

Effect of Water in Cationic Photopolymerizations: Reversible Inhibition

By Ruiping Huang,
Beth A. Ficek,
Shedric O. Glover and
Alec B. Scranton

In this contribution, the effect of water on cationic photopolymerizations of vinyl ethers is investigated by subjecting polymerization systems to nitrogen atmospheres of controlled humidity. Cationic photopolymerizations of dodecyl vinyl ether thin films were performed in environments of varying percent saturations while monitoring the monomer concentration using Raman spectroscopy. For conditions of constant humidity, it was found that the degree of inhibition increased with increasing humidity, and that a saturated atmosphere leads to complete inhibition. The inhibition was found to be reversible, with rapid polymerization observed when the system was flushed with dry nitrogen, even after 25 minutes in the dark.

Introduction

Photoinitiated cationic polymerizations offer many important advantages for industrial applications. They exhibit very high active center concentrations, and may achieve high reaction rates resulting in highly crosslinked polymers that offer excellent adhesion, abrasion resistance and chemical resistance. In contrast to free radical photopolymerizations, cationic polymerizations are not inhibited by oxygen and do not experience termination by combination or disproportionation and therefore may continue to cure for hours, even days after removal from a light source.¹⁻³ These features make cationic photopoly-

merizations attractive for a variety of applications. One potential disadvantage of cationic photopolymerization is its sensitivity to moisture.

Recently, a number of authors have investigated the effect of moisture on cationic photopolymerizations.⁴⁻⁹ For example, Lin and Stansbury used real time infrared spectroscopy (FT-IR), to investigate cationic polymerizations of vinyl ethers containing water added directly to the formulation, and found that the monomer structure had an important impact on the inhibition mechanism. For monomers containing hydroxyl groups, increasing amounts of water resulted in large reductions of polymerization rate but similar induction times and final conversions.⁴ It was concluded that the hydroxyl-terminated vinyl ethers undergo an unusual self-polyaddition in which the hydroxyl group will react with the vinyloxy functionality of another monomer resulting in formation of polyacetals. Water slows this polyacetal formation, but does not have a significant affect on the final polymer properties.

The water inhibition for cationic photopolymerizations of vinyl ether monomers, which do not contain hydroxyl groups, has been recently studied by both Lin and Stansbury⁴ and Crivello *et al.*⁵ Lin and Stansbury reported the induction times of the polymerization increase with increasing water content, but the overall polymerization rate and final conversion remain

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unaffected. The authors concluded that for these monomers, water will react with the cationic active center in a chain transfer reaction producing another active center, as shown in Figure 1a. The hydroxyl formed in this reaction may carry out a second chain transfer reaction to consume a second propagating chain and produce a second proton. In both of these chain transfer reactions, the resulting proton is much more reactive to water than vinyl ether monomers. The proton will participate in the reaction, shown in Figure 1b, to produce a hydronium ion that is not active for initiation of the monomer, therefore decreasing the active center concentration.⁴ Crivello *et al.* investigated cationic photopolymerizations of vinyl ethers containing water introduced from the atmosphere

rather than being mixed into the original formulation. Using optical pyrometry, the authors again concluded that cationic active centers will preferentially react with water until water is depleted from the system and only then will the remaining cationic active centers polymerize the monomer.

In this contribution, the effect of water on the cationic photopolymerization of a hydroxyl-free vinyl ether monomer was further investigated to determine whether the inhibition by water could be reversed simply by changing the atmospheric conditions. Specifically, 30-50 micron films were photopolymerized in a custom-made chamber, which allowed polymerizations to be carried out under conditions of controlled nitrogen atmosphere while the monomer concentration is monitored *in situ* by Raman spectroscopy. The

experimental design allowed the relative saturation of the nitrogen atmosphere to remain constant, or to be changed at will, thereby allowing new aspects of the inhibition by water to be investigated.

