Development of a Cationic UV Curable Inkjet Ink – Formulation Effect on Curing Behavior

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Abstract

Two alternative curing mechanisms may be used; free radical polymerization and cationic polymerization. Free radical polymerization currently dominates because of its low cost and the ease of design afforded by a wide selection of usable monomers. Cationic polymerization is a new process but has become to get many attracts because of its unique advantages. One of the challenges of the cationic polymerization is the tendency to be affected by moisture. Studying about the polymerization under several moisture levels, we found the reactivity of monomers controlled the effect of moisture. We will report results of mechanistic study of the effect as well as ink performances at high humidity environment.

Introduction

UV curable inkjet systems have proliferated because they can be used with non-absorbing media and because they fix quickly. Two alternative curing mechanisms may be used, free radical polymerization or cationic polymerization. Free radical polymerization currently dominates because of its low cost and the ease of design afforded by a wide selection of usable monomers.

However, free radical polymerization has an inherent disadvantage: oxygen inhibits their polymerization. Inkjet inks have lower viscosity than conventional off-set inks, and atmospheric oxygen can diffuse into inks with lower viscosity. Consequently, inhibition takes place more easily in inkjet inks than in off-set inks.[1]

Cationic polymerization, the alternative curing mechanism,[2] avoids these difficulties by adopting a different polymerization mechanism that is free of oxygen inhibition. Key component for the polymerization is photo-generated acid. The acid protonates cyclic ether oxygen. It can be cleaved to carbonium cation (a). Unprotonated cyclic ether reacts with the cation to form alkyl oxonium cation (b). The oxonium cation can also be formed by the reaction of the cation (a) with unprotonated ether in S_N2 type reaction. The cation (b) reacts with the ether sequentially to form polyethers.

One of the issues of the cationic polymerization is the tendency to be affected by moisture. It was said that water molecule can react with the cation intermediate to terminate the polymerization because of its higher reactivity.[3]

In this paper, we present our results with a focus on effects of water on curing performance as well as mechanistic study.

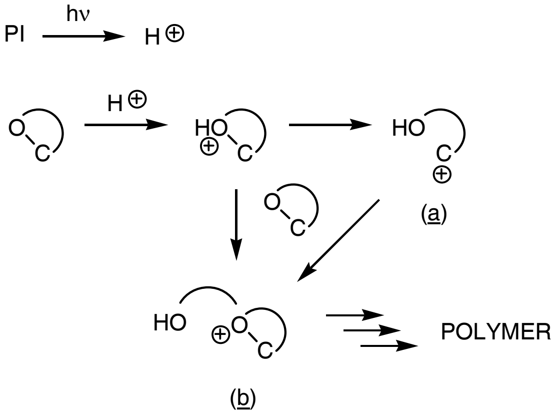


Figure 1 Cationic polymerization mechanism

Experimental

Epoxide (2) was synthesized by a conventional method.[4] Other monomers and photo-initiator used in this study are commercially available. Monomers and the photo-initiator were mixed with under yellow light and used for the study. Curing speeds were measured with FT-IR spectrophotometer.

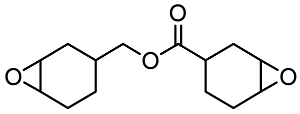
Results and Discussions

Effect of water on ring-opening reaction of epoxides

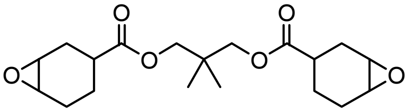
The effect of water on ring-opening reaction of epoxides was evaluated by using real time FT-IR spectroscopy at high and low humidity environments.

We mixed epoxide monomers, (1), (2), and (3) with photo-initiator (4) separately. The mixtures were irradiated with high pressure mercury lamp and a decay of peak intensity at 775 cm^{-1}, which was assigned to the absorption of epoxide ring, was monitored to evaluate the reaction rate. The measurements were carried out at 20%RH and 80%RH environments and the results were summarized in figure 2.

The curves showed the rate of ring-opening reaction of epoxide. Epoxide (1) and (2) showed higher rates while epoxide (3) showed slower rate at 20%RH. At high humidity environment, 80%RH, all the ring-opening rates were retarded greatly. In particular, epoxides (2) and (3) showed a big retardation.



