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PHOTOINITIATED CATIONIC POLYMERIZATION OF 3-ETHYL-3-(PHENOXYMETHYL)-OXETANE IN NITROGEN ATMOSPHERE

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Key Words: Photoinitiated cationic polymerization; Oxetane; Nitrogen atmosphere; Radical-induced cationic polymerization

ABSTRACT

The photoinitiated cationic polymerizations of 3-ethyl-3-(phenoxy-methyl)-oxetane (PhO) and phenyl glycidyl ether (PhE) with diphenyl-4-thiophenoxyphenyl sulfonium hexafluoroantimonate as the cationic photoinitiator were carried out in air and nitrogen atmospheres. A real-time FT-IR method was used to estimate the polymerization rates. The number-average molecular weight (M_n) of the resulting polymers were measured by gel permeation chromatography. In nitrogen, the photopolymerization rate of PhO was more than four times greater than in air, while there was no essential difference for PhE. The M_n of the PhO

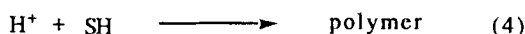
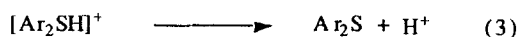
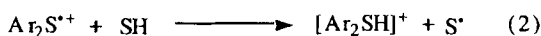
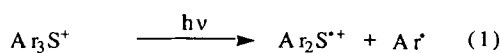
polymer increased from 13,900 (in air) to 61,200 (in nitrogen) at the peak top. The fast polymerization mechanism in nitrogen was postulated to be the radical-assisted decomposition of the sulfonium salt.

INTRODUCTION

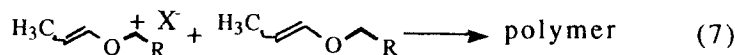
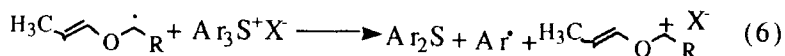
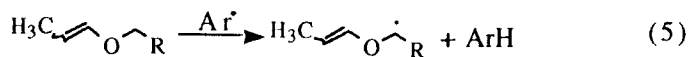
Photoinitiated cationic polymerization methods are of considerable interest because of their high throughput, low energy requirements, and solvent-free nature. Among the commercially available monomers, oxiranes are widely used for the photoinitiated cationic polymerization system. Although the photopolymerized oxirane resins exhibit excellent mechanical and chemical properties, the polymerization rates of oxiranes toward cationic polymerization are rather slow, which can be explained by their low basicity. Oxetanes possess a much higher basicity and a slightly lower ring strain energy than oxiranes and, therefore, are very attractive for improving the slow polymerization of oxiranes while maintaining the good properties of cured resins.

Previously, we reported the higher reactivity of novel oxetanes compared with that of oxiranes during photoinitiated cationic polymerization [1, 2], and thus we began to study the application of oxetanes as monomers for coating and adhesion materials. During the investigation of oxetanes, we recently found that the photoinitiated cationic polymerization rates of mono- or dioxetanyl monomers in nitrogen are extremely accelerated when compared to those in air [3].

Onium salts, which are used as photoinitiators for photoinitiated cationic polymerization, undergo photolysis through a radical reaction (Eqs. 1-4) [4].



Crivello and Jo proposed a "free radical-induced decomposition mechanism" to explain the variation in the experimental results of the photoinitiated cationic polymerization of propenyl ethers (Eqs. 5-7) [5]. They suggested that α -ether radicals, which are generated through hydrogen abstraction by the aryl radical, work as reducing agents for the photoinitiator and, as a result, the acid generation efficiency is increased. A similar mechanism has also been independently proposed [6, 7].



