Molecular Design of Cationically Polymerizable Monomers and Polymers

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This paper reviews our recent studies on the syntheses of new monomers and polymers that have cationically polymerizable groups such as vinyl ethers, cyclic ethers. A variety of vinyl ether monomers containing silicon or phosphorus atoms were successfully prepared by the regioselective reaction of glycidyl vinyl ether with dichlorosilanes or phosphorus dichlorides. Calixarene derivatives with propargyl, vinyl ether groups were prepared. Calixarene derivatives containing cyclic ethers such as oxirane, oxetane, and spiro orthoesters were also prepared. Polyimides containing propargyl, vinyl ether, and cyclic ether groups aforementioned were successfully prepared using diamines containing the functional groups. Photoinitiated cationic polymerization of the prepared monomers and polymers using suitable photoinitiators in the film state proceeded efficiently to produce crosslinked films. Behaviors of photoinitiated cationic polymerizations of the materials are also described.

Keywords: photoinitiated cationic polymerization, calixarene, polyimide

1. Introduction

UV and EB curing systems have been of great interest [1, 2], and have been widely used in the fields of coatings, printing inks, photofabrications, adhesives, and solder masks. Recently, these UV and EB curing systems have been further extended in some new technology fields such as microelectronics, micromachines, three-dimensional fabrications, liquid crystal displays, optical media, and optoelectronic materials. In these curing systems, radically polymerizable polyfunctional (meth)acrylate monomers and oligomers have been used with appropriate photoinitiators, because these monomers and oligomers have high photochemical reactivity to produce the crosslinked insoluble lumps or films having excellent mechanical and physical properties. However, it was pointed out that some (meth)acrylate monomers with low viscosity cause skin irritability, an undesirable property for handling them during these processes.

Photo-initiating cationic polymerizations of polyfunctional epoxy compounds and

polyfunctional vinyl ether compounds have been of interest [3] as second generation's UV curing materials, since these monomers and oligomers have also high photochemical reactivity in the presence of appropriate photo-generating cationic catalysts and seem to cause little skin irritability.

The authors have reported [4, 5, 6] new methods for the synthesis of polyfunctional vinyl ether monomers and oligomers based on the regioselective addition reaction of glycidyl vinyl ether with active chlorides followed by the condensation reaction of the resulting monomers containing reactive chloromethyl groups with dicarboxylic acids using quaternary onium salts or crown ethers as catalysts. Crivello *et al.* reported [7, 8] that polyfunctional 1-propenyl ether monomers, which have mostly the same photochemical reactivity with polyfunctional vinyl ether monomers, were prepared by the isomerization of the corresponding allyl ether monomers.

Recently, it was suggested that calixarenes have unique characteristics such as small

molecular size, good film-forming properties [9, 10] high glass transition temperature (T_g), excellent thermal stability many reactive groups such as hydroxyl groups in small molecule, and so on. For example, Fujita et al. found⁸ that hexa-acetate of *p*-methylcalix[6]arene could be used as a negative type resist with ultrahigh resolution in electron beam lithography.

Photosensitive polyimides with excellent electrical and thermal properties have been used as a circuit framing materials and as an electrical insulation membrane between the layers. The authors recently developed new synthesis of polyimides containing cationically polymerizable groups in the side chains using diamines with the aforementioned groups, and using polymer reaction of polyimides with carboxyl groups.

In this article, we report on the synthesis, characterization, and photochemical reaction of new monomers, oligomers, and polymers with cationically polymerizable groups such as vinyl ether, propargyl ether, oxirane, oxetane groups. Calixarene derivatives containing the groups and polyimides containing the groups are designed as high performance materials for new UV curing systems.

2. Synthesis of vinyl ether monomers based on the regioselective addition reaction of glycidyl vinyl ether [11]

It is well known that organic materials containing silicon or phosphorus atoms have flexibility at low temperature and flame retardancy. The authors designed some vinyl ether monomers with silicon or phosphorus atoms using glycidyl vinyl ether (**1**) as a starting material.

Silicon-containing monomers with vinyl ether groups were easily synthesized by the reaction of **1** with silyl chlorides catalyzed by quaternary onium salts under very mild conditions. The reactions of **1** with dichlorosilanes such as diphenyldichlorosilane (**2a**) or dimethyldichlorosilane (**2b**) proceeded using TBAB at 0 °C for 1 h and then at ambient temperature for 23 h, and the corresponding vinyl monomers (**3a** and **3b**) were obtained with high yield (Scheme 1). Silicon-containing vinyl ether monomers with disilylalkylene structure (**3c**) and siloxane structure (**3d**) were also synthesized by the reaction of **1** with 1,1,4,4-tetramethyl 1,4-dichlorosilylethylene (**2c**) and 1,7-dichlorooctamethyltetrasiloxane (**2d**), respectively. All of the synthesized

silicon-containing vinyl monomers were clear liquids.