(1)



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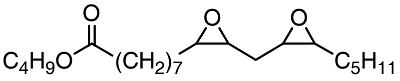

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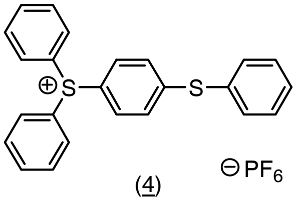

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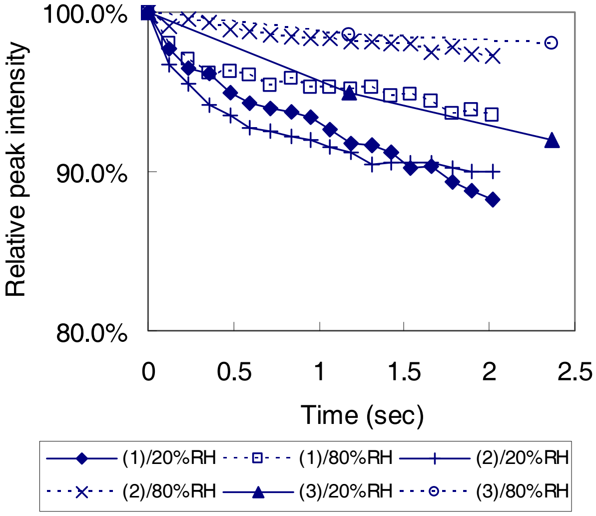


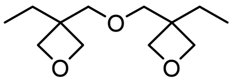
Figure 2. Ring-opening reaction of epoxides at 20%RH (solid lines) and 80%RH (dashed lines)

Effect of water on curing behavior of oxetane-epoxide mixtures

It was reported that mixture of oxetane and epoxide showed good curing behavior for practical use of cationic polymerization as UV curable ink.[2] Although the epoxide used in the literature showed higher reaction rate alone at initial stage of polymerization, its conversion ratio stayed low. Although the oxetane used showed higher conversion ratio alone, its reaction rate was low at the initial stage. It was found the mixture of the epoxide and the oxetane showed a synergistic effect on curing behavior; the epoxide gave higher reaction rate and oxetane gave higher conversion rate.

To evaluate the effect of water on practical usage, we then measured the effect of water on curing sensitivity with coatings of the mixture of oxetane (5) and above mentioned epoxides. We mixed the oxetane with epoxides and the photo-initiator to form model inks. The ratio was 67/28/5 in weight. The mixtures were coated on PET with wire bar, and the thickness of the coating was adjusted to be 3 μm. Then they were irradiated with high pressure mercury lamp at 3 humidity levels, 20%RH, 50%RH, and 80%RH. To compare the curing sensitivity at every humidity level, we measured irradiated energy that was necessary to become durable against scratch. The results were summarized in figure 3.

In figure 3, we observed similar effect of water to that of on ring-opening reaction. Efficiency of polymerization was decreased as humidity level was increased. Much energy was necessary at higher humidity levels. Combining with the result in figure 2, it seemed that the ring-opening reaction rate affected the curing sensitivity. Epoxide (1), which showed the highest rates at both high and low humidity alone, showed higher polymerization efficiency with the oxetane. Epoxide (3), which showed the slowest rates, showed lower polymerization efficiency.



(5)

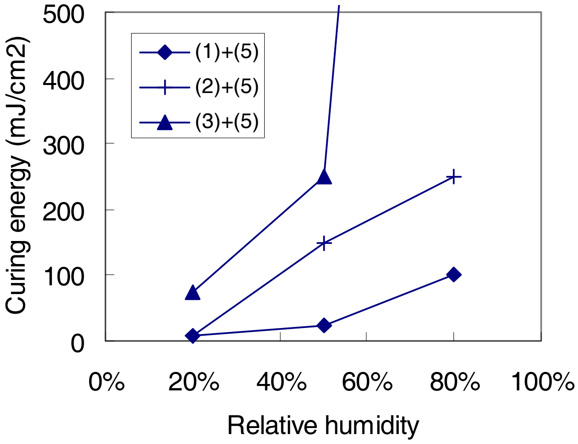


Figure 3 Humidity dependence of curing sensitivity.