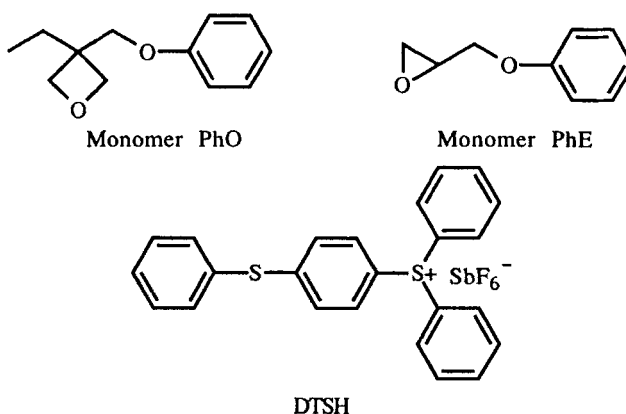
For the radiation-induced polymerization of 3,3-bis(chloromethyl) oxetane (BCMO) formulated with maleic anhydride (MA), Okamura et al. proposed a radical-induced cationic polymerization mechanism [8]. They suggested that the active species for cationic polymerization of BCMO are generated through radical reaction between BCMO and MA.

Oxygen is known as a strong radical scavenger. Considering the previous results, the fast polymerization of oxetanes in a nitrogen atmosphere might be explained by a radical reaction that facilitates cationic polymerization, which is inhibited by oxygen in air.

Although a number of such radical-assisted cationic polymerization mechanisms has been reported [5-8], no characterization of the resulting polymer has been done. Multifunctional monomers, possessing more than two reactive moieties in the molecule, result in an insoluble network gel whose characterization is very difficult by authentic analysis. To investigate the fast polymerization mechanism of oxetane in nitrogen, we depict 3-ethyl-3-(phenoxyethyl)-oxetane (PhO) as a monofunctional oxetane monomer which results in a linear and soluble polymer. As a reference, we also carried out the photopolymerization of oxirane monomer, phenyl glycidyl ether (PhE), which possesses the same phenyl group as PhO. For the characterization of the polymers, we used gel permeation chromatography. We also employed a real-time FT-IR method which was developed by Yang [9] for the evaluation of reactivities.

Using these methods, we report the fast photopolymerization of PhO with a sulfonium salt (diphenyl-4-thiophenoxyphenyl sulfonium hexafluoroantimonate: DTSH) as a cationic photoinitiator in nitrogen.

Monomers and photoinitiator



EXPERIMENTAL

Materials

PhE was purchased from Tokyo Kasei Co. All other starting materials and solvents were of reagent quality and were used as received. PhO was prepared by

the phase-transfer reaction of 3-(chloromethyl)-3-ethyl-oxetane and phenol. DTSH used as a photoinitiator was prepared according to the procedures of Crivello [10].

Polymerization and Real Time Infrared Measurement

The conversions of monomers to polymers were measured using real-time FT-IR spectroscopy employing the method of Yang [9]. The apparatus used for these measurements consisted of a Nicolet Magna-IR 550 FT-IR spectrometer equipped with a Ushio Spot Cure UIS-25102 (250w) fitted with a fiber optic cable. The probe of the fiber optic cable was positioned so that the UV irradiation was directed onto the sample. Air and/or nitrogen are introduced into the sample chamber of the FT-IR spectrometer through a glass tube filled with silica gel to keep them dry. Polymerizations were carried out at room temperature on samples of the monomers containing 0.5 mol% DTSH coated onto an aluminum plate (sample thickness = 10 μm) in air and nitrogen. The nitrogen atmosphere was established by the 10-minute substitution of air with nitrogen in the sample chamber of the FT-IR spectrometer (no absorption of CO_2 was detected). All the samples were irradiated at UV intensities of 44.2 mW/cm^2 . The UV irradiation intensity measurements were made with the aid of a Ushio UNIMETER UIT-102 radiometer at 365 nm. During the irradiation, the decrease in the absorbances at 995 cm^{-1} for the oxetane and at 865 cm^{-1} for the epoxide were monitored. After the decrease in absorbance had ceased, the conversions of the monomers were calculated by comparing the initial and final absorbances.