Scheme 1

3. Synthesis of phosphorous-containing vinyl monomers and oligomers [11]

Phosphorous-containing vinyl ether monomers can be synthesized by the reaction of **1** with phosphoric dichlorides (Scheme 2). The reaction of **1** with phenylphosphonic dichloride (**4a**) using TBAB proceeded regioselectively at 90 °C in toluene to provide a vinyl ether monomer (**5a**). Other phosphorous-containing vinyl ether monomers (**5b**, **5c**) are also synthesized in good yield from the reaction of **1** with phenyldichlorophosphate and propylphosphonic dichloride.

Based on the reactivity of the prepared vinyl ether monomers that have two reactive chloromethyl groups, polycondensation of **5a** with dicarboxylic acids (**6**) can be carried out using DBU to provide phosphorous-containing oligomers (**7**) with vinyl ether groups in the side chain. A hybrid type oligomer (**7e**) is successfully prepared by the polycondensation of **5a** with fumaric acid DBU at 70 °C for 48 h in DMSO. The molecular weight (M_n) of the obtained oligomers is controlled as from 3600 to 5800 by feed ratios of each monomer. The oligomers with M_n of about 4000 are liquid, those with M_n of about 5000 are semi-solids, and those with higher M_n than 5000 are solids.

Scheme 2

Scheme 3

4. Synthesis of calixarenes containing propargyl, allyl, and vinyl ether groups [12]

Calixarene containing cationically polymerizable groups such as propargyl, allyl, and vinyl ether groups were prepared by the substitution reactions of **8a** or **8c** with certain unsaturated alkyl halides, propargyl bromide, allyl bromide, and 2-chloroethyl vinyl bromide using KOH or NaH and TBAB (Scheme 4). The substitution reactions proceeded smoothly with 100% degree of substitution to give the targeted calixarene derivatives with good isolated yields. These results mean that *p*-alkylcalixarenes such as **8a** and **8c** can be modified easily to provide new functional calixarene derivatives by the substitution reaction of potassium or sodium salts of **8a** or **8c** with appropriate alkyl halides using phase-transfer catalysis under mild reaction conditions.

The isomerization of calixarene **10a** containing allyl ether groups was carried out using *tert*-BuOK in NMP at 80 °C according to the reported method by Crivello et al. [7, 8]. The reaction proceeded quantitatively under the same reaction condition, and the corresponding calixarene **12a** containing 100 mol% of *Z*-1-propenyl ether groups

Scheme 4

Scheme 5

Scheme 6

T_g s of calixarene derivatives **9a–13a** are summarized in Table III. This result shows that the calixarene derivatives **9a–13a** containing cationically reactive groups have high T_g values, which is an important characteristic of photo-curable oligomers. The temperature at 10% loss of mass ($T_d^{10\%}$) of calixarene derivatives **9a–13a** excepting calixarene **9a** showed higher temperature than 350 °C. This means that these calixarene derivatives have excellent thermal stability as photo-curable oligomers.

5. Synthesis of calixarenes containing cyclic ether groups [13, 14]

Synthesis of calixarene derivatives containing oxirane groups by the substitution reaction of calixarenes with epibromohydrin (EBH) was performed using inorganic bases in MNP.

Table 1 UV spectra and thermal properties of calixarene derivatives

Calixarene	$\lambda_{\max}^a$ (nm)	T_g^b (°C)
9a	280	314
10a	272	203
11a	280	245
11c	279	177
12a	280	226
13a	280	148

^a Measured at film state.^b T_g: Glass transition temperature.^c T_d^{10%}: The temperature at 10% loss of mass.

When the reactions were carried out using weak inorganic bases such as Na₂CO₃, K₂CO₃, or Cs₂CO₃, soluble products were produced. The targeted *p*-methylcalix[6]arene derivative **14a** was successfully prepared with 88% yield from the reaction of **1a** with 1.2 times amount of EBH and 1.2 times amount of Cs₂CO₃ at 50 °C for 48 h. *p*-*tert*-butylcalix[8]arene containing oxirane groups **14c** and *C*-methylcalix[4]resorcinarene containing oxirane groups **14d** were also prepared with good yields.

Scheme 7

We designed new polyfunctional oxetane oligomers with calixarene backbones as new materials for photoinitiated cationic curing system. (3-Methyloxetan-3-yl)methyl-4-toluenesulfonate (MOMT) and (3-ethyloxetanyl-3-yl)methyl-4-toluenesulfonate (EOMT), as starting materials for the synthesis of calixarenes containing oxetane groups, were synthesized by the reaction of *p*-toluenesulfonyl chloride with 3-hydroxymethyl-3-methyl oxetane and 3-hydroxymethyl-3-ethyloxetane, respectively. Substitution reactions of calixarenes **8a**, **8c**, and **8d** with MOMT or EOMT were performed using KOH and TBAB. Calixarenes containing 3-methyloxetane groups **15a**, **15c**, and **15d** with 100 % degree of

substitution were obtained in good yields by the reaction of **8a**, **8c**, and **8d** with slightly excess amount of MOMT at 70 °C for 24 h in NMP. Calixarenes containing 3-ethyloxetane groups **16a**, **16b**, and **16c** were also prepared by the reaction with EOMT under the same conditions as applied for the synthesis of calixarenes **15a**.