Reaction mechanism of cationic polymerization

Although the carbonium cation derived from epoxide was reported to be a key intermediate and its formation step is rate-determining of the polymerization, the effect of water did not reported.[2] To clarify the effect, we studied the reaction mechanism of the polymerization of oxetane-epoxide system in the presence of water.

We evaluated tendency of protonation by photo-generated acid of the materials, oxetanes, water, and epoxides, by comparing their basicity, pKb values.

The basicity of oxygen atoms of oxetane and epoxide were reported as shown below. Oxetane-oxygen has the biggest pKb value; it means that oxetane has the highest basicity of the three. The photo-generated proton will be added on the oxetane-oxygen in higher ratio. The oxonium cation derived from the oxetane, however, was reported to be much stable than the oxonium cation derived from epoxide; the polymerization will be promoted only from the epoxide-derived oxonium cation.

	oxetane	water	epoxide
pKb	3.1	7.0	7.4

When the polymerization will be carried out at higher humidity environment, the ink can absorb certain amount of water. Water molecule is less basic than oxetane but much basic than epoxide. Water molecule can trap the photo-generated proton and retard to form the epoxide-derived oxonium cation (B). The concentration of the oxonium cation will be decreased, and the polymerization will be retarded accordingly. The mechanism was proposed in figure 4.

If the ring-opening reaction of the epoxide-derived oxonium cation (B) is fast, much amount of epoxide (A) will be protonated through the equilibrium *EQ*. Consequently, efficiency of the polymerization with such epoxide will be improved as shown in figure 3.

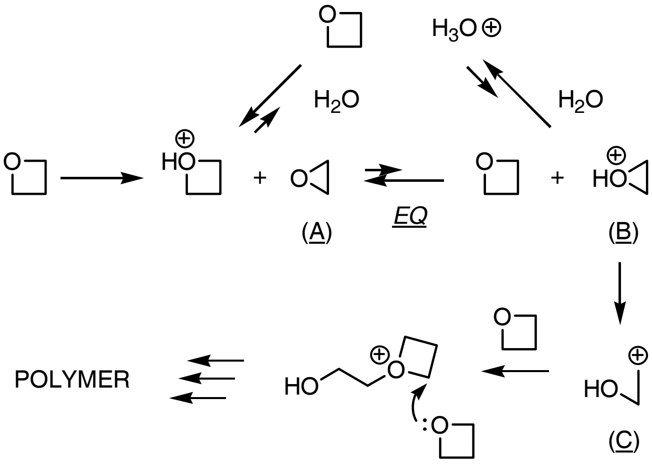


Figure 4. Polymerization mechanism in the presence of water

Conclusion

We evaluated the effect of water on ring-opening reaction of epoxides by using real time FT-IR spectroscopy. The ring-opening reactions were retarded greatly at high humidity environment. We also evaluated the effect of water on curing behavior of oxetane-epoxide mixture system. The curing sensitivity was also affected by moisture and much amount of energy was necessary at high humidity environment to be cured.

Comparing pKb values of materials, epoxide was found to be less basic than oxetane and water. The generation of the key intermediate, oxonium cation (B), will be affected by water accordingly. The concentration of the cation will be decreased by water and the polymerization will be retarded accordingly.

From the mechanism, it was considered that accelerating of the ring-opening reaction will suppress the effect of water on the curing. Epoxides with higher ring-opening rate showed good curing behavior even at high humidity environment.

References

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[3] "UV curable materials", Johokiko co.,ltd, 11(2006)
[4] Japanese Patens, No.3770274

Author Biography

Atsushi Tomotake received his Ph.D. degree in Synthetic Organic Chemistry in University of Tsukuba in 1987. He joined Konica Corporation in the same year. He was working to develop new materials for color silver halide photographic paper for many years. Now his interest is focused on the materials for color hard copy, such as thermal dye transfer printing and ink jets.