Photopolymerization for GPC Measurement

The photopolymerization was carried out under the same conditions as previously mentioned. The irradiation time was 30 seconds for full conversion of the monomers, and the total irradiated energy was 1.33 J/cm^2 . After irradiation, the resulting polymer was dissolved in THF containing a small amount of ammonium hydroxide (to neutralize any remaining acid). The molecular weight distribution was measured using gel permeation chromatography (GPC) in THF at 40°C on a TOSOH S8010 GPC system equipped with five polystyrene gel columns [TSK Gel G-7000HXL, 5000HXL, 4000HXL, MHXL (2 columns)] and a refractive index detector. The number-average molecular weight (M_n) was calculated from the GPC curves on the basis of the polystyrene calibration.

RESULTS AND DISCUSSION

Real-Time FT-IR Method

Figure 1 shows plots for the conversions of PhO and PhE versus irradiated time in air and nitrogen using the real-time FT-IR method. The polymerization reactivity of PhO, possessing the same phenyl group as PhE, was significantly affected by the atmosphere. In air, the conversion curve of the oxetanyl group showed an S-type curve indicative of the induction period up to 2 seconds of UV irradiation and reached 80% conversion after 5 seconds. In nitrogen, however, the photopolymerization of PhO was extremely accelerated and the conversion reached

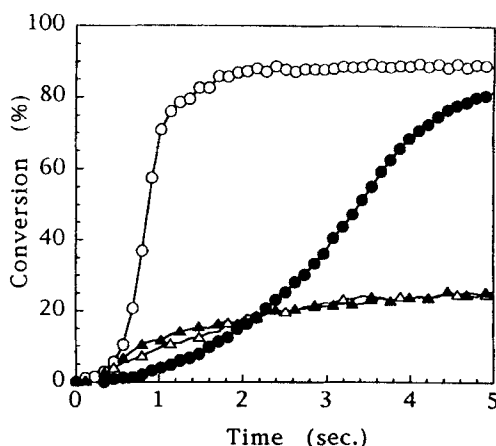


FIG. 1. Conversion versus irradiation time curves using 0.5 mol% photoinitiator at a UV intensity of 44.2 mW/cm². In air atmosphere: PhE (▲), PhO (●). In nitrogen atmosphere: PhE (△), PhO (○)

80% with less than 1 second of UV irradiation. During this fast polymerization of oxetane in nitrogen, the induction period was shortened but was still observed at up to 0.5 seconds.

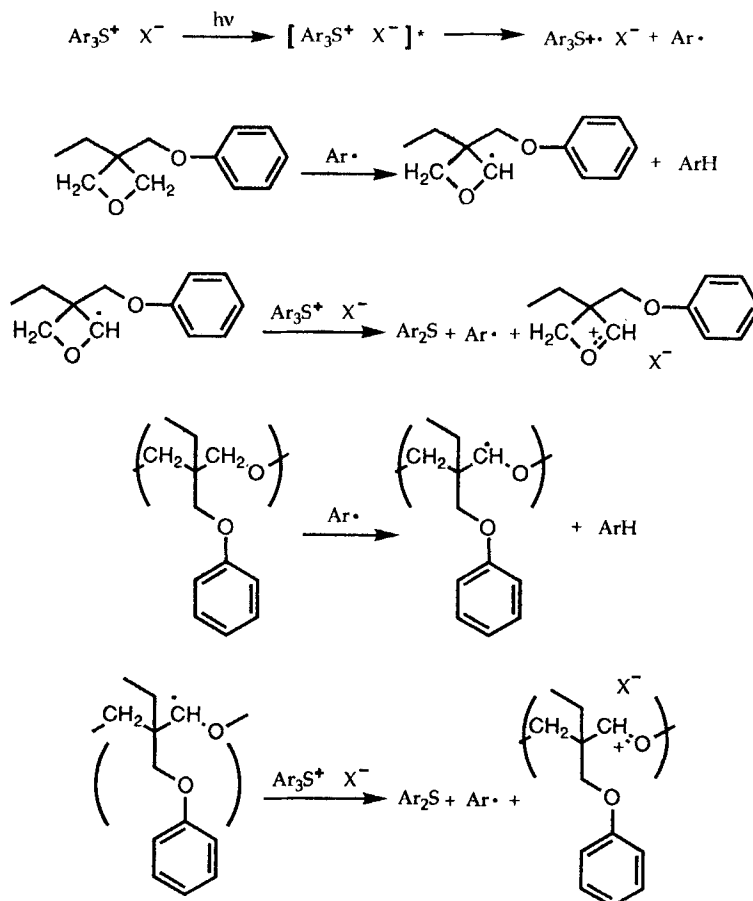
The mechanism of cationic ring-opening polymerization of cyclic ethers has been proposed to undergo an S_N2 reaction. For the initiation stage, an acid first attacks a cyclic ether, and a dialkyl oxonium cation is generated in the equilibrium reaction. Another monomer attacks the oxonium cation in an S_N2 fashion to form a trialkyl oxonium cation. Once the trialkyl oxonium cation is generated, the propagation goes through an S_N2 mechanism. Because the protonation of the cyclic monomer is in equilibrium, the ring-opening reaction of the dialkyl oxonium cation (generation of a trialkyl oxonium cation) is considered to be the rate-determining step for the initiation stage. The trialkyl oxonium cation is the actual propagating species, and the overall polymerization rate is governed by the generation rate of the trialkyl oxonium cation (i.e., the concentration of the cation). In a previous study, using a semiempirical method (AM1), we reported that the polymerization path of the oxetane seems to go through an S_N2 mechanism [11]. The induction time of PhO can be explained by the first step of the initiation stage of the S_N2 reaction (generation of the dialkyloxonium cation in equilibrium). After a sufficient generation of reactive chain ends (the trialkyl oxonium cation), the propagation of PhO proceeds with a high polymerization rate due to its high basicity. The existence of an induction period both in air and in nitrogen implies that both photopolymerizations proceed through the same S_N2-type mechanism.

