● Application of Oxetane Compounds to Photo-Cationic Curing Systems

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1. Introduction

In a photocuring system, polymerizable functional groups polymerize under exposure to light such as UV, resulting in three-dimensional cross-linking. Solvent-free photocuring materials based on such cross-linking systems have been proposed. Photocuring materials were first put to practical use as a filling coat material for woodworking materials. Although the scope of their application was limited at first due to their relatively slow curing speed, it has expanded to include a wide variety of materials today, with the development of acrylate-based materials with excellent photocuring properties. This can be attributed to the fact that the inherent characteristics of photocuring systems, such as reduced resource use, reduced space requirements, reduced waste, room-temperature curing, and high productivity, aligned with the demands of the times. In addition, with regard to global environmental issues that have been attracting attention in recent years, the photocuring systems are essentially solvent-free and do not contain organic solvents that could cause ozone depletion, air pollution, or other adverse environmental effects. Photocuring also requires less energy for curing and produces less carbon dioxide, resulting in a low environmental impact.

Conventional photocuring systems can be roughly classified into two types according to the polymerization-initiating species generated: radical and cationic. When compared to photo-radical curing systems, the most significant feature of the cationic type is that it is not affected by oxygen in the air. In the late 1970s, it was discovered that non-nucleophilic strong acids such as hexafluoroantimonate can be efficiently generated by the photolysis reaction of onium salts, and the possibility of practical application of photo-cationic curing systems was quickly raised[1)]. Iodonium salts, sulfonium salts, etc. have been developed so far as photoinitiators[2) 3)].

It has been known for some time that cationic polymerization using acidic substances as initiators can polymerize a wide variety of functional groups such as electron-dense vinyl groups with electron-donating groups (vinyl ether compounds, styrene derivatives, etc.) and heterocyclic compounds (epoxy compounds with oxirane rings, lactone compounds, etc.). To date, development of cationic UV curing materials has used both ring-opening-polymerizable cyclic ethers such as epoxy groups and addition-polymerizable vinyl compounds such as vinyl ether. Of these, epoxy-based materials have been widely examined for use because of their relatively low cost and the availability of existing compounds with various structures developed for thermal curing[4)5)]. However, despite these favorable properties, epoxy-based materials (especially inexpensive glycidyl ether-based materials) are known to suffer from low polymerizability (curability) in photo-cationic polymerization, and this low curability is sometimes a problem that inhibits practical application[6)].

We have been studying cyclic ether compounds, which are analogous compounds of oxirane rings, with the aim of developing compounds with new functional groups that can maintain the properties of epoxy-based materials while offering improved curability.

Cationic ring-opening polymerization of cyclic ether compounds involves nucleophilic attack of neutral molecules on oxonium ions, and is generally considered to proceed via an S_N2 reaction. In this case, factors that may have significant effects on the polymerization rate include the ring strain energy, nucleophilicity (basicity), and steric hindrance of the cyclic ether compound[7)]. In other words, ring strain energy is the factor governing the ease of ring opening when it is attacked by a monomer, and nucleophilicity is a measure of the strength of the attack on the active terminal. Comparison of the unsubstituted oxirane and oxetane rings shows no significant difference in ring strain energy at 27.3 and 25.5 (kcal/mol), respectively[8)]. However, the pKb values are 7.4 and 3.1, respectively, indicating that the oxetane ring is much more basic than the oxirane ring[9)10)].

Furthermore, we need to consider the chain transfer reaction in addition to initiation and growth reaction when we examine the curability. For oxirane rings, chain transfer from the active polymerization terminal to the ether oxygen in the polymer main chain occurs readily, because the ether oxygen of the polymer main chain is more basic than that of oxirane monomer. This results in a decrease in polymerization rate and a decrease in degree of polymerization due to the formation of cyclic oligomer byproducts[11)].

Oxetane compounds, which are four-membered ring ethers that have a high ring strain comparable to that of oxirane rings and higher basicity, may be more reactive than oxirane rings to cationic ring-opening polymerization. In this article, we describe the synthesis of oxetane compounds containing oxetanyl groups as cationic polymerizable groups, along with their photo-cationic polymerization properties, with a focus on our research results.

2. Molecular design of oxetane compounds

2.1 Synthesis of oxetane rings

Various methods for synthesizing oxetane rings have been proposed so far. They can be roughly classified into the following three types by the type of raw materials used.

- 1,3-diol derivatives
- Compounds containing carbonyl groups and vinyl compounds
- Epoxy compounds

Fig 1 shows the synthetic schemes for the oxetane ring using these raw materials.

