

Creation of New Organic Reactions of Oxetanes and Their Application to the Synthesis of Photo-curable Polymers and Oligomers

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ABSTRACT

We succeeded in developing new ring-opening addition reactions of oxetanes with certain reagents such as acyl chlorides, silyl chlorides, phosphonyl chlorides, aryl esters, thio esters, phosphonic acids, carboxylic acids, thiols, and phenols using suitable quaternary onium salts or crown ether complexes as catalysts. More recently, we also found anionic ring-opening polymerization of oxetanes containing hydroxyl groups such as (3-methyl-3-hydroxymethyl)oxetane and (3-ethyl-3-hydroxymethyl)oxetane using potassium *tert*-butoxide and 18-crown-6-ether complex as a catalyst, and anionic ring-opening alternating copolymerization of oxetanes with cyclic carboxylic anhydrides. These reaction systems have been widely applied to the synthesis of new functional polymers. In this paper, I would like to introduce the application of these reaction systems to the synthesis of photo-curable polymers and oligomers containing pendant or terminal (meth)acryloyl groups.

1. INTRODUCTION

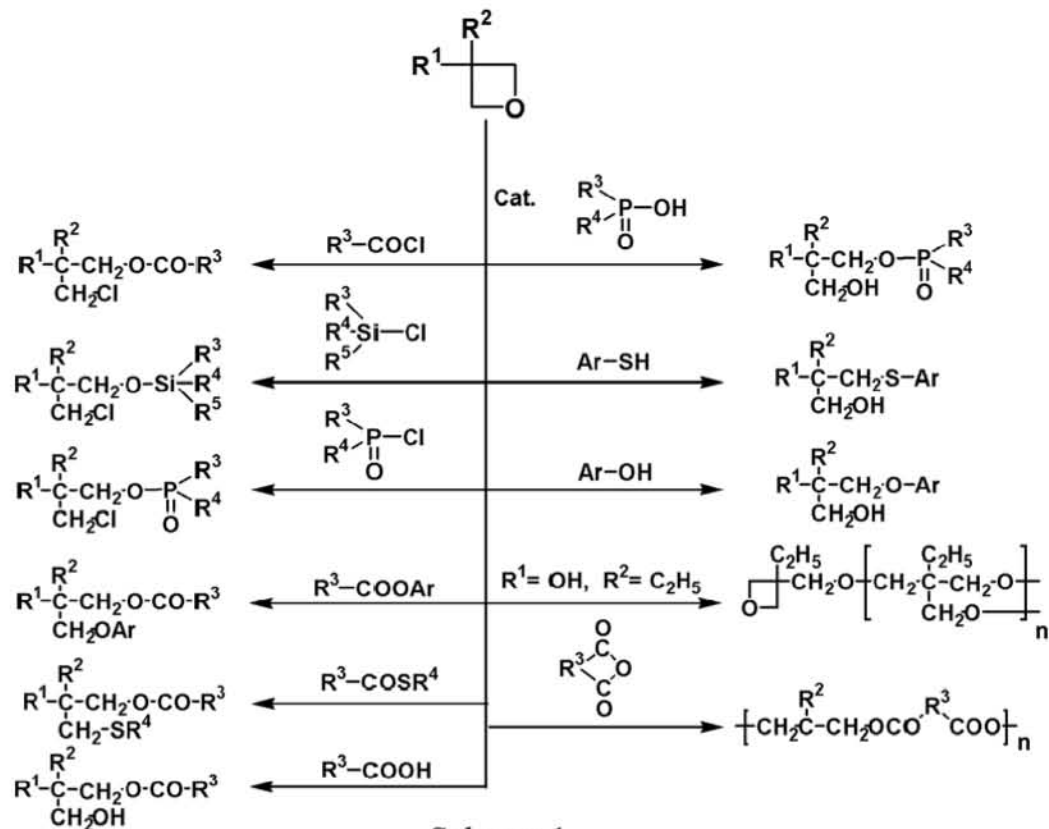
4-Membered cyclic ethers, oxetanes have high strain energy (107 kJ/ mol) as 3-membered cyclic ethers, oxiranes, and the former ethers have higher basicity than the latter ethers. Therefore, the cationic ring opening polymerization of oxetanes proceeds¹ very smoothly with suitable catalysts to afford the corresponding poly(ether)s. The first commercial oxetane resin is poly[(3,3-bis(chloromethyl)oxetane] (PENTON®) from Hercules, which was prepared by the ring-opening polymerization of (3,3-bis(chloromethyl)oxetane (BCMO). More than 10 years ago, Crivello and his co-workers² reported the photo-initiated cationic polymerizations of oxetanes with appropriate photo-acid generators (PAG)s, which proceed very smoothly at room temperature. This photo-initiated cationic polymerization system composed from polyfunctional oxetanes (oxetane resins) with PAG has been developed by Sasaki and Kuriyama³ into high performance photo-curing system. Ukaji and his co-workers⁴ have reported an application of the photo-initiated cationic polymerization system of oxetanes to three-dimensional photo-fabrication, because this reaction system has high photochemical reactivity and excellent physical properties of the cured materials. However, any other useful organic reactions of oxetane compounds have not been reported.

