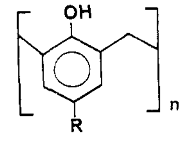
Polymer Research Institute, Polytechnic Institute of New York, Brooklyn, New York 11201, and Materials Research Laboratory, Industrial Technology Research Institute, Hsinchu, Taiwan. *Received June 25, 1985*

ABSTRACT: Polymer blends based on proton donor-acceptor interactions were used to study polymer miscibility. Four para-substituted poly[(1-hydroxy-2,6-phenylene)methylenes] (*o,o*-PHMP's), viz., the H, Cl, NO$_2$, and *tert*-butyl derivatives, were synthesized and blended with poly(methyl methacrylate) (PMMA). Hydrogen bond dissociation energies were determined by Fourier transform infrared spectroscopy (FT-IR) and interaction characteristics were determined by differential scanning calorimetry, (DSC). The hydrogen-bonding interaction between the various PHMP's and PMMA was manifested by a shift of ~25 cm^{-1} in the infrared stretching frequency of the carbonyl group. The acidic strength and size of the substituent on the PHMP have a direct effect on the hydrogen-bonding strength in the blend. Blends of all systems show single T_g's and their magnitudes indicate slightly stronger hydrogen-bonding interaction effects for the *p*-NO$_2$- and *p*-Cl-PHMP's.

Introduction

There is increasing interest in understanding specific interactions in polymer blends because they play an important role in achieving compatibility.[1-3] Hydrogen bonds based on proton donor-acceptor interactions have been credited to yield miscibility in many systems.[4] Compatibility may be investigated by Fourier transform infrared (FT-IR) spectroscopy[5] and differential scanning calorimetry (DSC)[6] as well as other techniques.

Various novolac resins have been previously found to be compatible with polymers containing ether, nitrile, sulfone, and carbonyl groups.[6] In this paper, four poly[(1-hydroxy-2,6-phenylene)methylenes] (*o,o*-PHMP's) were synthesized and characterized for blending studies with poly(methyl methacrylate) (PMMA). These studies were conducted to gain insight into the effect of the strength



o,o-PHMP