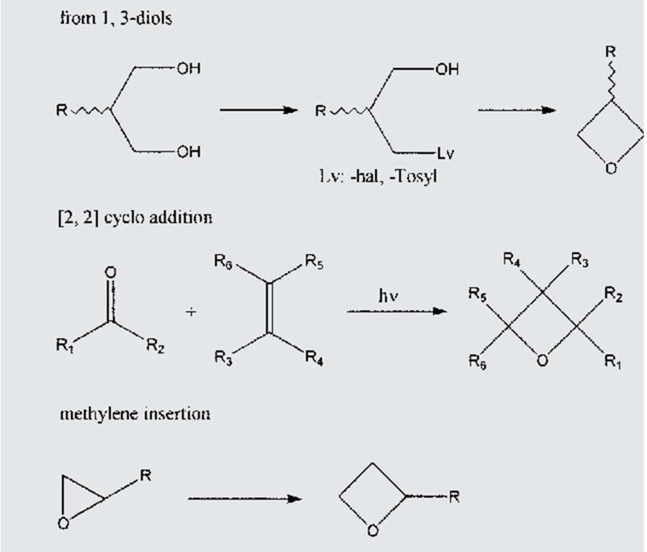


Figure 1: Synthetic paths of oxetane rings

When a diol derivative is used as the raw material, the oxetane ring can be formed in a two-step reaction in which a halogen atom or tosyl group is introduced as a leaving group, followed by a cyclization reaction through an elimination reaction with a base such as an alkali.[12) 13)]

Oxetane rings can also be synthesized by photodimerization reaction between a compound containing a carbonyl group and a vinyl compound, which is known as the Paterno-Bucci reaction[14)-16)]. Various compounds have been investigated so far, and reports have shown that the formation rate of oxetane rings differs greatly depending on the substituent of each substrate used as the raw material.

An example of the synthesis of an oxetane ring by inserting a methylene group into an epoxy ring using an ylide compound has also been reported[17)].

2.2 Molecular design of compounds containing oxetanyl groups

Oxetane alcohol (OXA) is one of the useful raw materials for synthesizing compounds containing oxetanyl groups. It has been previously reported that the synthesis of OXA with an oxetane ring and a hydroxyl group in one molecule results in relatively high yield when a triol such as trimethylolpropane and an alkyl carbonate are used[18)]. By utilizing this hydroxyl group, various monomers containing oxetanyl groups can be synthesized via ether, ester, carbonate, or urethane linkages.[19)20)]

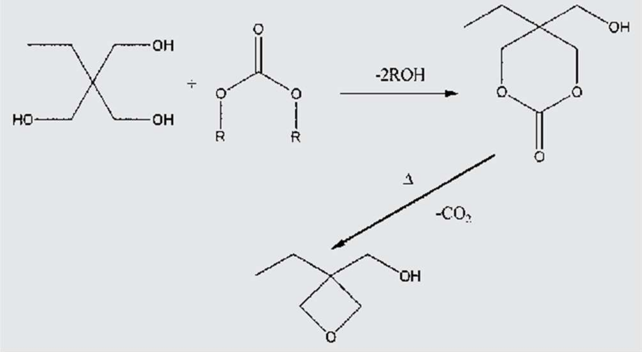


Figure 2: Synthesis of oxetane alcohol (OXA)

When used as a photocuring material, oligomer materials may be needed in addition to relatively low-molecular-weight monomers. While there is a method to synthesize oligomers containing oxetanyl groups in one step by direct reaction with OXA as described above, it is difficult to design a variety of oligomers with this method. Another possible method to synthesize oligomers with a wide range of properties is a two-step reaction in which a reactive functional group is introduced into OXA and the oligomer is synthesized using that functional group.

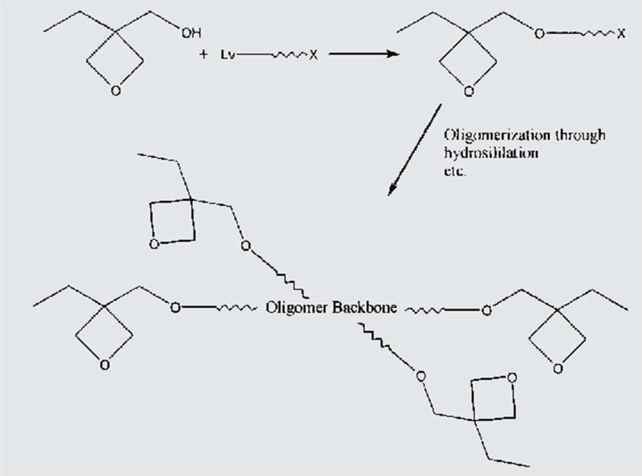


Figure 3: Synthetic tactics for oligomer

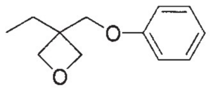
For example, oligomers with silicone main chains can be synthesized by hydrosilylation when allyl groups are used[21)]. In addition, various oligomers can be synthesized by exploiting the difference in reactivity between the oxetane ring and the oxirane ring, when a glycidyl group is introduced. When glycidyl oxetane is reacted with phenols, derivatives containing oxetanyl groups can be synthesized by ring-opening addition reaction of the oxirane ring. By anionic polymerization of only the oxirane ring in this monomer, reactive polymers containing cationic polymerizable oxetanyl groups in the side chain can be synthesized[22)].

