The Pursuit of Rapid Curing
in UV Cationic Polymerization

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Abstract

Recently, the UV cationic polymerizations of cyclic ether compounds are employed in a various commercial applications. For this reason, the UV cationic polymerization has advantage of low shrinkage as compared with UV radical polymerizations. However, it's problem that UV cationic polymerization speed is slow. So, we pay attention to the initiation reaction and utilize a carbocation, which is formed by α-2 –substitution epoxy resins or vinyl ether derivatives, and radical initiator as accelerator. Consequently, we found out the system, which is equal to the polymerization speed of a general UV radical polymerization.

Introduction

In recent years, UV cationic polymerizations of cyclic ether compounds are employed in a variety of commercial applications. The reason is explained by the advantage that UV cationic polymerization has small shrinkage as compared with UV radical polymerization system.[1,2] However, that polymerization speed is slow for developing still more broadly. Generally, after UV irradiation, UV radical polymerization advances immediately and completes in a few seconds. On the other hand, UV cationic polymerization has the long induction period after UV irradiation. As a result, UV cationic polymerization speed is slow as compared with UV radical polymerization (Scheme I)[3].
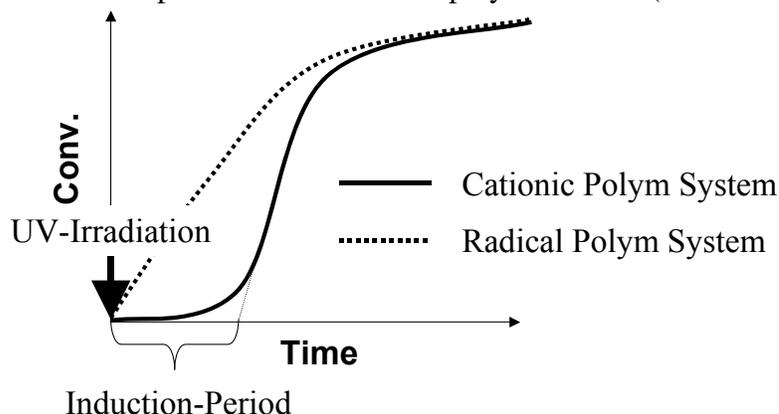
Scheme I

The study of the UV cationic polymerization of cyclic ether monomers has been an area of long-term interest. Saegusa have reported that adding oxirane monomer to oxetane monomer improves polymerization speed.[4] Sasaki has reported the mechanism in detail[3,5]. That is, the oxirane monomer caused the initiation reaction and the propagation reaction is advanced by the oxetane monomer. As a result, a rapid polymerization realized. However, the sufficient polymerization speed could not be acquired as compared with UV radical polymerization.

It is known that the optical propagation speed in cationic polymerization will be governed by a kind of

monomer and counter anion. As shown in Scheme II a propagation reaction repeats ring opening of the cyclic ether monomer by the attack to the generated oxonium-ion. This process advances rapidly.

On the other hand, the initiation reaction in UV cationic polymerization goes on as follows.

In the first step, the UV irradiation of the photo cationic initiator results in excitation and then fragmentation of the photo initiator into a variety of radical and cationic species. The further reaction of those species with the monomer, solvent, or other protogenic components present yields the Brønsted acid H^+X^- The photogenerated strong acid very rapidly protonates(k_1) the cyclic ether. The secondary oxonium species that is formed(k_2) undergoes attack by the nucleophilic cyclic ether to yield the tertiary oxonium species(k_3) as result of ring opening of heterocyclic ring. Finally, the attack by a cyclic ether on the tertiary oxonium ion leads to chain growth. The rate of k_2 and k_3, respectively, are different because secondary oxonium ion and tertiary oxonium ion have different ring strains, steric hindrance, and electronic charge distributions. Generally, the process of forming tertiary oxonium ion is rate limiting, and so k_3 is greater than k_2. However, the relative magnitudes of k_2 and k_3 depend on the specific monomer undergoing polymerization. For example, in the cationic photo polymerization of highly strained cycloaliphatic epoxide both of k_2 and k_3 are large, and the observation of the effects of the difference in the rates is difficult.[6]

