

at 80 °C for more than one week, adding more CAN during the reaction. Water (300 mL) was added, and the reaction mixture was extracted several times with CH₂Cl₂. The combined organic layer was washed successively with aqueous NaHCO₃ and water, dried (MgSO₄), and evaporated under reduced pressure. The crude product was chromatographed (SiO₂, benzene : Et₂O, 20 : 1) to give 30 mg (8.2%) of **10** and 10 mg (2.5%) of **11**; ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.15 (m, 23H, ArH), 2.37 (s, 3H, ArCH₃); EIMS m/z (relative intensity) 638 (22.3, M⁺), 578 (28.3), 386 (33.7), 282 (49.3), 236 (48.1), 148 (100); HRMS calcd for C₄₃H₂₆O₆ 638.1729, found 638.1077. **11**; IR (KBr) 3040, 2944, 1776, 1644, 1456, 1065, 1036, 1004, 988, 912, 748; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.25 (m, 23H, ArH), 5.11 (s, 2H, CH₂O), 2.05 (s, 3H, C=(O)CH₃); EIMS m/z 696 (M⁺).

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- Reduction of 4-methylphthalic anhydride with LAH followed by monobromination of the resulting 1,2-bis(hydroxymethyl)-4-methylbenzene with HBr in benzene gave rise to two isomeric benzyl alcohols, 2-(bromomethyl)-4-methylbenzyl alcohol and 2-(bromomethyl)-5-methylbenzyl alcohol, which were protected with dihydropyran in the presence of catalytic amounts of *p*-TsOH to give **1a** and **1b** (69% overall yield from 1,2-bis(hydroxymethyl)-4-methylbenzene).
- The precursor of the dilithio reagent **7**, bis(2-bromophenyl)methane was prepared by modification of the literature procedures: Lee, W. Y.; Park, C. H.; Kim, Y. D. *J. Org. Chem.* **1992**, *57*, 4074 and references therein.
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Photopolymerization of Methacrylic Acid with Disilanes

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Today photopolymerization technology applicable conveniently is extensively used on a commercial basis in the areas of surface coatings, photoresists, adhesives, and holography. A wide variety of unsaturated vinyl derivatives can be polymerized *via* a free-radical chain process, only a few unsaturated compounds will undergo chain photopolymerization with 250-500 nm wavelength light which is the most convenient wavelength range for experimental work.¹ Although the detailed mechanism forming the propagating radicals is not completely apprehended, it apparently involves the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.² The capability performing a thermodynamically feasible polymerization depends upon its kinetic feasibility on whether the process proceeds at a reasonable rate under a given set of reaction conditions. Hence, an initiator (or promotor) is often needed to attain the kinetic feasibility. In addition, a chain transfer agent is often used in controlling the molecular weights.

Hydrosilanes have participated in versatile catalytic reactions such as free radical reduction of organic halides,³ nucleophilic reduction of carbonyl compounds,⁴ dehydropolymerization,⁵ cross-dehydrocoupling with alcohols and amines,⁶ and hydrosilation of olefins.⁷ The hydrosilation has been also applied for the preparation of many interesting types of silicon containing dendrimers⁸ and copolymers.⁹ We reported the bulk photopolymerization of methyl methacrylate (MMA) with various silanes to produce poly(methyl methacrylates), poly(MMA)s containing the corresponding silyl moiety probably as an end group.¹⁰ We recently described the bulk photopolymerization of methacrylic acid (MA) with primary and secondary silanes.¹¹ In this paper we wish to report the bulk photopolymerization of MA with disilanes such as 2-phenyl-1,3-disilapropane (PhCH(SiH₃)₂) **1** and 1,2-diphenyldisilane (PhSiH₂SiH₂Ph) **2** giving poly(methacrylic acids), poly(MA)s containing the disilyl moiety presumably as an end group.