3. Reactivity of oxetane compounds

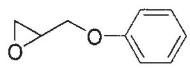
We have previously studied the photo-cationic polymerization properties of oxetane compounds containing oxetanyl groups as cationic polymerizable reactive groups[23)]. The results of these studies are shown below.

3.1 Comparison of reactivity between oxetane compounds and epoxy compounds

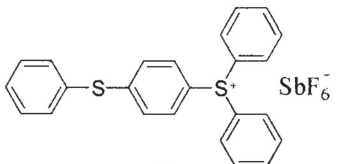
Fig. 4 shows the results of comparing reaction properties in the single polymerization of oxetane compounds by the Realtime FT-IR method. The compounds used were phenyl oxetane (PHO), phenyl glycidyl ether (PGE), which has a similar structure to PHO, and a tetraarylsulfonium salt diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate (PI).



PHO



PGE



PI

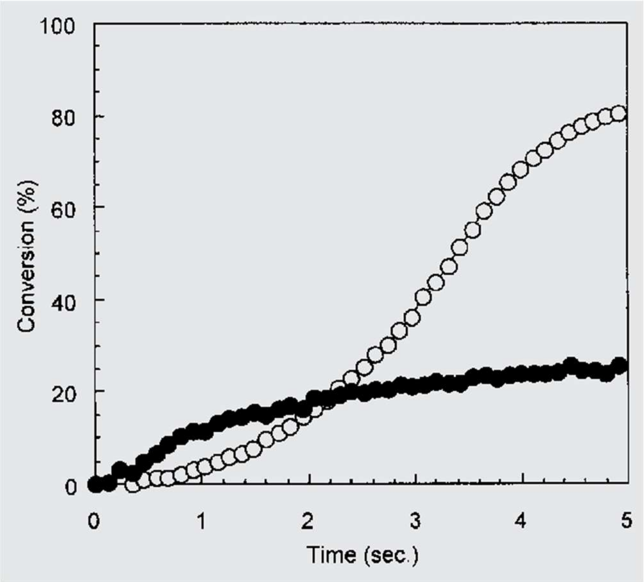


Figure 4: Time-Conversion curves for PHO (○) and PGE (●) using 0.5 mol% of PI at a UV intensity of 44.2 mW/cm^2

In the photo-cationic polymerization of PHO, the disappearance curve of the oxetanyl group showed an S shape with a clear induction period. After the induction period, polymerization proceeded at an almost constant rate, reaching a conversion of 80% or higher after 5 seconds of irradiation. On the other hand, the polymerization rate rapidly decreased at about 20% conversion in the photo-cationic polymerization of PGE, even though no induction period was observed.

In general, it is believed that the cationic ring-opening polymerization of cyclic ethers proceeds via the S_N2 reaction as shown in **Fig. 5**.

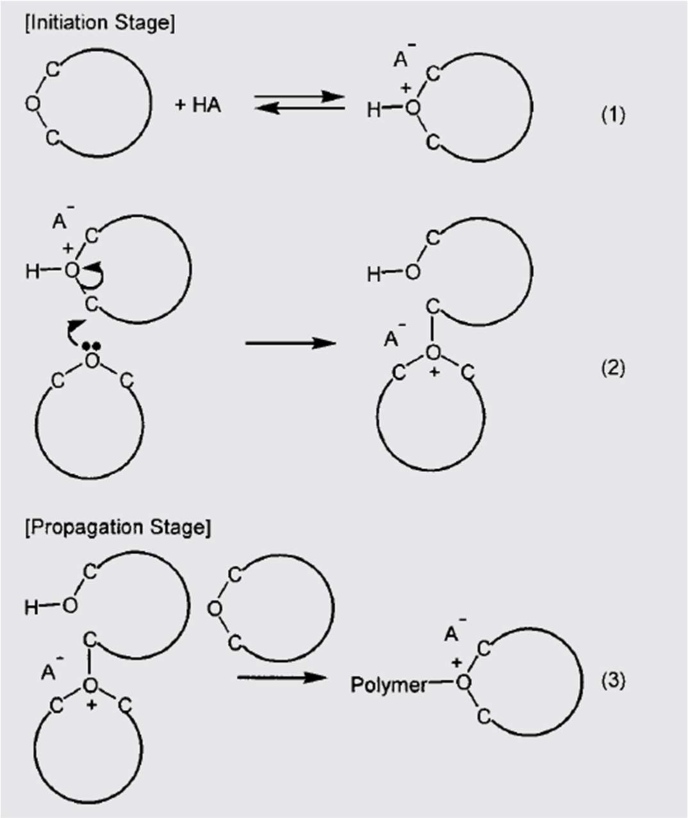


Figure 5: Cationic ring opening polymerization of cyclic ether monomer

In the initiation reaction, the addition of acid forms a dialkyl oxonium cation (Formula 1), which the next monomer attacks to form a trialkyl oxonium cation (Formula 2). Since dialkyl oxonium cation is less susceptible to ring-opening reactions, it is assumed that the reaction to produce trialkyl oxonium cation (Formula 2) is the rate-limiting step in polymerization, and that the rate of its formation (or its concentration) governs the polymerization rate.