Initiation

Propagation
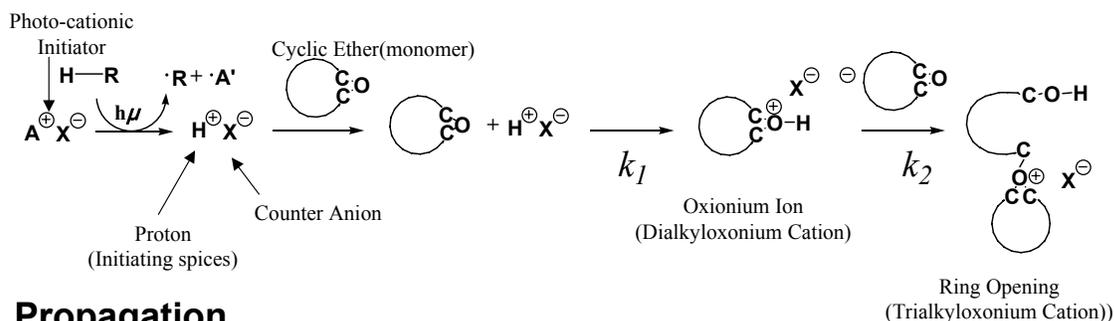
Scheme II

Generally it is supposed that cation ring opening polymerization of cyclic ether is gone on via S_N2 reaction as shown in scheme II.

In an initiation reaction, a dialkyloxonium cation generates by addition of an acid, the following monomer attacking is generated a trialkyloxonium cation. In this process, science a dialkyloxonium cation cannot receive ring opening reaction easily, the reaction which generates a trialkyloxonium cation is a rate-determining step of this polymerization, and it is thought that the generation rate governs a polymerization speed.

In this study, we examined how to avoid this rate-determining step. As a result, it found out a rapid curing system of UV cationic polymerization by adding a specific cyclic ether and vinyl ether which do not generate a trialkyloxonium cation.

Experiment

Materials

As an oxirane monomer, phenyl glycidyl ether (PGE), bisphenol A diglycidyl ether (BPA-EP) were used. As an oxetane monomer, 3-ethyl-3-phenoxymethyl-oxetane(POX) was used.

As the oxirane monomer which has an alkyl substituent in alpha carbon, terpinolene dioxide was used. It was with the commercial item. Isobutyl vinyl ether(IBVE) was distilled and used on CaH_2. Isobutoxy ethylacetate(IBEA)was compounded by the method of Aoshima[6] et.al, and on molecularsieve 4A, it dried one whole day and night, and it was used.

As a UV cationic polymerization initiator, tetrakis(pentafluorophenyl) borate4-methylphenyl [4-(1-methylethyl (phenyl))] iodine(PCI-1) was used.

As a UV radical polymerization initiator, IRGACURE 184 hydroxycyclohexyl-phenyl-ketone was used as an assistant catalyst.

Formulation

The glue for evaluation was prepared in screw vial. In the case of using the oxirane monomer which has an alkyl substituent in alpha carbon, vinyl ether, its derivative, and photo radical initiator, they are added the last in order to be prevent from reacting

Evaluation of polymerization speed

Equipment : EYE CURE UGHT SPOT UP 350G (light source: quantity mercury lamp 20mW/cm^2) by an eye graphics company is used.

Several drops of glue were applied on the glass(2x25x45mm). The time from UV irradiation to gelation was measured with the stopwatch. The time is called gelation time.

The molecular weight of the obtained polymer was measured in GPC (made by Showa Denko K.K.).