On the other hand, various ring-opening polymerizations of 3-membered cyclic ethers, oxiranes have been reported¹ using many catalyst systems such as tertiary amines, imidazoles, Lewis acids, or their complexes. The photo-initiated cationic ring-opening polymerization of oxiranes with PAG was also noted⁵ as a novel photo-curing system in can coatings and three-dimensional photo-fabrications as well as that of the photo-initiated curing system of oxetane resins. It is well known that the anionic ring-opening alternating copolymerization of oxiranes with cyclic carboxylic anhydrides proceeds very smoothly using quaternary onium salts as catalysts. The typical example of this reaction system is the synthesis of photo-curable poly(ester)s⁶ containing pendant methacryloyl groups by the copolymerization of glycidyl methacrylate (GMA) with certain dicarboxylic anhydrides. Furthermore, it has been reported that addition reactions⁷⁻¹⁰ of oxiranes with amines, phenols, thiols, carboxylic acids, acyl chlorides, active alkyl halides, active aryl halides, silyl chlorides, phosphonyl chlorides, active esters, active phosphonyl esters, and active ethers proceed very smoothly under appropriate reaction conditions to produce corresponding adducts. These reaction systems have been widely applied to the thermal curing reaction of epoxy resins, and chemical modifications of polymers and oligomers containing pendant epoxide groups such as poly(glycidyl methacrylate)s¹¹ and many epoxy resins¹². Especially, the thermal curing reactions of epoxy resins are practically used in many application fields⁸ such as paints, coatings, adhesives, and electronic materials for printed wiring boards (PWB), encapsulant, and intermetal dielectrics for semiconductors.

That is, useful organic reaction of oxetane compounds excepting the cationic ring-opening polymerization has not been reported, although many useful organic reactions of oxiranes such as cationic- and anionic ring-opening polymerizations, anionic alternating ring-opening polymerization, and many ring-opening addition reactions with certain reagents such as amines, carboxylic acids, phenols and thiols have been reported, and these reaction systems of oxiranes have been widely used in industry.

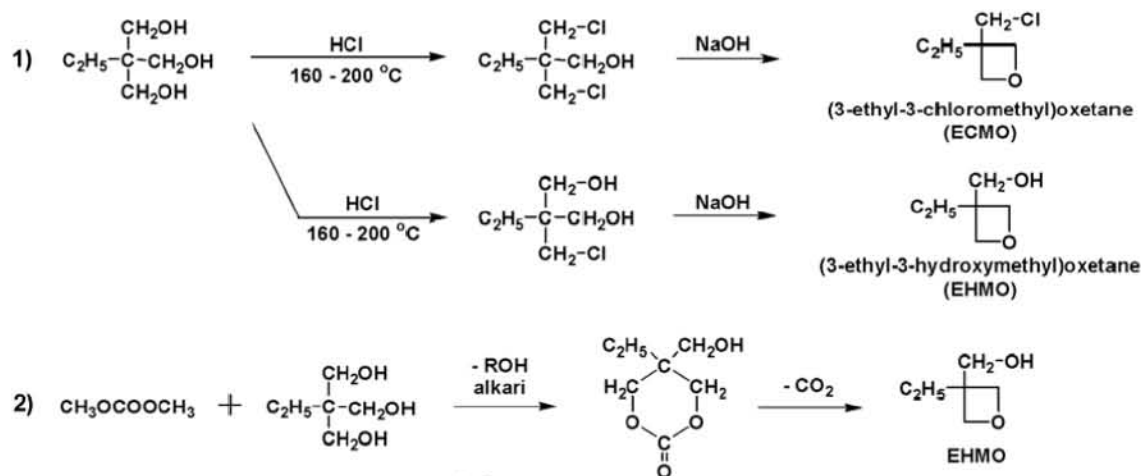
From these background, about 15 years ago, I was interested in developing new reactions of oxetanes, and successfully found¹³⁻¹⁵ certain new ring-opening addition reactions of oxetanes with acyl chlorides, active esters, thio esters, silyl chlorides, and phosphonyl chlorides. We also examined the development of further new ring-opening addition reactions¹⁶⁻¹⁸ of oxetane with phenols, thiols, carboxylic acids, and phosphonic acids. More recently, we succeeded¹⁹⁻²¹ in developing novel anionic ring-opening polymerization of (3-hydroxymethyl)oxetanes using potassium *tert*-butoxide and 18-crown-6-ether complex as a catalyst and anionic ring-opening alternating copolymerization of oxetanes²² with cyclic dicarboxylic anhydrides using appropriate quaternary onium salts as catalysts. All these reactions proceed very smoothly to give the corresponding adducts and polymers in satisfactorily high yields (Scheme 1).