The induction period observed in the polymerization of PHO may have occurred because the formation of the cyclic trialkyl oxonium cation in Formula 2 is rate-limiting, as the polymerization proceeds via the S_N2 reaction.

Since no induction period is observed with PGE, it suggests that trialkyl oxonium cation may be formed from an early stage in the polymerization of the oxirane ring. In addition, the decrease in the polymerization rate is attributed to the formation of strain-free trialkyl oxonium cations through chain transfer of active species to the product polymer chain, which effectively stops the polymerization.

Fig. 6 shows the measurement results of the molecular weight of each polymer formed by photo-cationic polymerization. The number-average molecular weights at the peak were 2390 and 13900, respectively, indicating that the molecular weight of the polymer formed from PHO was about five times larger than the one formed from PGE. This difference in molecular weight of the product polymer is attributed to the higher likelihood of chain transfer occurring in the polymerization of PGE, resulting in the formation of macrocyclic compounds as byproducts, while PHO forms polymers of relatively high molecular weights as it is less prone to chain transfer reactions during the polymerization reaction due to the high basicity of the oxetane ring.

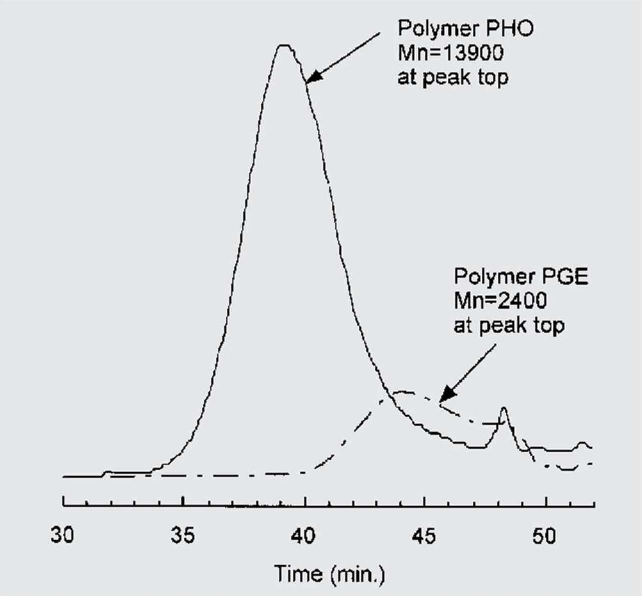


Figure 6: GPC elution of polymer PHO and PGE using 0.5 mol% of PIat a UV intensity of 44.2 mW/cm^2 and a total irradiation energy of 1.33 J/cm^2

3.2 High-speed polymerization of oxetane compounds with addition of epoxy compounds

Previously, Saegusa et al. reported that epoxy compounds acted as accelerators in the cationic polymerization system of oxetane compounds using Lewis acids[24]. Regarding this acceleration effect, a mechanism has been proposed, in which the oxirane ring undergoes cationic ring-opening polymerization more readily than the oxetane ring to form trialkyl oxonium cations. However, the reaction has not been studied in detail.

We examined the effect of the addition of PGE on the photo-cationic polymerization of PHO, and found that the rate of disappearance of the oxetane ring was accelerated by a factor of 7 or more (**Fig. 7**). **Fig. 8** shows the GPC elution curves of the polymers formed by photo-cationic polymerization. The molecular weight of the polymers formed had decreased with the addition of the epoxy compound.

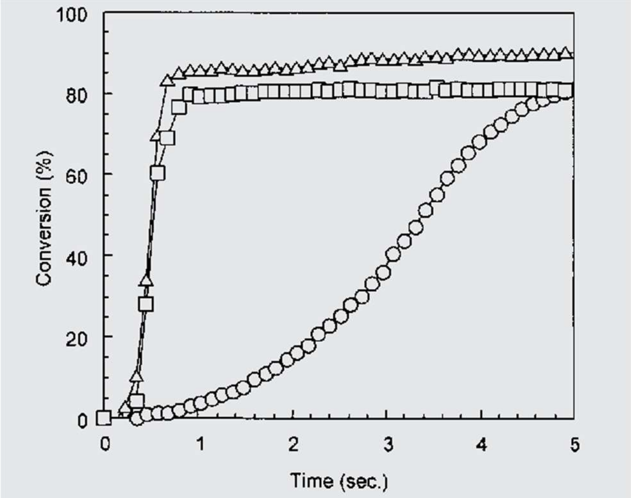


Figure 7: Time-Conversion curves for PHO (○) and PHO/PGE=95/5 mol/mol (△) and 90/10 mol/mol (□) using 0.5 mol% of PI at a UV intensity of 44.2 mW/cm^2