Experimental Section

Materials and Instrumentation. All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were used throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recor-

ded on a Bruker ASX 32 (300 MHz) spectrometer using DMSO- d_6 /DMSO- H_6 as a reference at 2.49 ppm downfield from TMS. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in THF and separately eluted from an Ultra-styragel GPC column series (sequence 500, 10^3 , 10^4 , 10^5 Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 570. Reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) of different concentration (c in g/dL) of polymer solutions in DMF were obtained by measuring three satisfactory readings of the efflux time (polymer, t ; solvent, t_0) with an Ostwald-Fenske viscometer immersed in the constant-temperature bath maintaining at 25 ± 0.01 °C and by substituting the mean of three readings into the known equations.¹² The extrapolation of the two viscosities to the same intercept as c approached to zero afforded the intrinsic viscosity $[\eta]$ in dL/g. Thermogravimetric analysis (TGA) of polymer sample was performed on a Perkin Elmer 7 Series thermal analysis system under a nitrogen flow (50 mL/min). The polymer sample was heated from 25 to 700 °C at a rate of 10 °C/min. TGA residue yield (for convenience' sake, read at both 400 and 600 °C) is reported as the percentage of the sample remaining after completion of the heating cycle. Differential scanning calorimetry (DSC) of the polymer sample was performed on a Perkin-Elmer 7 Series thermal analysis system under an argon flow. Polymer sample was heated at 20 °C/min. For the photolysis experiments a Raynot photochemical reactor (model RPR-2080) made by the Southern N. E. Ultraviolet Co., which has merry-go-round system in order to uniformly irradiate all samples, was used. The built-in monochromatic UV light sources (RUL-300 nm UV lamp; lamp intensity = 6.93×10^{18} hv mL⁻¹min⁻¹) was positioned approximately 17 cm from the reaction quartz tube. Methacrylic acid (Aldrich Chemical Co.) was saturated with NaCl (to remove the bulk of the water), then the organic phase was dried with CaCl₂ and distilled under vacuum before use. Disilanes 1 and 2 were kindly provided by Dr. I. N. Jung of the Korea Institute of Science and Technology and Prof. J. F. Harrod of McGill University, respectively.

Bulk Photopolymerization of MA with 1. Bulk photopolymerization of MA with different mole ratio of PhCH(SiH₃)₂ (10 : 1 and 7 : 3) was performed. In a typical experiment, a quartz test tube (1 cm × 20 cm) charged with MA (1.72 g, 20 mmol) and 1 (0.30 g, 2.0 mmol) was degassed, sealed, and irradiated with 300 nm UV-light for 6 h. The polymer was taken in methanol, precipitated in diethyl ether, filtered off, and dried to give 1.90 g (94%) of white solid (TGA residue yield at 400 and 600 °C: 62 and 10%, respectively). ¹H NMR (δ , DMSO- d_6 , 300 MHz): 0.9-1.1 (br, 3H, C-CH₃), 1.8-2.1 (br, 2H, CH₂), 7.1-7.4 (m, ArH), 12.3 (br, 1H, OH). The SiH resonance was not clearly observed in the ¹H NMR spectrum for uncertain reasons. IR (KBr pellet, cm⁻¹): 3400 br s (ν_{O-H}), 2163 w (ν_{Si-H}), 1705 s ($\nu_{C=O}$). Intrinsic viscosity: 0.64 dL/g. The polymers were extracted with toluene. Nothing was left after removal of volatiles at reduced pressure.

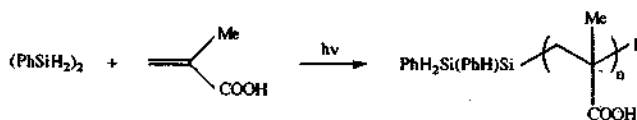
Bulk Photopolymerization of MA with 2. Bulk pho-