For PhO, there are many ether-linked α -methylene groups on the ring and at the substituent group in the 3-position of the ring. Radical species, which are primarily formed from the photoinitiator, easily abstract hydrogen from the α -methylene groups. After the generation of the α -ether radical, the fast polymerization mechanism of oxetane in nitrogen can also be explained by the single electron transfer (SET) reaction [5-7] from the radical to the sulfonium salt, resulting in the

generation of the initiating cationic species (Scheme 1). The polymerization rate of oxetane should be affected by the generation rate of cationic species formed through the radical reaction. The fast polymerization of oxetane is caused by the lack of oxygen in the nitrogen atmosphere, because molecular oxygen is an effective radical trapping agent and delays the radical reaction.

On the other hand, PhE exhibited almost no difference when in air or in nitrogen; the same results reported by Decker [12]. PhE showed a different conversion curve from PhO both in air and in nitrogen. No induction period was observed, and initially the curve had a steeper slope, indicative of a higher reactivity than that of PhO. After a 1-second irradiation (around 10% conversion), the polymerization rate suddenly slowed down and the conversion reached only about 30% after 5 seconds of irradiation.

In a previous study, possibilities of an S_N1 (or an S_N1 -like) through the α -cleavage and of an S_N2 through β -cleavage were implied for oxirane [11]. The absence of an induction time indicates a fast initiation reaction, which can be



SCHEME 1. Reaction mechanism of radical-induced cationic polymerization of oxetane (PhO).

explained by the spontaneous ring opening of the oxirane without an equilibrium reaction of the dialkyl oxonium cation and direct generation of a carbenium ion. The sudden drop in the polymerization rate implies the stabilization of the carbenium ion by the ether oxygen on the polymer main chain due to the low basicity of the oxygen atom on the oxirane ring. For the photopolymerization of PhE, radical species from the photoinitiator should mainly abstract hydrogen from the α -position on the oxirane ring, thus generating a more stable tertiary radical. The previously mentioned SET mechanism is governed by the free energy of the reaction, which depends on the difference in potential between the oxidation of the free radical and the reduction potential of the onium salt. For the single electron transfer to take place, the value of ΔG must be negative [5]. The oxidation potential of the tertiary radical of PhE might not be enough to reduce the sulfonium salt (DTSH) used in this study.