Scheme 8

Calixarenes containing spiro orthoester groups were also prepared. The substitution reaction of **1a**, **1c**, and **1d** with methyl α -bromoacetate (MBA) was conducted using Cs₂CO₃ and TBAB in NMP at 70 °C for 48 h, and corresponding calixarenes with spacer moieties were obtained in good yields. Then, the hydrolysis of the obtained calixarenes was performed using excess amount of KOH and TBAB in the mixed solvent of 1,4-dioxane and water to give calixarene derivatives with carboxymethoxy groups in good yields. Calixarenes containing spiro ortho ester groups **18a**, **18c**, and **18d** were prepared in good yields by the substitution reaction of calixarene derivatives with carboxymethoxy groups with excess amount of BMTSN using DBU as a base in NMP.

It is found that calixarene derivatives containing cyclic ether groups and spiro ortho ester groups have excellent thermal stability as new photo-functional materials. The temperatures T_d^{5%} and T_d^{10%} of all calixarene derivatives containing oxirane and oxetane groups recorded higher than 350 °C. The temperatures T_d^{5%} and T_d^{10%} of calixarenes derivatives containing spiro ortho ester groups were higher than 315 °C.

Scheme 9

Interestingly, calixarene derivatives with C-methylcalix[4]resorcinarene structures had higher thermal stability than the corresponding calixarene derivatives with *p*-methylcalix[6]arene or *p*-*tert*-butylcalixarene structures.

6. Photoinitiated cationic polymerization of calixarenes containing cationically polymerizable groups [15]

The photoinitiated cationic polymerizations of calixarenes **9a**, **11a**, **11c**, **12a**, and **13a** were examined using 5 mol% of 4-morpholino-2,5-dibutoxybenzenediazonium hexafluorophosphate (MDBZ) or DPSP as a PAG in the film state using a 250-W high-pressure mercury lamp. When MDBZ was used, the rate of the photochemical reaction increased as following order, **9a** > **11a** > **11c** > **12a** > **13a**. On the other hand, when DPSP was used, the rate of the photochemical reaction increased as following order, **11a** > **11c** > **13a** > **12a** > **9a** (Figure 1).

It has been reported⁸ that the photoinitiated cationic polymerization of 1-propenyl ether groups in liquid monomers proceeded very smoothly as did as the photoinitiated polymerization of vinyl ether groups. However, the photoinitiated cationic polymerization of 1-propenyl ether groups in calixarene **12a** did not proceed smoothly. This may be due to the steric hindrance of calixarene structures or due to the inhibition of molecular motion of 1-propenyl ether groups bonded directly to the rigid calixarene backbone. From these results, it was found that combination with photo-acid generators is a very important factor for the photo-crosslinking reaction of calixarene

derivatives containing certain cationically polymerizable groups.

Figure 1. Rates of photochemical reaction of calixarenes **9a**, **11a**, **11c**, **12a**, and **13a** with DPSP (5 mol %): (■) calixarene **9a**, (●) calixarene **11a**, (□) calixarene **11c**, (▲) calixarene **12a**, (○) calixarene **13a**.

7. Synthesis of new polyimides containing cationically polymerizable groups

The authors developed synthetic method of diamines [16, 17] with propargyl, vinyl ether, and spiro ortho ester groups. The diamines were successfully prepared in one-step by the reaction of 4,4'-diamino-3,3'-dicarboxydiphenylmethane (**19**) with propargyl bromide, 2-chloroethyl vinyl ether, and 2-bromomethyl-1,4,6-trioxaspiro[4.4]nonane using DBU as a base. The reactions proceeded chemoselectively without any protection of the amino group to provide the corresponding diamines. The syntheses of diamines containing oxirane or oxetane groups by the method were not successful due to side reactions.

Scheme 10

New polyimides (**21a**, **21b**, **21c**) containing cationically polymerizable groups were synthesized by the diamines (**20**) with tetracarboxylic dianhydrides following chemical cyclization (Scheme 10).

Polyimides (**22a**, **22b**) [18, 19] containing oxiranes and oxetane groups were prepared by

polymer reactions of the polymer having pendant carboxyl groups, which was prepared by the polymerization of **19** and tetracarboxylic dianhydrides, with glycidyl tosylate or 3-methyl-3-oxetanylmethyl tosylate (Scheme 11).

The photoinitiated cationic polymerization of the prepared polyimides [16, 17, 18, 19] using a

suitable photo-acid generator proceeded under UV irradiation to provide crosslinked materials.

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