Experimental

Materials

The monomer dodecyl vinyl ether (DVE) was purchased from Sigma Chemical. This monomer, whose chemical structure is shown in Figure 2, was selected because it is a mono (vinyl ether) with a low vapor pressure that contains no hydroxyl groups. An iodonium triflate (IT) salt supplied by Dow Corning was used as the cationic photoinitiator at concentrations of 0.15 mol% (Figure 3).

Methods

The reaction chamber was constructed out of glass with the exception of the top surface, which was quartz to allow UV illumination from above. The bottom glass surface was cooled with circulated water to keep the temperature constant (23°C). A type 61 IR Card (3M Corp.) was used to maintain a well-defined film thickness of 30-50 microns. Raman scattering was induced with 200 mW of 514.5 nm radiation from a Coherent Innova 70 argon ion laser. The Raman probe beam was focused and entered the glass bottom at large angle (> 70 degree) to increase the light path in the mixture. A low-pressure mercury lamp (Oriel, Model 6034) was used as the UV-light source. To test the effects of moisture, the chamber was purged with nitrogen (ranging from dry to water-saturated) at a rate of at least 0.5 L/minute. The Raman signal was collected using a Spex 1877 Triplemate monochromator, and the light was focused onto a liquid-nitrogen-cooled CCD detector (EG&G Princeton Applied Research Model 1530C/CUV). The data were analyzed with an OMA 4000 detector

FIGURE 1A

Reactions of water and cationic active centers in vinyl ether polymerization systems without hydroxyl end groups

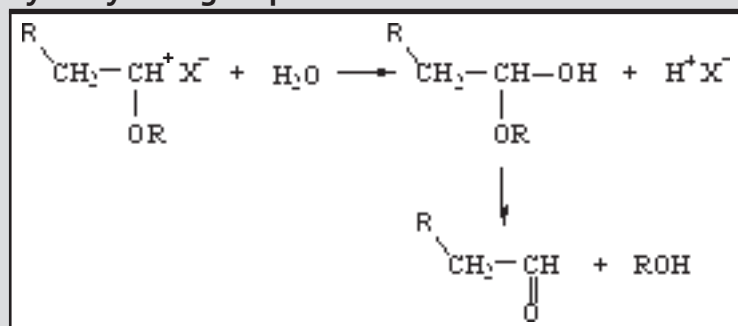


FIGURE 1B

Proton produces a hydronium ion



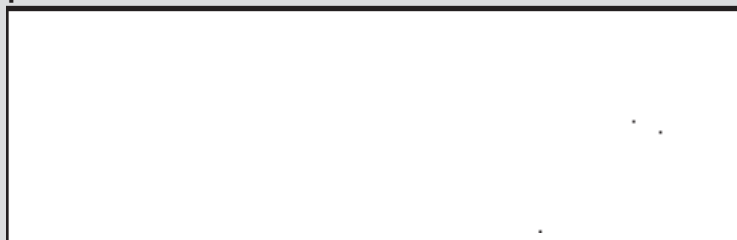
FIGURE 2

Structure of cationic monomer dodecyl vinyl ether (DVE)



FIGURE 3

Structure of iodonium triflate salt (IT) cationic photoinitiator



controller and software. The monomer conversion was determined by monitoring the peak area of the doublet at 1630 cm⁻¹, which arises from the double bond and represented the concentration of non-polymerized vinyl. The peak area at 1460 cm⁻¹, which arises from the wagging and bending of the ethyl ether carbon-hydrogen bonds, was used as internal standard.