In this paper, I would like to report the synthesis of oxetane monomers, development of new reactions of oxetanes, synthesis and photochemical reaction of new (meth)acrylate oligomers and polymers by the reaction of oxetanes, and synthesis and photochemical reaction of high performance oligomers and polymers containing pendant oxetane groups.

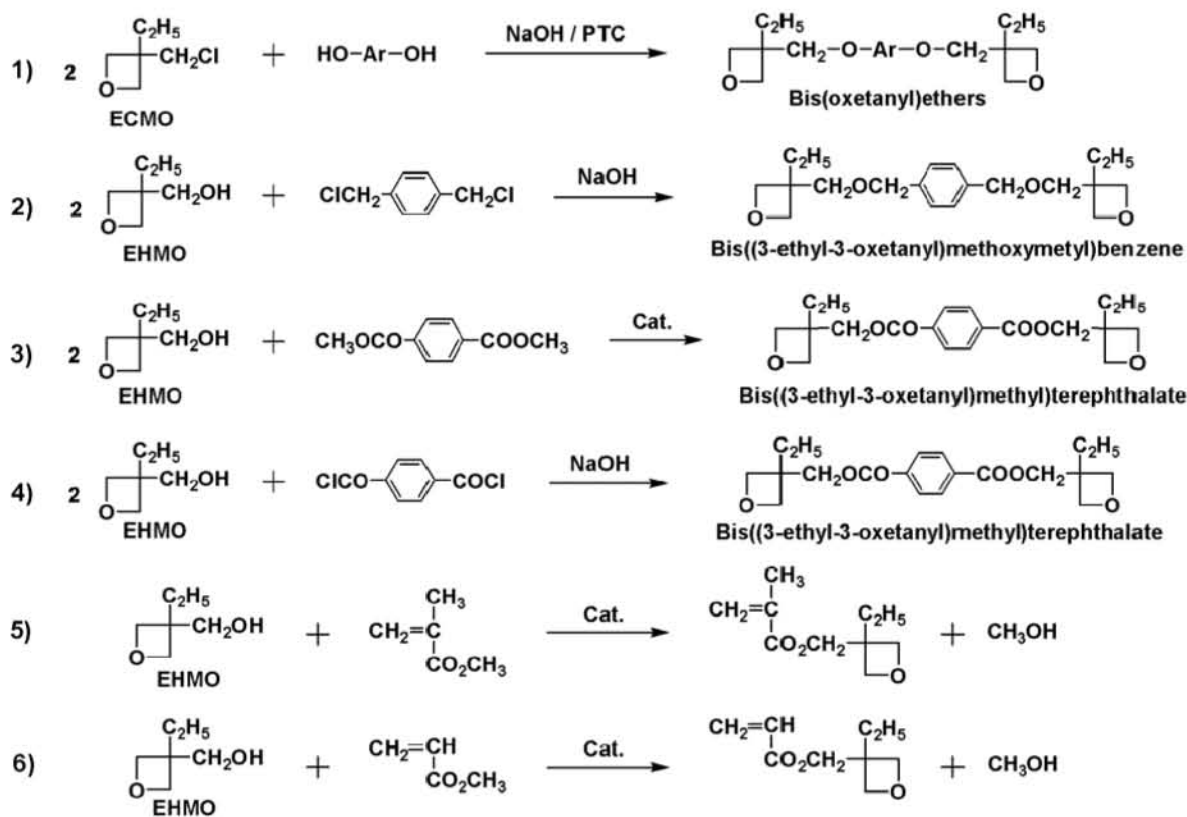


2. SYNTHESIS OF OXETANE MONOMERS

In order to create an oxetane chemistry and industry, it is a very important factor to supply the oxetane monomers with reactive groups to the market at reasonable prices. There are many methods for the synthesis of oxetane compounds from the viewpoint of material supply; however, useful industrial procedures are limited to the following two methods: 1) Synthesis of (3-ethyl-3-chloromethyl)oxetane (ECMO) or (3-ethyl-3-hydroxymethyl)oxetane (EHMO) by the substitution reaction of trimethylolpropane with hydrogen chloride following the reaction with NaOH. 2) Synthesis of EHMO by the reaction of dimethylcarbonate with trimethylolpropane through a cyclic carbonate intermediate (Scheme 2).