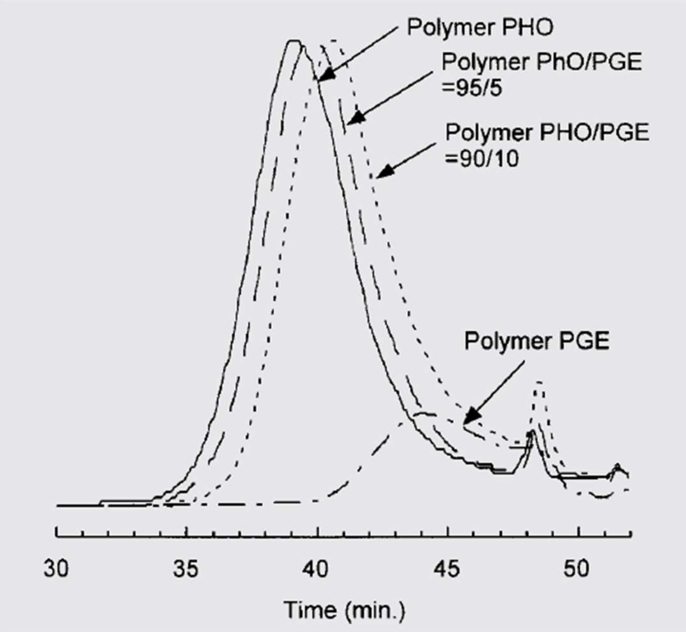
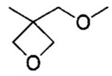


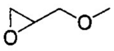
Figure 8: GPC elution of polymer PHO, PGA and formulations using 0.5 mol% of PI at a UV intensity of 44.2 mW/cm^2 and a total irradiation energy of 1.33 J/cm^2

As described previously, when comparing the unsubstituted oxirane and oxetane rings, the oxetane rings have a much higher basicity, even though there is no significant difference in ring strain energy. If the polymerization proceeds only via the S_N2 reaction, it is unlikely that the cationic ring-opening properties of the less basic oxirane ring would differ significantly due to this slight difference in ring strain energy.

3.3 Examination of reaction mechanism by computational chemistry

As shown in **3.1**, an initial induction period was observed in the single polymerization of PHO, which may be due to the fact that polymerization proceeds via the S_N2 reaction and that the formation of cyclic trialkyl oxonium cations is rate-limiting. Since no induction period was observed with PGE, it is possible that the high-speed polymerization of oxetane compounds with the addition of epoxy compounds does not proceed solely via the S_N2 reaction. In order to elucidate the polymerization mechanism of this high-speed polymerization of oxetane compounds, we examined the polymerization initiation mechanism by semiempirical molecular orbital method (AM1) using 3-methyl-3-methoxymethyloxetane (MEO) and methyl glycidyl ether (MGE) shown below, as model compounds.


MEO


MGE

3.3.1 Initiation mechanism of epoxy compounds

Fig. 9 shows a comparison of the carbon-oxygen bond distances of protonated MGE and the changes in energy of the heat of formation obtained by the reaction coordinate calculation. The long bond distance between MGE and α-carbon suggests that this bond is easily broken.

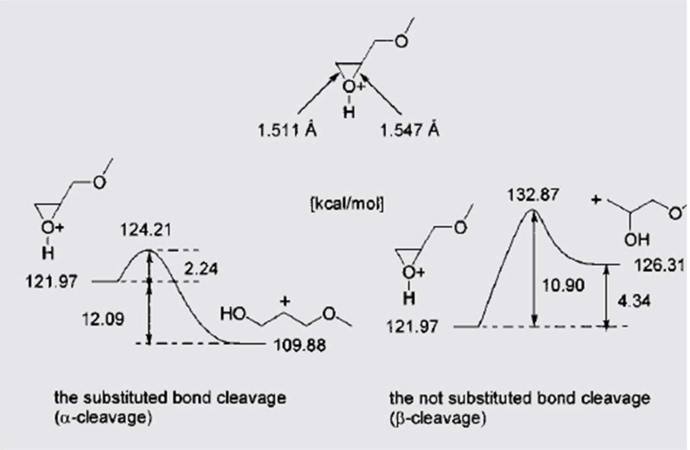


Figure 9: Reaction diagram of ring-opening reaction of protonated oxirance MGE

The results of reaction coordinate calculations show that the reaction barrier energies are 2.24 and 10.90 kcal/mol, respectively, with α-cleavage being considerably smaller, and that the α-cleavage results in a stabilization of 12.09 kcal/mol. These results confirm that in the oxirane ring, α-cleavage to form a secondary carbocation is kinetically and thermodynamically favorable.