topolymerization of MA with different mole ratio of PhSiH₂SiH₂Ph (10 : 1 and 7 : 3) was carried out. The following procedure is representative of the polymerization reactions. A quartz test tube (1 cm × 20 cm) was loaded with MA (1.72 g, 20 mmol) and 2 (0.43 g, 2.0 mmol). The mixture was degassed, sealed, and UV-irradiated for 6 h. The polymer was dissolved in methanol, precipitated in hexane, filtered off, and dried to give 1.40 g (65%) of white solid (TGA residue yield at 400 and 600 °C: 62 and 19%, respectively). ¹H NMR (δ , DMSO- d_6 , 300 MHz): 0.9-1.1 (br, 3H, C-CH₃), 1.8-2.1 (br, 2H, CH₂), 7.2 - 7.6 (m, ArH), 12.3 (br, 1H, OH). The SiH resonance was not clearly shown in the ¹H NMR spectrum for uncertain reasons. IR (KBr pellet, cm⁻¹): 3400 br s (ν_{O-H}), 2132 w (ν_{Si-H}), 1692 s ($\nu_{C=O}$). For this sample the molecular weights were obtained with GPC instead of intrinsic viscosity because of its low molecular weight and its solubility in THF: $\bar{M}_w = 3400$, $\bar{M}_n = 2300$. The polymers were extracted with toluene. Nothing was found after removal of volatiles at vacuum.

Results and Discussion

The poly(MA)s containing 2-phenyl-1,3-disilapropyl moiety with intrinsic viscosities of 0.23-0.64 dL/g and TGA residue yields of 62-73% at 400 °C and 10-17% at 600 °C were prepared in 55-94% yields by bulk photopolymerization of MA with different mole ratio of 1 (MA : 1 = 10 : 1 and 7 : 3). The polymers were soluble in DMF, DMSO, and methanol. The characterization data of the resulting poly(MA)s are summarized in Table 1.

Bulk photopolymerization of MA with different mole ratio of 2 (MA : 2 = 10 : 1 and 7 : 3) produced the poly(MA)s containing 1,2-diphenyldisilyl moiety with weight average molecular weights of 2500-3400 and TGA residue yields of 62-74% at 400 °C and 19-30% at 600 °C in 37-65% yields.



The polymers were soluble in THF, DMF, DMSO, and methanol. The characterization data of the resulting poly(MA)s are listed in Table 2.

It is known that high-molecular-weight polymer is formed instantly and that the weight average molecular weight gene-

Table 1. Characterization of Photopolymerization of MA with 1^a

Mol ratio (MA : 1)	Yield (%)	Intrinsic viscosity ^b $[\eta]$	Relative intensity ^c IR (ν_{SiH})	% TGA residue yield at 400 °C
10:1	94	0.64	1.0	62 (10) ^d
7:3	55	0.23	1.5	73 (17) ^d

^aUV-irradiation for 6 h. ^bMeasured in DMF at 25 °C; unit, dL/g. ^cRelative ratio with respect to the intensity of ν_{SiH} (MA : 1 = 10 : 1). ^d% TGA residue yield read at 600 °C.

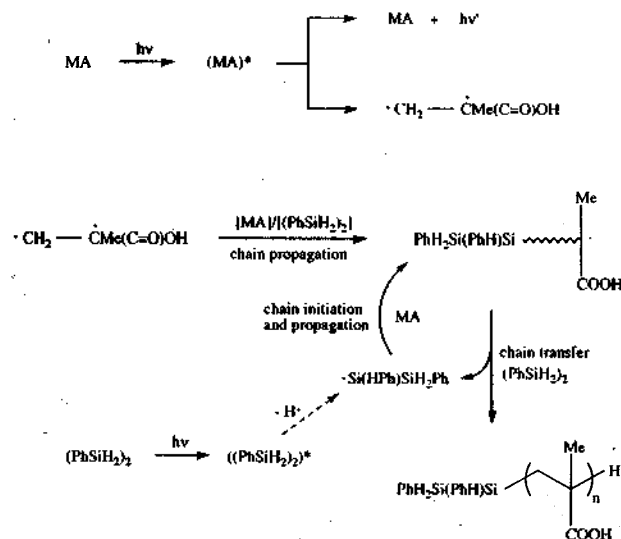
Table 2. Characterization of Photopolymerization of MA with 2^a