Results and Discussion

Moisture Inhibition

The effect of atmospheric moisture on the photopolymerization of DVE is illustrated in Figure 4, which shows the DVE conversion for three different nitrogen atmospheres: dried nitrogen (0% relative saturation), 50% relative saturation, and 100% relative saturation. The figure illustrates that the polymerization proceeds rapidly with no induction time under dry conditions (with 50% converted in 5 seconds), and is completely inhibited when the polymerization is carried out in a

nitrogen atmosphere that is saturated with water vapor (no conversion was noted even after 150 seconds of illumination). For the system polymerized in a 50% saturated

nitrogen atmosphere, an induction time of 10 seconds is observed during which the conversion remains essentially zero. At the end of this induction time, the reaction proceeds at a slower rate than the dry system. The effects of the atmospheric relative saturation on the induction time and the time to reach 50% conversion are summarized by the data in Table 1. Since these reactions are carried out in films that are exposed to nitrogen atmospheres of constant humidity, water is able to enter the system from the atmosphere. Therefore, water that is consumed by the reaction shown in Figure 1b can be replenished from the atmosphere, and in the case of 100% relative saturation, this prevents the polymerization from taking place. For the case of 50% relative saturation, the shape of the polymerization profile depends upon both the initially dissolved water and the additional water that enters from the atmosphere.

Reversible Water Inhibition

In this study, the reversibility of the water inhibition is explored by

FIGURE 4

Conversion vs. time for cationic photopolymerizations of DVE containing 0.15 mol.% IT in nitrogen atmospheres of 0%, 50% and 100% relative saturation

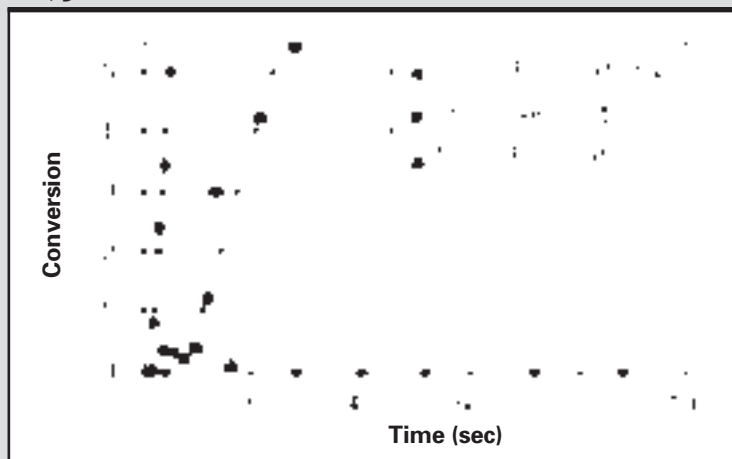


TABLE 1

Induction time and time to reach 50% conversion for cationic photopolymerizations of DVE containing 0.15 mol.% IT in nitrogen atmospheres of 0%, 50%, and 100% relative saturation

Atmospheric Relative Saturation	Induction Time (Seconds)	Time to reach 50% conversion
0%	0 sec	5 sec
50%	10 sec	~25 sec
100%	∞	∞

monitoring the monomer conversion while the relative saturation of the nitrogen atmosphere is changed from 100% relative saturation to dry conditions. In this experiment, the thin film of vinyl ether monomer is illuminated for one minute while it is exposed to a nitrogen atmosphere of 100% relative saturation. The active centers produced during this time are quickly inhibited by reaction with water (Figure 1b), and no perceptible polymerization occurs (Figure 5). At

the end of one minute, the lamp is shuttered off and the system is maintained in the dark; therefore, no additional active centers are produced after the first minute. At a pre-determined time (25 minutes), the water saturated nitrogen atmosphere was replaced with a dry nitrogen atmosphere while maintaining dark conditions. If the inhibition reaction shown in Figure 1b is reversible, the depletion of water by evaporation will move the equilibrium toward the left

side of the reaction, and hydronium ions will be converted to free protons capable of initiating cationic polymerizations of the vinyl ether monomer.