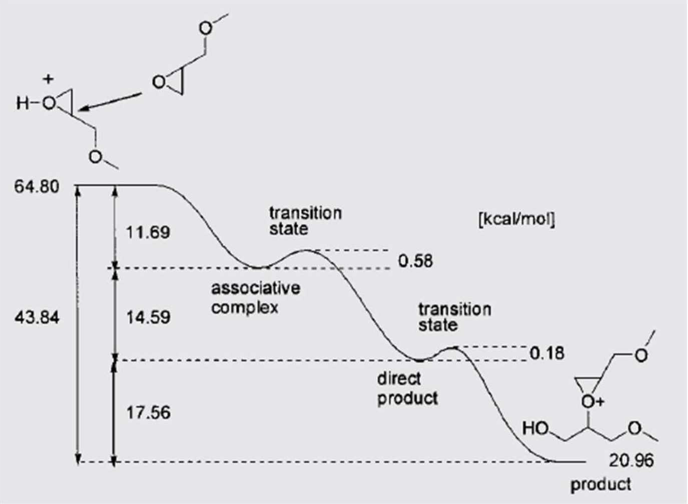


Figure 10: Reaction diagram of second initiation stage of MGE through S_N2 mechanism on α-carbon

Fig. 10 shows the results of reaction coordinate calculations for nucleophilic attack on the α-carbon of protonated MGE. Two transition states were obtained, and in the first transition state, although the distance between the attacking nucleophile's oxygen and the α-carbon was relatively long, the distance of the bond being cleaved had already increased. Results of intrinsic reaction coordinate calculations from this transition state indicated that a compound containing a secondary carbocation with the oxirane ring unimolecularly opened was formed. We carried out reaction coordinate calculations from this product, and obtained a reaction system in which the nucleophile attacked the secondary carbocation. Based on this, we infer that unimolecular ring-opening of the oxirane ring occurred with the nucleophile's oxygen pre-coordinated to the α-carbon during the attack. That is, the reaction was proceeding via an S_N1 mechanism. On the other hand, when the β-carbon was attacked, the reactants formed via the S_N2 reaction were calculated by the intrinsic reaction coordinate calculations from the transition state. It has been reported that not only head-to-tail structures but also head-to-head and tail-to-tail structures were present in the product polymers of polymerization using epoxy compounds. Based on these experimental results and our calculation results, we confirmed the possibility that cationic polymerization of epoxy compounds could also proceed via the S_N1 reaction.

3.3.2 Initiation mechanism of oxetane compounds

In our examination of MEO in a similar fashion to MGE, we found that the ring-opening reaction of the proton adduct had the reaction barrier energy of 14.84 kcal/mol, and that the heat of formation in the most stable structure of the product was destabilized by 13.74 kcal/mol compared to that of the reactant. Calculation results of the respective bond distances of the bond to be cleaved and the bond to be formed in the transition state of the second step of the initiation reaction also indicated that the S_N2 reaction was proceeding reasonably well.

3.3.3 Reaction mechanism of high-speed polymerization

Based on our examination of the initiation mechanism, we infer that the S_N1-like reaction via carbocations may also proceed in the polymerization of epoxy compounds. When an epoxy compound is added in the polymerization of an oxetane compound, the acid generated from the photoinitiator upon light irradiation is added to the oxirane ring, partially causing ring-opening in a unimolecular reaction and forming a secondary carbocation. This carbocation derived from the oxirane ring readily attacks the oxetane ring to form a trialkyl oxonium cation, which is the polymerization active species, and the growth reaction proceeds when the oxetane compound attacks it.

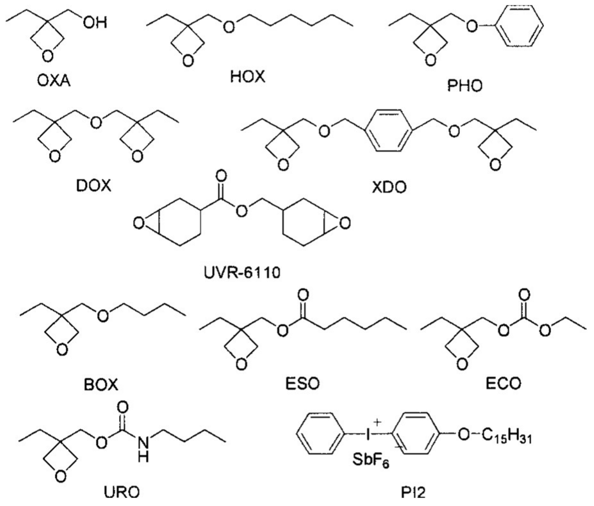
We believe that the addition of the epoxy compound increased the rate of formation of trialkyl oxonium cations via carbocations, and that it resulted in the elimination of the induction period that had been observed in single polymerization and increase in the polymerization rate. The decrease in molecular weight due to the addition of epoxy compounds can be explained by an increase in the concentration of active species.