Mol ratio (MA : 2)	Yield (%)	Mol wt ^b \bar{M}_w	Mol wt ^b \bar{M}_n	Relative intensity ^c IR (ν_{SiH})	% TGA residue yield at 400 °C
10:1	65	3400	2300	1.0	62 (19) ^d
7:3	37	2500	1400	1.2	74 (30) ^d

^aUV-irradiation for 6 h. ^bMeasured with GPC in THF. ^cRelative ratio with respect to the intensity of ν_{SiH} (MA : 2 = 10 : 1). ^d% TGA residue yield read at 600 °C.

rally increases with increase of polymerization yield in the radical polymerization of vinyl monomers.¹ The intrinsic viscosity is directly related to the weight average molecular weight of polymer.¹² The disilanes showed the similar trends as the other arylsilanes did.¹¹ As shown in Table 1 and Table 2, while the polymerization yields and intrinsic viscosities $[\eta]$ (or molecular weights) decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the mole ratio of disilane over MA augmented. These facts can be rationalized as follows (*vide infra*). The absorption of light may produce an excited singlet state of MA which will either fluoresce or be converted to an excited and long-lived triplet excited state, diradical of MA monomer. Attack on the other MA by this diradical yields a new diradical of MA dimer which either reverts to the ground state two MA molecules or attacks on the other MA that ultimately initiates polymerization.² At neat condition the latter will be a predominant process to produce poly(MA) radicals. At high MA or low silane concentrations, chain propagation will be able to compete with chain transfer over the poly(MA) radicals. However, the chain transfer will eventually beat the chain propagation with increasing the disilane concentration. The chain transfer might produce a disilyl radical which, in turn, leads to chain initiation, resulting in the production of poly(MA) containing the disilyl moiety as an end group as shown in Scheme 1.

It is known that polysilyl radicals generated from the photochemical homolysis of polysilanes may initiate the free-radical chain polymerization of some vinyl monomers.¹³ The disilanes seem to considerably affect on the photopolymerization as both chain initiation and chain transfer agents by operating competitively and simultaneously. The direct chain transfer constants of the disilanes for radical polymerization of MA are not found in the literatures. Nevertheless, it could serve as an excellent chain transfer agent because $PhSiH_3$ has low Si-H bond energy of 88.2 kcal/mol¹⁴ which is comparable to S-H bond energy of mercaptans, known to date to be one of most powerful chain transfer agents, of 87 kcal/mol.¹⁵ In fact, it has been reported that chain transfer constant for radical polymerization of MMA at 60 °C is 2.7 for thiophenol and 0.12 for triphenylsilane.¹⁶ The Si-H bond energies of silanes are known to be mostly uniform except the silanes with strongly electron-withdrawing and/or silyl substituents in the α -position.³ It is recently reported that the substitution of methyl group on a silane decreases the hydrogen donation ability of the silane, but the substitution of phenyl group increases it.¹⁷ The hydrogen donation ability

**Scheme 1.** postulated Mechanism for Photoreaction of MA with 1,2-Diphenyldisilane.

of a silane appears to be not related always to the Si-H bond energy of a silane. This might suggest that the aryl group of an arylsilane first absorbs the energy and then transfers it into the silicon center, which leads to the photochemical homolysis of Si-H bond. The energy transmission could be at short range. However, we are not sure of this hypothesis yet. A study for verifying the matter is in progress using fluorophotometer.