GPC Measurement

The GPC curves of polymers PhE (PPhE) and PhO (PPhO) in air and nitrogen are shown in Figs. 2 and 3, respectively. The M_n of PPhE was around 2400 at the peak top in air and was slightly higher (3600) in nitrogen. The low M_n of PPhE is explained by a chain-transfer reaction or backbiting, resulting in a cyclic oligomer during polymerization because of the low basicity of the oxygen atom on the oxirane ring. The slight difference between the M_n s of PPhE in air and nitrogen also indicates that the polymerization mechanism of PhE is not affected by atmosphere.

On the other hand, the M_n of PPhO in nitrogen was more than four times higher than that in air [13,900 (in air) to 61,200 (in nitrogen) at the peak top]. During the fast polymerization mechanism of oxetane which was previously proposed, the number of active chain ends in nitrogen should be higher than those in air. If the hydrogen abstraction by radical species primary formed from the photoinitiator occurs only on the α -methylene group of the oxetane ring, the M_n of PPhO should be lower than that in air. The ease of hydrogen abstraction from the ether-linked α -methylene of either the oxetane ring or the open chain ether, such as the polymer main chain, should be almost the same. The higher M_n of PPhO in

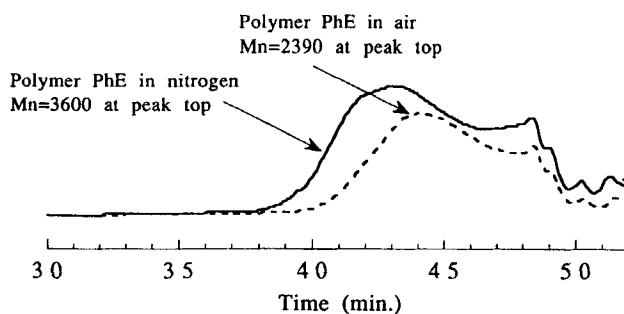


FIG. 2. GPC elution curves of polymer PhE in air and nitrogen atmosphere using 0.5 mol% photoinitiator at a UV intensity of 44.2 mW/cm^2 and a total irradiated energy of 1.33 J/cm^2 .

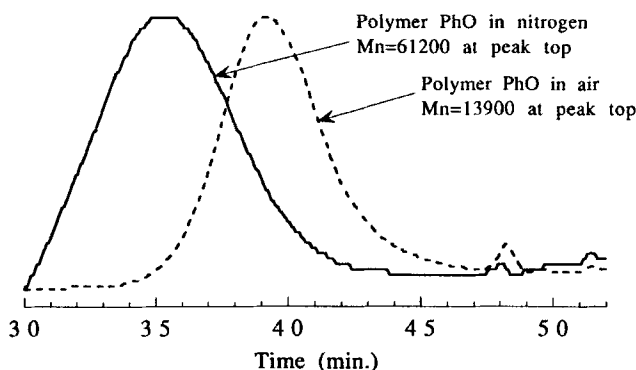


FIG. 3. GPC elution curves of polymer PhO in air and nitrogen atmosphere using 0.5 mol% photoinitiator at a UV intensity of 44.2 mW/cm² and a total irradiated energy of 1.33 J/cm².

nitrogen suggests that the hydrogen abstraction and subsequent oxidation by the onium salt also occurs on the α -methylene group of the polymer main chain, and the branched polymer will be generated from the resulting carbenium ion on the polymer main chain (Scheme 1).

CONCLUSIONS

The fast polymerization mechanism of oxetane toward photoinitiated cationic polymerization in a nitrogen atmosphere was investigated by using PhO as a mono-functional oxetane monomer. A real-time FT-IR measurement revealed that the photopolymerization rate of PhO was extremely accelerated in nitrogen. The M_n of PPhO polymerized in nitrogen was more than four times higher than that in air. The fast polymerization mechanism in nitrogen was explained by the radical-assisted decomposition of the sulfonium salt. This additional decomposition mechanism contributes to the increased efficiency of acid generation, which results in an elevated efficiency of the photopolymerization of oxetanes, and to the higher molecular weight of the resulting polymer.

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