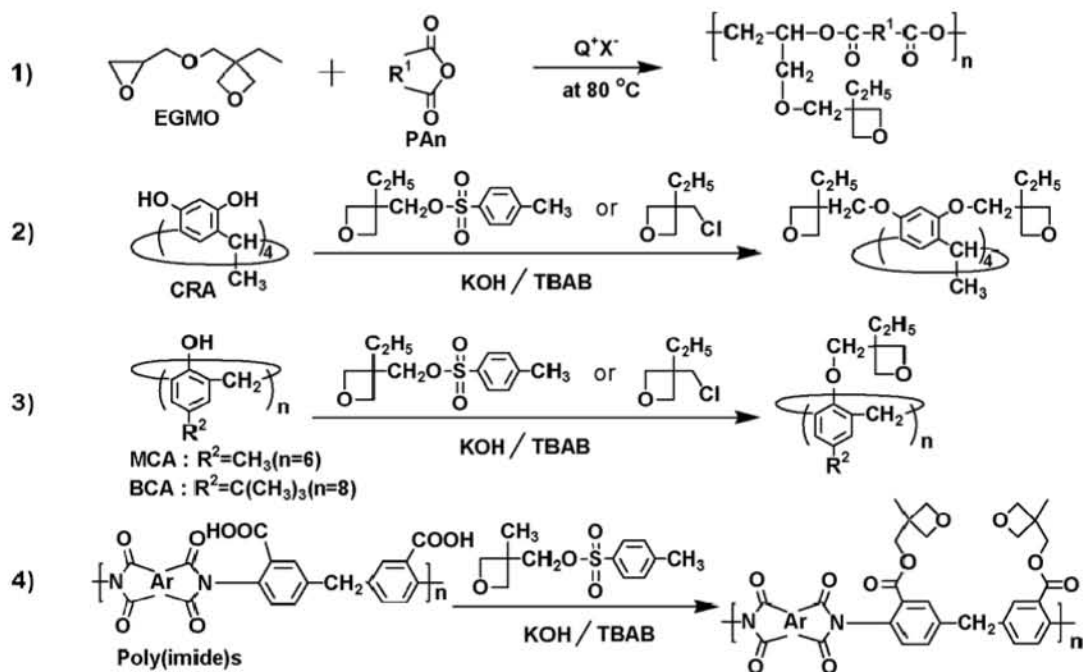
Certain poly-functional oxetanes were practically prepared in Toagosei Co., Ltd., Ube Industries Ltd., and Osaka Organic Chemistry Industry Ltd. in Japan. For instance, ether type bis(oxetane)s are prepared by the reaction of ECMO with bisphenols or the reaction of EHMO with *p*- (or *m*-) xylene dihalides, and ester type bis(oxetane)s are also prepared by the inter-esterification reaction of EHMO with dimethylterephthalate or the condensation reaction of EHMO with terephthalic chloride. (Meth)acrylate monomers with pendant oxetane group (Osaka Organic Chemistry Industry) are synthesized by the inter-esterification reaction¹² between EHMO with methyl methacrylate (MMA) and methyl acrylate (MA). Poly(methacrylate)s or poly(acrylate)s containing pendant oxetane groups have been prepared easily by radical polymerization of these monomers or radical copolymerization of these monomers with other comonomers (Scheme 3).