In this study we employed two different types of disilanes to check whether they could serve as a cross-linking agent in the photopolymerization of MA. **1** is a primary alkylsilane with a methylene spacer between two silicon atoms and **2** is a secondary arylsilane with a direct Si-Si bond. We anticipated that **2** might be a good cross-linking agent because the disilane has two silyl units and low Si-H bond energy due to the silyl substituent.^{3a} We aware the possibility of the Si-Si bond scission of **2** under the 300 nm UV-irradiation condition. However, we believe that the disilane oligomer unlike polysilane should have the much less chance of the Si-Si bond scission. We also trust that the disilane oligomer should have the much less chance of the Si-Si bond making than polysilane under the photochemical condition.¹³ The argument was supported by an experiment which attempted to extract polysilanes, if any, from the poly(MA) samples. No polysilane was observed at all. The disilane **1** was expected to have the higher cross-linking chance (due to smaller steric effect and more Si-H bonds) and the lower inclination of chain transfer (due to weaker hydrogen donation ability) under the photopolymerization conditions than the disilane **2**. We also expected that **1** will produce a poly(MA) in as low yield as the alkylsilane $PhCH_2SiH_3$ does in the photopolymerization of MMA.^{10b} Contrary to our expectations, the photopolymerization of MA with **1** possessing an extra electron-donating SiH_3 group gave the poly(MA)s in good yields and the cross-linking seems not to be significantly occurred under the photopolymerization conditions.

As shown in Table 1 and Table 2, the disilane **1** afforded poly(MA)s with somewhat higher molecular weights in higher polymerization yields than the disilane **2**. The MA

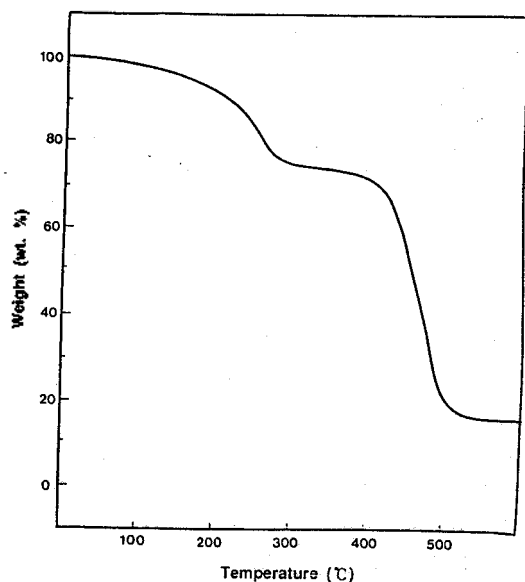


Figure 1. TGA thermogram of poly(MA) obtained from the photopolymerization of MA with **1** (mole ratio, 7:3).

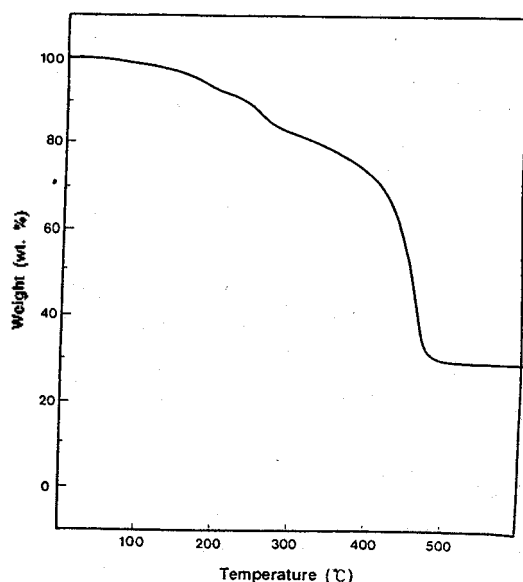


Figure 2. TGA thermogram of poly(MA) obtained from the photopolymerization of MA with **2** (mole ratio, 7:3).

photopolymerization yields with the disilanes were much higher than the MMA photopolymerization yields with the disilanes.^{10c} The polymerizability of MA by the silyl radical seems to be naturally higher than that of MMA. The TGA residue yields of poly(MA)s with the disilyl moieties were much higher than those of poly(MMA)s with the disilyl moieties.^{10c} Compared to the photopolymerization of MA with primary silane, phenylsilane,^{11a} the photopolymerization of MA with the disilanes produced the lower-molecular-weight polymers in lower polymerization yields, but the polymers produced with phenylsilane and disilanes had similar TGA residue yields at 400 °C. The photopolymerization of MA with **1** afforded poly(MA)s with similar molecular weights and TGA ceramic yields compared to the photopolymerization