A result and consideration

UV cationic polymerization system of oxirane / oxetane

The glue consists of POX and BPA-EP is prepared at rate of POX/BPA-EP:100 / 0 - 0/100. PCI-1 as photo cationic initiator was used 3wt%. The gelation time estimated a polymerization speed. A result is shown in Figure.1, gelation time was plotted against molar ratio of the oxirane / oxetane The local minimum of the gelation time exists in about an oxirane / oxetane mol ratio=2/1. Then the gelation time is 9 seconds (=180mJ/cm^2). When the oxetane mol ratio was increased, it was note that a gel time becomes very long. It seems that k_1(Scheme II) is the same as oxirane's and oxetane's, but k_2 of oxirane is greater than oxetane's. On the other hand, k_3 of oxirane is smaller than oxetane's. So, the optimum
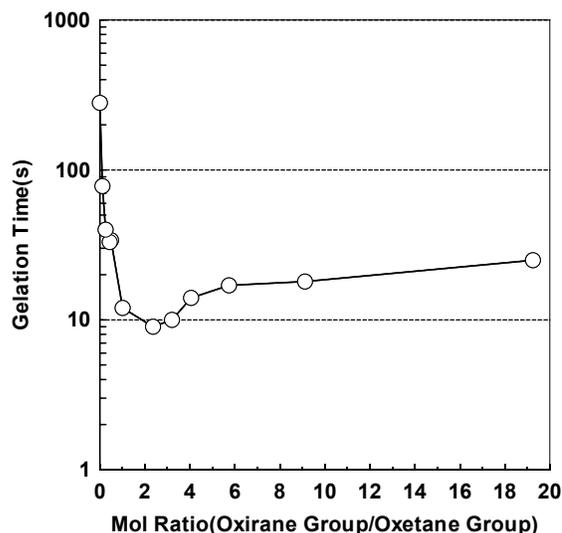
Figure 1 Gelation Time of **POX/BPA-EP/ PCI-1** system
POX/BPA-EP/ PCI-1 =100~0/0~100/3(pbw)

amount of an initiation reaction and propagation reaction both exists.

The effect of an alpha-2 substitution oxirane monomer

The glue consists of POX, BPA-EP and terpinolene dioxide as oxirane monomer which has an alkyl substituent in alpha carbon is prepared at rate of POX/BPA-EP/ terpinolene dioxide:98 / 0/2 - 0/98/2. PCI-1 as photo cationic initiator was used 3wt%. The gelation time estimated the hardenability of this obtained the glue.

A result is shown in Figure 2. The gelation time was drastically shortened by the addition of the oxirane monomer which has alpha alkyl substituent.

In this case, the local minimum of the gelation time exists in about an oxirane / oxetane mol ratio=0.7. Then the gelation time is 4 seconds ($=80mJ/cm^2$).

This phenomenon is suggested this system is different from the conventional initiation reaction model which exists the oxonium ion.
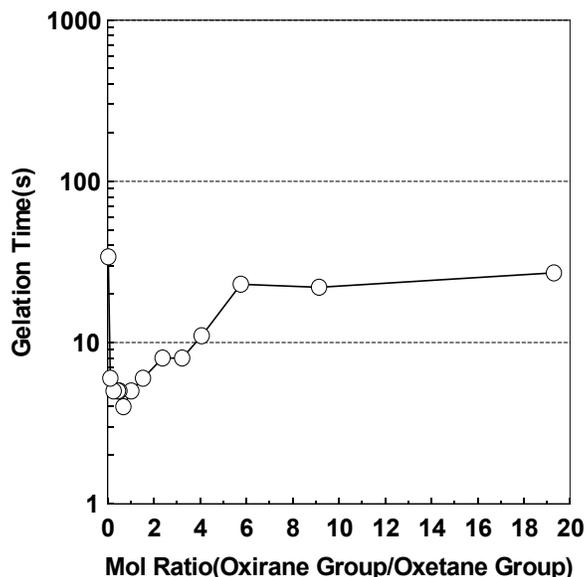
Figure 2 Gelation Time of **POX/BPA-EP/Terpinolene Dioxide/PCI-1** System
POX/BPA-EP/ Terpinolene Dioxide/PCI-1=98~0/0~98/2/3(pbw)

The computations suggestion for the mechanism

Then, the initiation reaction model was compared with each cyclic ether monomer by using calculation chemistry. The heats of addition reaction of a proton and a methyl cation to various cyclic ether was calculated by first-principles calculation (B3LYP/6-31G*) (scheme III)

The computations suggest that the oxirane monomer which has alpha alkyl substituent have reactivity high as much as oxetane to a cation. Especially, they have high reactivity to the proton while initiation reaction. Moreover, the oxirane monomer which has alpha alkyl substituent stabilizes to a ring- opening formation (carbenium cation) irreversibly by proton addition, it is surmised that the efficiency of an initiation reaction is increased. (Table 1)
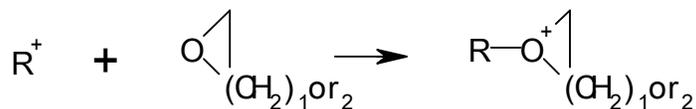
Scheme III