Results for the experiment described are shown in Figure 5. The figure illustrates that, as expected, no reaction is observed while the system is maintained in a nitrogen atmosphere of 100% relative saturation (during both the one minute of illumination and the subsequent 25 minutes in the dark). Therefore, any cations that exist in the system during this time are not active for cationic polymerization of the vinyl ether monomer. When the atmospheric conditions are changed to dry nitrogen, the figure illustrates that the polymerization is immediately observed even though the system continues to be maintained in the dark. Since all other conditions are constant, the observed polymerization must be a direct result of the changing atmospheric conditions, therefore the polymerization can be attributed to the evaporation of water. Figure 6 provides a more detailed view of the shape of the polymerization profile upon switching the atmosphere to dry nitrogen. The figure illustrates that a slow polymerization begins immediately after the dry nitrogen is introduced, and that after approximately 60 seconds, the polymerization rate accelerates considerably. The shape of this polymerization profile is influenced by the time for the water in the system to diffuse to the exposed surface, and subsequently evaporate into the atmosphere. All experimental observations are consistent with the conclusion that the inhibition reaction is reversible and that the active centers can be regenerated after remaining as unreactive hydronium ions for an extended period of time.

Conclusion

This contribution further enhances knowledge of water inhibition in

FIGURE 5

Monomer conversion vs. time for DVE containing 0.15 mol.% IT under fully saturated nitrogen atmosphere that is switched to dry nitrogen atmospheric conditions after 25 minutes

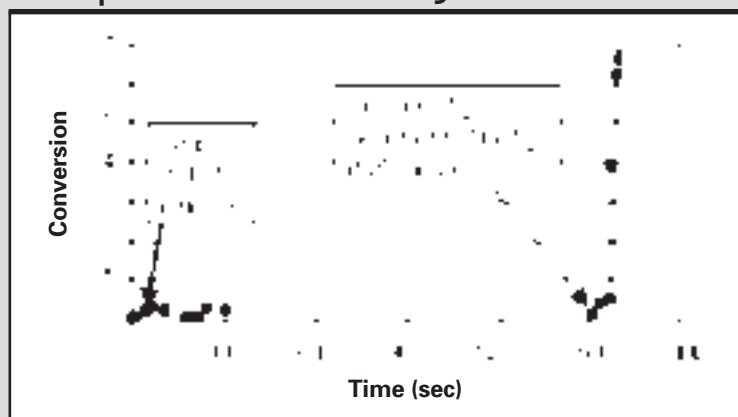
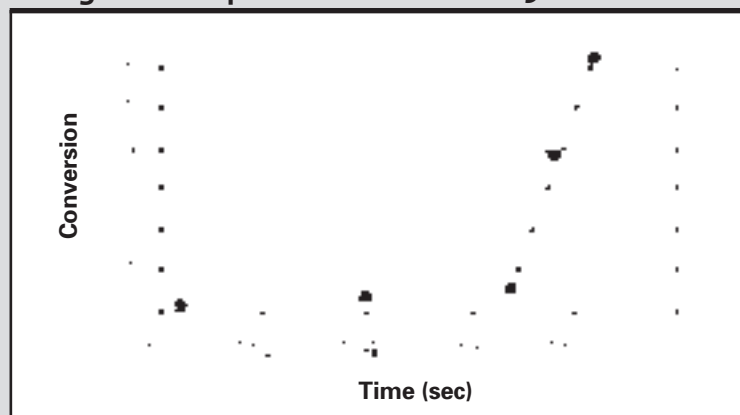


FIGURE 6

Monomer conversion vs. time for DVE containing 0.15 mol.% IT immediately after a fully saturated nitrogen atmosphere that is switched to dry nitrogen atmospheric conditions at 25 minutes



cationic photopolymerizations. For conditions of constant humidity in thin film systems, it was found the degree of inhibition increased with increasing humidity, and that a saturated atmosphere leads to complete inhibition. Furthermore, it was shown that a completely inhibited system can experience a rapid polymerization, even after 25 minutes in the dark, when the system was purged with dry nitrogen causing the water to evaporate and the inhibition reaction to be reversed. These results illustrate the potential of vinyl ether cationic photopolymerization to be controlled temporally by the water concentration in the atmosphere. ▀

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—Ruiping Huang is with the Department of Medicine at Michigan State University, East Lansing, Mich. Beth A. Ficek and Alec B. Scranton are with the Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa. Shedric O. Glover is employed at Dow Corning Corporation, Midland, Mich.

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