3.4 Other characteristics

It has been reported that the polymerization proceeds at a high speed in photo-cationic polymerization of oxetane compounds in nitrogen[25)26)]. Although the details of this high-speed polymerization mechanism are not known, it is presumed that the redox reaction of the photoinitiator onium salt, which also involves the oxetane compounds, increased the initiator decomposition efficiency.

4. Application to photo-cationic curing materials

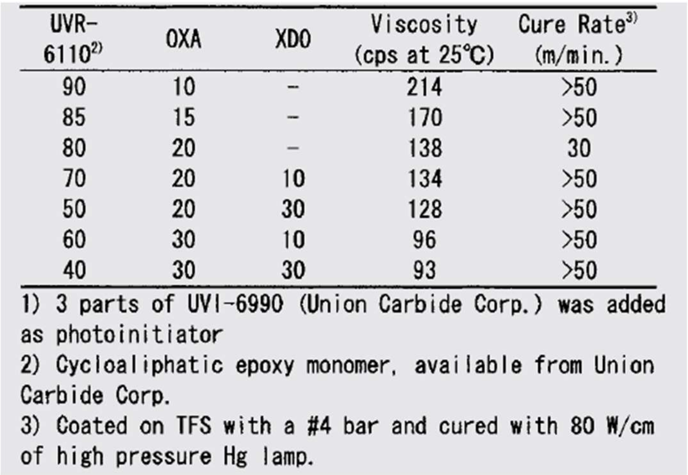
As shown in the previous section, oxetane compounds have been shown to have different polymerization characteristics from epoxy compounds in photo-cationic polymerization. This difference in polymerization characteristics could be used to design novel photo-curing resins. In this section, we present the results of our examination of the following oxetane compounds and their application to photo-cationic curing materials.



4.1 Use of OXA

OXA has a ring-opening polymerizable oxetane ring and a hydroxyl group in one molecule. Since hydroxyl groups are known to act as chain transfer agents in cationic ring-opening polymerization of cyclic ether compounds, OXA may be effective as both a polymerization accelerator and a crosslinking component, through the chain transfer from the hydroxyl group to the active polymerization terminal, in addition to the participation of the oxetane ring in ring-opening polymerization. OXA is also effective as a diluting component because of its very low viscosity. **Table 1** shows the results of our study on the curability of formulation systems of OXA and commercially available alicyclic epoxy compounds.

Table 1: Formulation of OXA and epoxy monomer with or without XDO[1)]



UVR-6110[2)]	OXA	XDO	Viscosity (cps at 25℃)	Cure Rate[3)] (m/min.)
90	10	–	214	>50
85	15	–	170	>50
80	20	–	138	30
70	20	10	134	>50
50	20	30	128	>50
60	30	10	96	>50
40	30	30	93	>50

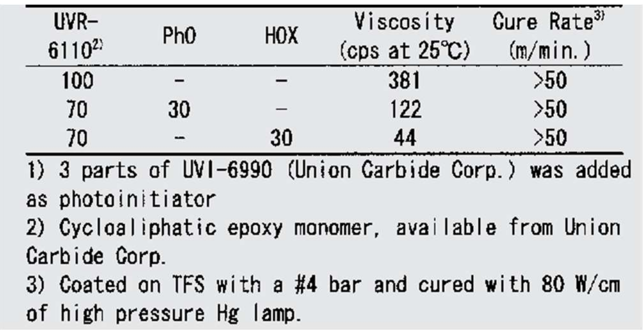
1) 3 parts of UVI-6990 (Union Carbide Corp.) was added as photoinitiator
2) Cycloaliphatic epoxy monomer, available from Union Carbide Corp.
3) Coated on TFS with a #4 bar and cured with 80 W/cm of high pressure Hg lamp.

While the viscosity of the formulation could be reduced depending on the amount of OXA added, a decrease in surface curability occurred when 20 parts were added. This is presumably due to the high hydroxyl equivalent of oxetane alcohol, which causes unreacted hydroxyl groups to remain even after light irradiation, resulting in reduced surface curability. We also confirmed that by using the bifunctional compound XDO in combination with oxetane alcohol, the viscosity could be lowered while maintaining the surface curability even when the amount of oxetane alcohol added was increased to 30 parts. This is assumed to be the result of high-speed polymerization of bifunctional XDO, which caused a rapid network formation.

4.2 Use of monofunctional oxetane compounds

Table 2 shows the curability evaluation results of formulations of monofunctional oxetane compounds. Unlike oxetane alcohol, we confirmed that the viscosity of the formulation could be greatly reduced with no decrease in curability even when 30 parts were added.