Table 1 Reaction heats of addition reaction with H⁺ or CH₃⁺ to cyclic ethers

Heats of Reaction (kcal/mol)	(oxirane)	(methyloxirane)	(dimethyloxirane)	(ethyloxirane)	(oxetane)	(methyloxetane)
H^+	0	-22.4	-28.4 Ring Openig Formation (-31.7)	-28.3(trans) -28.4(cis)	-27.7	-29.2
CH_3^+	0	-3.8	-8.5 Ring Openig Formation (-9.5)	-8.5(trans) -9.0(cis)	-11.8	-12.9

Next, the activation energy in ring opening reaction at the time of methyl cation addition was calculated with the same technique. As a result, in the case of oxirane group and the oxetane group, the activation energy in ring-opening reaction was high energy, so these ethers formed oxonium ion, without ring-opening (it ring-opens only after the following monomer adds, and distortion energy is released). On the other hand, in the case of the oxirane monomer which has alpha alkyl substituent, since its activation energy was lower than other ethers, it is very likely that the formation is a tert-carbeniumu cation (its distortion energy is released at the time of addition). These differences between oxonium ion (dialkyloxonium cation) and ter-carbenium cation influence shortening of the induction period in an initiation reaction. Thus, oxonium ion (dialkyloxonium cation) is stabile in case of iniation reaction, on the other hand carbenium cation is not stabile. So a carbenium cation attacks a monomer smoothly, and then reaction advances from initiation reaction to propagation reaction. (Scheme IV, Table 2)
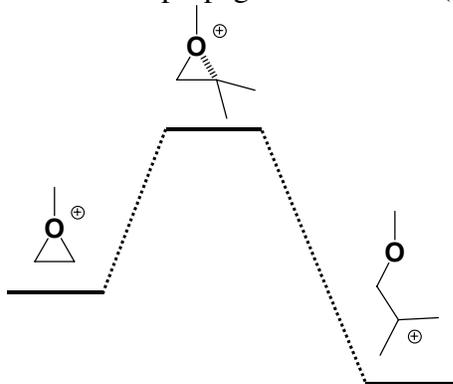
Scheme IV

Table 2 Activation energy on ring opening reaction

	(oxirane)	(methyloxirane)	(dimethyloxirane)	(ethyloxirane)	(oxetane)	(methyloxetane)
Activation Energy (kcal/mol)	27.3	18.7	7.3	19.4(trans) 19.3(cis)	29.5	28.0

UV radical polymerization initiator combined use system

It is known that there is the process of radical generation when the proton generate after UV irradiation of photo cationic initiator. Then, photo radical initiator was made to live together as other radical sources here. Irugacure184 of a photo radical initiator as the same number of moles in PCI-1 as a

photo cation initiator was added to the BPA-EP/POX/Terpinolene Dioxide/PCI-1 mixture system. In the gelation time in the presence of Irgacure184, it took half only two seconds without an additive (Irgacure184).

Acceleration by other sources of cation

The vinyl ether which gives the same carbo-cation from it having turned out that carbo-cation like carbenium ion is activating the cationic polymerization of cyclic ether by the above examination was used for polymerization of cyclic ether. It blended with the Shlenk tube by the molar ratio of IBVE/Cyclic Ether/PCI-1=0.0-0.4/1.0 - 0.6/1.0x10^{-3}. 500mg of obtained glue was put into the screw vial, and it hardened using the mercury lamp of 1000 mJ/cm^2. The molecular weight of polymer obtained form the glue mixture was measured by GPC. The gelation time is shown in Table 3 and the chromatogram of GPC is shown in Figure 3 and Figure 4.