Scheme 3

3. SYNTHESIS OF POLYMERS AND OLIGOMERS CONTAINING PENDANT OXETANE GROUPS

Recently, my research group synthesized poly(ester)s²³ containing pendant oxetane groups by chemo-selective alternating ring-opening copolymerization of (3-ethyl-3-glycidylloxymethyl)oxetane with carboxylic anhydrides. In order to develop high performance oxetane compounds with excellent thermal properties, we also examined the synthesis of certain calixarene derivatives containing oxetane groups²⁴ by the reaction of ECMO or EHMO tosyl ester with various calixarenes. Furthermore, we investigated the synthesis and photochemical reaction of high performance poly(imide)s²⁵ containing pendant oxetane groups (Scheme 4).



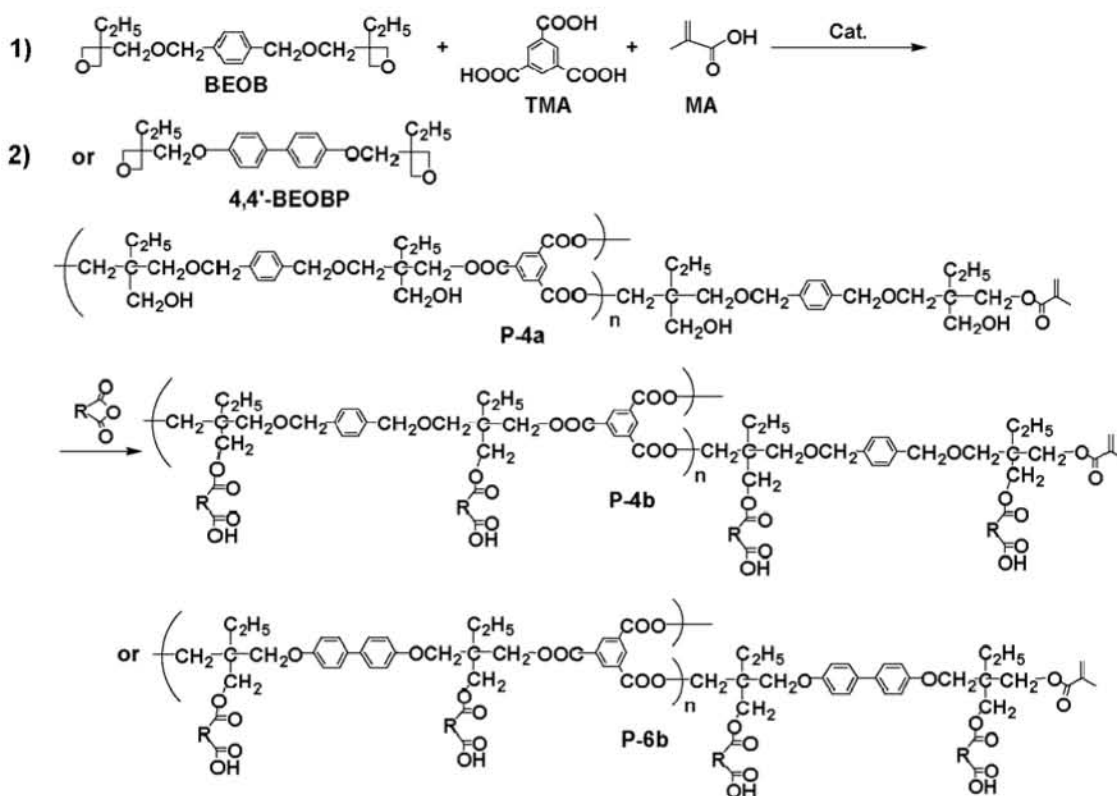
Scheme 4

4. SYNTHESIS OF OXETANE-ACRYLATE OLIGOMERS AND POLYMERS

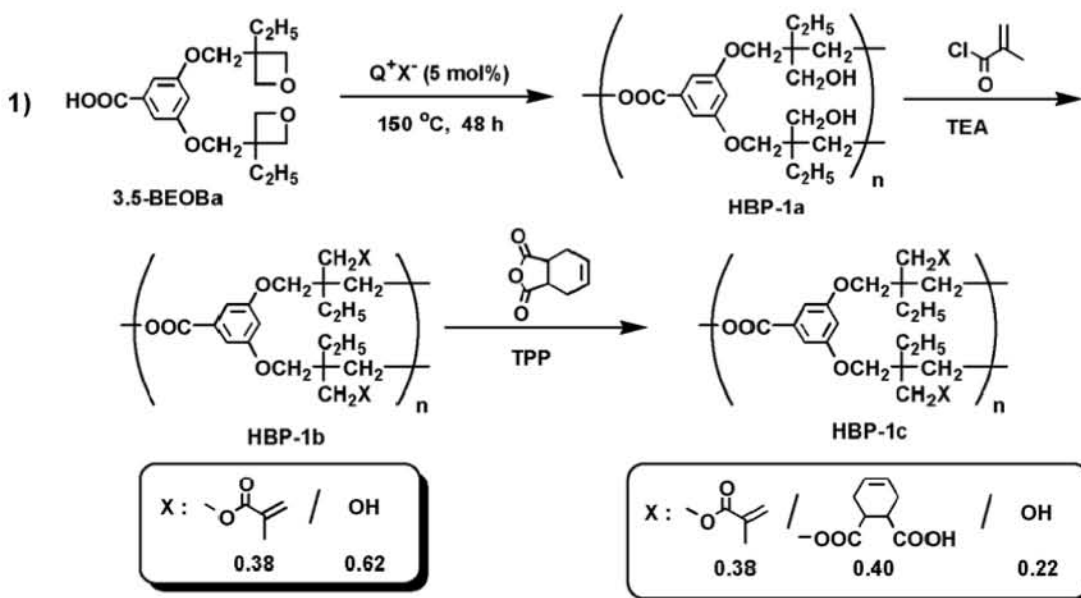
We found novel addition reactions of oxetane compounds with carboxylic acids and phenols. These reactions did not proceed under 110 °C at all. This suggests that these reactions can be applied to the creation of new thermo-setting resin with a single-component at room temperature. Another advantage of these reactions is that the produced primary hydroxyl groups do not react essentially with the oxetane groups under the normal conditions employed. This is unlike the reaction of epoxy compounds with carboxylic acids or phenols, and is important in terms of reaction control in the synthesis of linear polymers or modification of reactive