of MA with secondary silanes such as PhMeSiH₂ and Ph₂SiH₂.^{11b} Unlike the poly(MMA)s exhibiting the drastic transition of the TGA residue yields (at 400 °C) with changing both relative disilane concentration and type of disilane, the variation of the TGA residue yields (at 400 °C) of the poly(MA)s with changing both relative disilane concentration and type of disilane was very little. However, the TGA residue yields at 600 °C of poly(MA)s with **2** were found to be ca. two times higher than those with **1**. Thus, the disilane PhH₂SiSiH₂Ph seems to have the higher cross-linking chance due to stronger hydrogen donation ability under the pyrolysis conditions than **1**. It is interesting to note that while the weight loss of the poly(MMA)s was smoothly occurred up to 350 °C with few turning points, the abrupt weight loss of a narrow range of the poly(MA)s was occurred twice at the turning points around 150 °C and 250 °C before 350 °C (Figure 1 and Figure 2), although all the poly(MA)s and poly(MMA)s rapidly and exhaustively decomposed after 350 °C.

Two endotherms were observed at 135 °C and 257 °C in DSC. We believe that cross-linking reactions could be happened by the acidolysis between Si-H group and acid group in the different polymer chains at around 150 °C, yielding a silyl ester linkage¹⁸ and then by the dehydration between two acid groups in the different polymer chains at around 250 °C, forming an acid anhydride linkage.¹⁹ For the disilanes the little change of TGA residue yields at 400 °C of the poly(MA)s with increase of the relative disilane concentration may suggest that the cross-linking by the formation of acid anhydride linkage should contribute by far more than the cross-linking by the formation of silyl ester linkage. The silyl ester linkage is known to be thermally weak. Nonetheless, the cross-linking possibility might be slim under the photopolymerization conditions. The cross-linking processes could require high energy, which are anticipated only to occur during the pyrolysis.²⁰ However, we should admit at this moment that we cannot completely exclude the low degree of cross-linking possibility during the photopolymerization.

In conclusion, this work describes the photopolymerization of MA with disilanes such as 2-phenyl-1,3-disilapropane (**1**) and 1,2-diphenyldisilane (**2**). While the polymerization yields and molecular weights of the poly(MA)s containing the disilyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the mole ratio of the disilanes over MA increased. The polymerizability of MA by the disilyl radical seems to be naturally higher than that of MMA. The photopolymerization of MA with **1** produced higher-molecular-weight polymers having lower TGA residue yields when compared to the photopolymerization of MA with **2**. The disilyl moieties, once attached to the poly(MA) as an end group, could be left untouched before the pyrolysis process were suggested, based on the trend of the TGA residue yields. The disilanes appeared to competitively and concurrently function as both chain initiation and transfer agents in the photopolymerization of MA. A plausible mechanism for the photopolymerization of MA with the disilanes was provided.

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New Crown Ethers Containing Kemp's Triacid and Their Binding Properties with Alkali Metal Cations

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The development of neutral hosts for binding metal ions has been extensively pursued for the last two decades due to the potential applications in the various areas; analytical, environmental and biological chemistry.¹ Most works were based on the modification of crown ether by replacing the ethylene glycol units with other building molecules that may introduce different size, shape, and conformational properties of the binding sites.² For the development of efficient ion-selective electrodes and synthetic ion transporters, highly lipophilic molecules should be incorporated into crown ethers. Recently, Moriarty *et al.*³ reported that the rigid and compact hydrocarbons such as cubane are more relevant for this purpose than long-chain hydrocarbons that may increase lipophilicity but decrease mobility of the carrier.

Kemp's triacid, a highly rigid and compact molecule, has proven to be a versatile building block for the construction of synthetic molecular clefts⁴ and self-replicating molecules.⁵ Using its unique structural feature, U-shaped relationship between any two carboxyl functional groups, we recently introduced the alkali metal cation hosts such as bis(crown ether)s, functionalized podands, and cage-type molecules.⁶ We here report the synthesis and binding properties of new crown ethers in which one of the ethylene glycol units is