Table.3 Gelation time of copolymerizaiton of **IBVE** and cyclic ether

Polym System	Gelation Time(s)	Polym System	Gelation Time(s)
IBVE/POX [mol/mol]		IBVE/PGE [mol/mol]	
0.4/0.6	1.9	0.4/0.6	1.2
0.3/0.7	2.7	0.3/0.7	1.0
0.2/0.8	2.9	0.2/0.8	1.8
0.1/0.9	2.5	0.1/0.9	14.6
0.0/1.0	11.4	0.0/1.0	50.0

The polymerization of cyclic ethers in the presence of vinyl ethers has been speeding up than the polymerization of independently cyclic ethers. Moreover, the phenomenon of high molecular weight was seemed about POX.
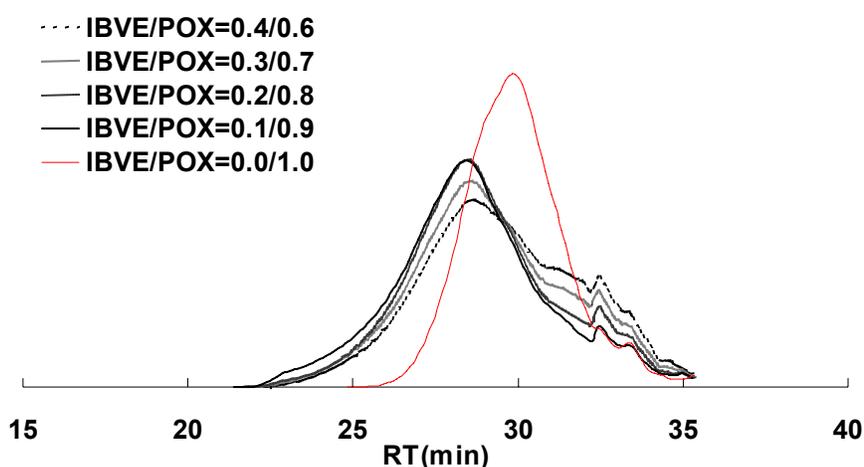
Figure.3 GPC curves obtained by copolymerization of **POX** and **IBVE**
[IBVE]/[POX]/[PCI-1] = 0.0-0.4/1.0 - 0.6 / 1.0x10^{-3} mol/g
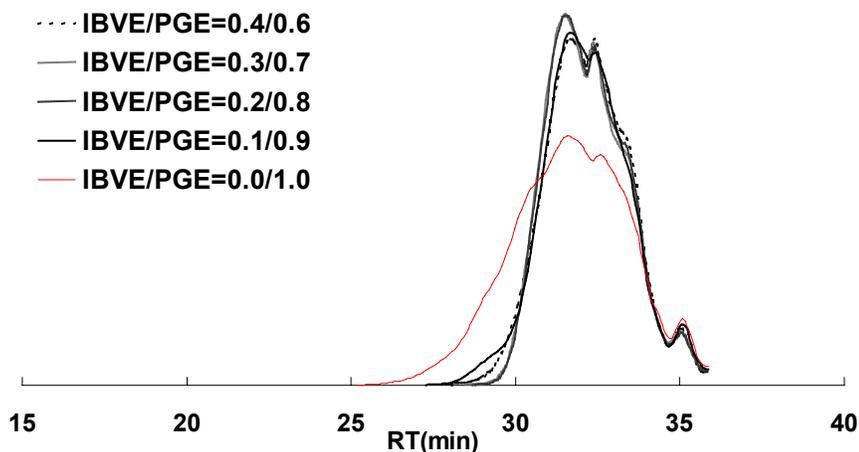
Figure.4 GPC curves obtained by copolymerization of **PGE** and **IBVE**
[IBVE]/[PGE]/[PCI-1] = 0.0-0.4/1.0 - 0.6 / 1.0x10^{-3} mol/g

The 1-iso butoxy ethyl acetate (IBEA) is provided from acetic acid and vinyl ether. IBEA has the hemiacetal structure, and gives carbo-cation potentially of accelerating cationic rig-opening polymerization. We try to use IBEA as additive in the polymerization of cyclic ethers. IBEA was used of the number of the mols same as PCI -1. The gelation time is shown in Table 4 and the chromatogram of GPC is shown in Figure 5.

It was confirmed that IBEA activated polymerization of cyclic ethers, too. More interestingly, IBEA influenced polymerization in quantity about the same as the amount of catalysts.