side chains. Furthermore, the polyaddition of polyfunctional oxetane compounds can be used for the synthesis of new (meth)acrylate monomers, oligomers, and polymers. Based on these results, we examined polyaddition of bis(oxetane)s with dicarboxylic acids and (meth)acrylic acids (AA or MAA). This reaction proceeds smoothly catalyzed by quaternary onium salts at 130-140 °C to produce linear poly(ester)s²⁶ (oxetane-acrylate) with primary pendant hydroxyl groups in the side chain and terminal (meth)acryloyl groups at the end of the polymer chain. This reaction system also can be applied to the synthesis of photo-curable hyperbranched polyesters²⁷ (hyperbranched oxetane-acrylate) containing many terminal (meth)acryloyl groups by the polyaddition of bis(oxetane)s with 1,3,5-benzenetricarboxylic acid (TMA) and MAA (or AA) (Scheme 5).

Furthermore, we succeeded²⁸ in the synthesis of alkaline developable hyperbranched poly(ester)s by the polyaddition of AB₂ type monomer 3,5-BEOBa, which had one carboxyl group and two oxetane groups in the molecule, followed by the reaction with (meth)acryloyl chloride (MAC) and cyclic carboxylic anhydride (Scheme 6).

The polyaddition of bis(oxetane)s with bis(phenol)s and MAA (or AA) affords poly(ether)s²⁹ with terminal (meth)acryloyl groups at the end of the polymer chain as well as polyesters. This reaction system can also be applied to the synthesis of photo-curable hyperbranched poly(ether)s containing many terminal (meth)acryloyl groups.