Table 2: Formulation of monofunctional oxetanes (PhO, HOX) with epoxy monomer[1)]



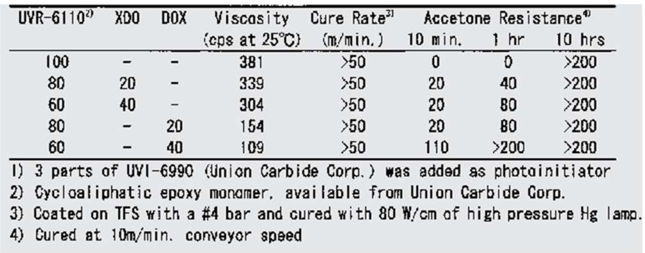
UVR-6110[2)]	PhO	HOX	Viscosity (cps at 25℃)	Cure Rate[3)] (m/min.)
100	–	–	381	>50
70	30	–	122	>50
70	–	30	44	>50

1) 3 parts of UVI-6990 (Union Carbide Corp.) was added as photoinitiator
2) Cycloaliphatic epoxy monomer, available from Union Carbide Corp.
3) Coated on TFS with a #4 bar and cured with 80 W/cm of high pressure Hg lamp.

4.3 Use of bifunctional oxetane compounds

Table 3 shows the examination results on XDO and DOX, which are bifunctional oxetane compounds with two oxetanyl groups in a molecule. In both formulations, high surface curability was maintained. Although the alicyclic epoxy compound alone had a significant post-curing contribution and exhibited little acetone resistance immediately after curing, formulation with a bifunctional oxetane compound improved acetone resistance immediately after curing. In particular, the improvement effect was significant when combined with DOX, which is assumed to shorten the distance between crosslinking points of the generated gel and form a strong network.

Table 3: Formulation of difunctional oxetanes (XDO,DOX) with epoxy monomer[1)]



UVR-6110[2)]	XDO	DOX	Viscosity (cps at 25℃)	Cure Rate[3)] (m/min.)	Accetone Resistance[4)] 10 min.	1 hr	10 hrs
100	–	–	381	>50	0	0	>200
80	20	–	339	>50	20	40	>200
60	40	–	304	>50	20	80	>200
80	–	20	154	>50	20	80	>200
60	–	40	109	>50	110	>200	>200

1) 3 parts of UVI-6990 (Union Carbide Corp.) was added as photoinitiator
2) Cycloaliphatic epoxy monomer, available from Union Carbide Corp.
3) Coated on TFS with a #4 bar and cured with 80 W/cm of high pressure Hg lamp.
4) Cured at 10m/min. conveyor speed

4.4 Impact of functional groups

In general, carbonyl groups in esters and urethane bonds are known to inhibit cationic polymerization. To confirm this effect, we examined the photo-cationic polymerization properties of compounds with various functional groups by the Realtime-IR method. **Fig. 11** shows the results[20)]. Compounds containing ester, carbonate, or urethane bonds showed significant polymerization inhibition effects.

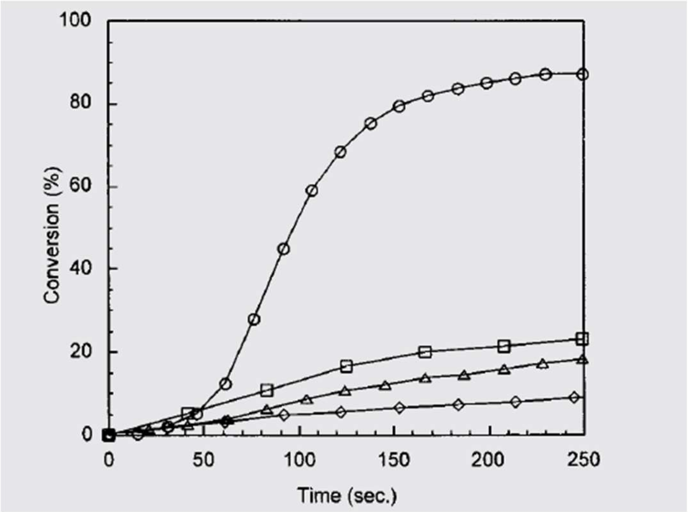


Figure 11: Time-Conversion curves for BOX(○),ESO(△), ECO (□) and URO(◇) using 0.5 mol% of PI2 at a UV intensity of 13 mW/cm²

4.5 Curing shrinkage

The curing shrinkage of a bifunctional xylylene dioxetane compound in photo-cationic polymerization has been measured and reported as relatively small at 3.9%[27].

5. Conclusion

Since photo-cationic curing materials have different characteristics from radical-curing materials, including not being inhibited by oxygen, their development is progressing rapidly in Japan. As described previously, oxetane compounds have polymerization properties that are not found in existing epoxy materials, and we are gradually seeing examples of their application to photo-cationic curing materials that exploit these properties. Some monomers are scheduled to be launched in the near future, and we expect that an expanding range of available monomers will enable the development of new materials with properties not achievable using radical-curing materials. The application scope of new photo-cationic curing materials is therefore expected to expand further.

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