Table.4 Gelation time of polymerization cyclic ether in the presence of **IBEA**

Polym system[mol/mol]	Gelation Time(s)
POX/IBEA=1.0/3.0×10^{-3}	**3.1**
POX/IBEA=1.0/-	**11.4**
PGE/IBEA=1.0/3.0×10^{-3}	**39.0**
PGE/IBEA=1.0/-	**50.0**
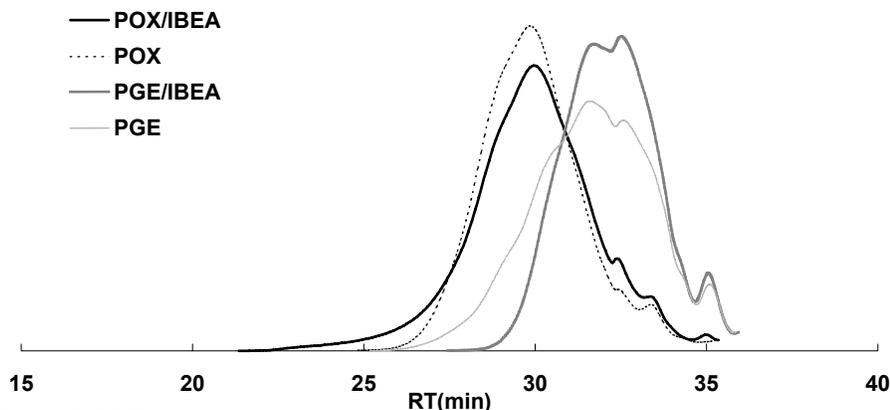
Figure 5 GPC curves obtained by polymerization of cyclic ether in the presence of **IBEA**

It seems that vinyl ether and its acetic acid accretionary compound are acting in assistant catalyst in an initiation reaction.

Namely, in the ring-opening cationic polymerization of cyclic ether, unlike the conventional polymerization, the carbo-cation generated from vinyl ether is advancing smoothly from initiation reaction to propagation reaction. (Scheme V)

Conventional System
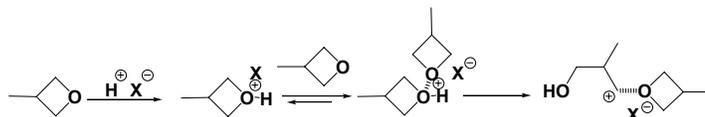
System in the Presence of Carbo-cation

IBVE

IBEA

Scheme V
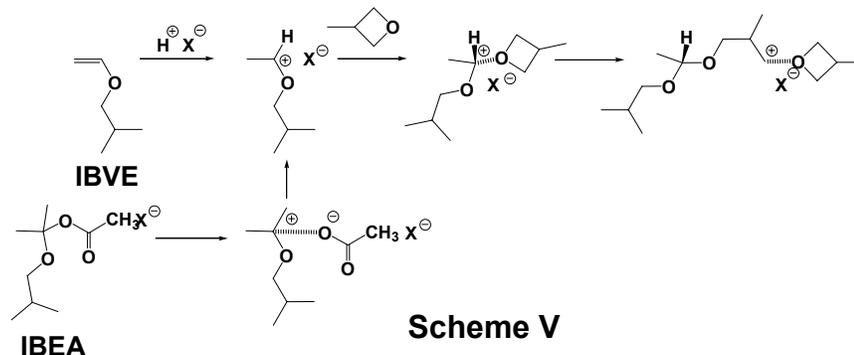
Conclusion

The rapid curing in UV cationic polymerization of oxirane was examined. In addition to the method of using the oxetane known as a means to accelerate the propagation reaction. We pay attention to the initiation reaction. It realized that a rapid polymerization which is equal to radical polymerization by utilizing oxirane monomer which has an alkyl substituent in alpha carbon. It's was suggested that stable oxonium ion transfer to carbenium ion during the initiation reaction. Furthermore, paying attention to radical in the decomposition process of photo cationic initiator, it found out that polymerization speed improved further by using photo radical initiator together.

Moreover, it found out that the vinyl ether known as a compound of carbo-cation activated UV cationic polymerization similarly.

Reference

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