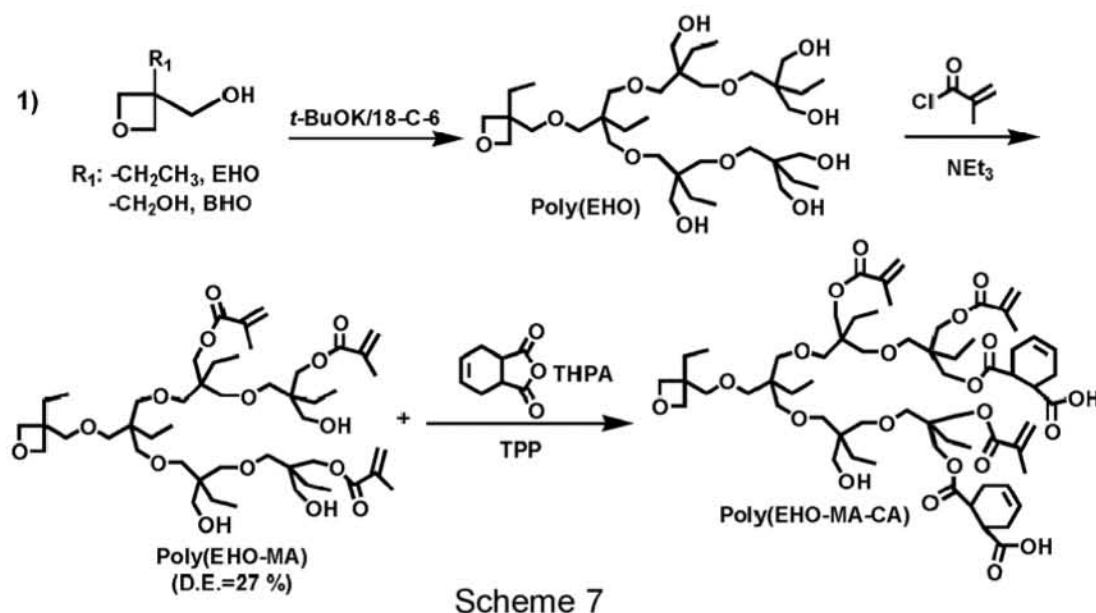


Scheme 5



Scheme 6

Hyperbranched poly(ether)s with an oxetane group and many terminal hydroxyl groups such as poly(EHO) and poly(BHO) were also synthesized¹⁹⁻²¹ by the anionic ring-opening polymerization of (3-alkyl-3-hydroxymethyl)oxetane or 3,3-bis(hydroxymethyl)oxetane using potassium *tert*-butoxide and 18-crown-6-ether as a catalyst at 120-180 °C. The obtained poly(EHO) was reacted with MAC using triethylamine as a base to give new photo-curable hyperbranched poly(ether)s [poly(EHO-MA) and poly(EHO-MA-CA)]³⁰, which have high photochemical reactivity (Scheme 7).

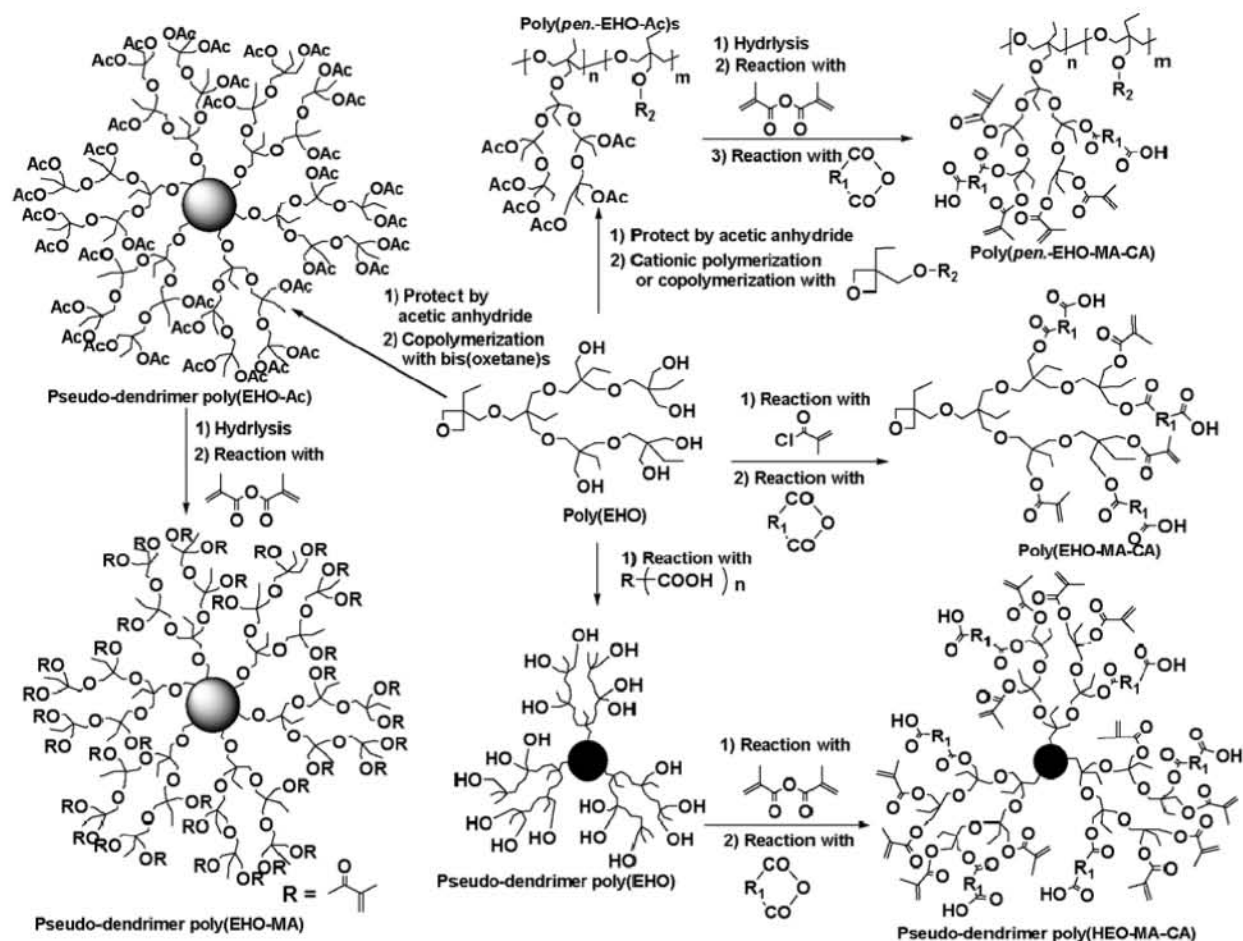


However, degrees of branching of poly(EHO) are not high enough (0.18-0.30 calculated from Frechet's equation). Therefore, we examined further chemical modification of poly(EHO) as follows (Scheme 8), and successfully synthesized certain photo-curable pseudo-dendrimers and pseudo-poly(dendron)s by the reaction of poly(EHO) (Scheme 8).

Poly(EHO-Ac) containing one oxetanyl group and many terminal acetoxy groups was synthesized²¹ by the reaction of poly(EHO) with acetic anhydride, and then the cationic polymerization of poly(EHO-Ac) and copolymerization with (3-ethyl-3-phenoyethyl)oxetane (EPO) were carried out using $\text{BF}_3 \cdot \text{OEt}_2$ as the catalyst. Resulting pseudo-poly(dendron)s [poly(*pen.*-EHO-Ac) and poly(*pen.*-EHO-Ac-EPO)] were converted to photo-curable pseudo-poly(dendron)s such as poly(*pen.*-EHO-MA) and poly(*pen.*-EHO-MA-CA) by the hydrolysis, followed by the chemical modifications with methacrylic anhydride and cyclic carboxylic anhydride.

Pseudo-dendrimers³¹ containing many terminal hydroxyl groups were prepared in good yields by the addition reaction of polyfunctional carboxylic acid such as TMA with poly(EHO). Then, photo-curable pseudo-dendrimers containing many terminal (meth)acryloyl groups were synthesized by the reaction of the resulting pseudo-dendrimers with methacrylic anhydride and cyclic carboxylic anhydride. Similar pseudo-dendrimer³² and photo-curable pseudo-dendrimer were also prepared by the cationic copolymerization of poly(EHO-Ac) with small amounts of bis(oxetane), followed by the hydrolysis and the reaction with methacrylic anhydride.

The photochemical reaction of the resulting pseudo-poly(dendron)s and pseudo-dendrimers with many terminal (meth)acryloyl groups were also examined.



Scheme 8

5. CONCLUSION

We examined the synthesis of new photo-reactive polymers and oligomers by novel ring-opening addition reactions of oxetane compounds or anionic ring-opening polymerization of (3-hydroxymethyl)oxetanes, and successfully synthesized certain linear and hyperbranched poly(ester)s or poly(ether)s containing pendant or terminal (meth)acryloyl groups. We also synthesized certain photo-reactive pseudo-dendrimers and pseudo-poly(dendron)s containing many terminal (meth)acryloyl groups by the further chemical modification of the resulting poly(HEO). Furthermore, high performance cyclic oligomers and poly(imide)s containing pendant oxetane groups were synthesized by the reaction of oxetane derivatives with the corresponding calixarenes and poly(imide)s.

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