Model for the Effects of Water on the Cationic UV-Curing of Cyclohexyl Epoxides

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The effect of relative humidity on the photoinduced curing kinetics of cyclohexyl epoxide and epoxide/polyol coating formulations was investigated in real-time using FTIR spectroscopy. In total, five formulations were used in this study, including a cyclohexyl epoxide without polyol, and four with polyols. The polyol formulations were varied with respect to ratio of epoxide to polyol, and molar functionality of the hydroxyl group. The formulations were exposed to a maximum of seven different relative humidities (6, 16, 20, 30, 51, 62, 75 RH). The curing speed and overall conversion of the epoxy group passed through a maxima for all the formulations. The polyol had an effect on the hydrophilicity of the overall formulation. It was also found that water and polyols had a synergistic effect on the UV-curing kinetics, in effect lowering the relative humidity to achieve a maxima. A model for UV-curing mechanisms at low, medium, and high relative humidity was proposed for both systems with and without the polyols.

INTRODUCTION

Over the last 15 years UV-curable coatings have become one of the fastest growing coatings markets especially for heat sensitive substrates.[1] There are two classes of UV-curable coatings: (a) free radical and (b) cationic. Cationically curable coatings are principally used in can and low dielectric coatings. Due to greater internal ring strain, cyclohexyl epoxides react faster than other types of epoxides, and consequently are the more widely used.[2,3] The reactivity of the cycloaliphatic epoxide is controlled by the cyclohexyl group fused to the oxirane ring resulting in a twisted boat conformation as previously reported.[4] As a neutral molecule, the fused cyclic structure is too stericly hindered to allow for nucleophilic attack; however, when protonated, the oxirane bonds lengthen to allow for nucleophilic attack.

The homopolymers of cyclohexyl epoxides are usually too brittle to be used alone for coatings. Typically, flexible crosslinkers such as di- and tri-functional polyols (especially ε-caprolactone derived polyols) are often added into the formulations to improve the flexibility.[5] The presence of polyol influences the kinetics of the photopolymerization. It has been reported that 1,4-butanediol accelerated the UV-curing speed of 3,4-epoxycyclohexane carboxylate using di(4-methylphenyl)-iodonium hexafluorophosphate as a photoinitiator.[6] In contrast, the UV-curing speed of 2,3-epoxypropyl phenyl ether was found to decrease with an increase in alcohol concentration.[7] The curing speed was also found to be independent of alcohol concentration when magnesium perchlorate was used as an initiator.[8]

Although cationic photopolymerization is not inhibited by oxygen, it is influenced by the presence of nucleophiles, and in particular the most ubiquitous nucleophile, water. In an industrial setting, water is sometimes an uncontrollable parameter due to the seasonal variations. The effect of water on cationic polymerization has been widely investigated.[9-11] It was

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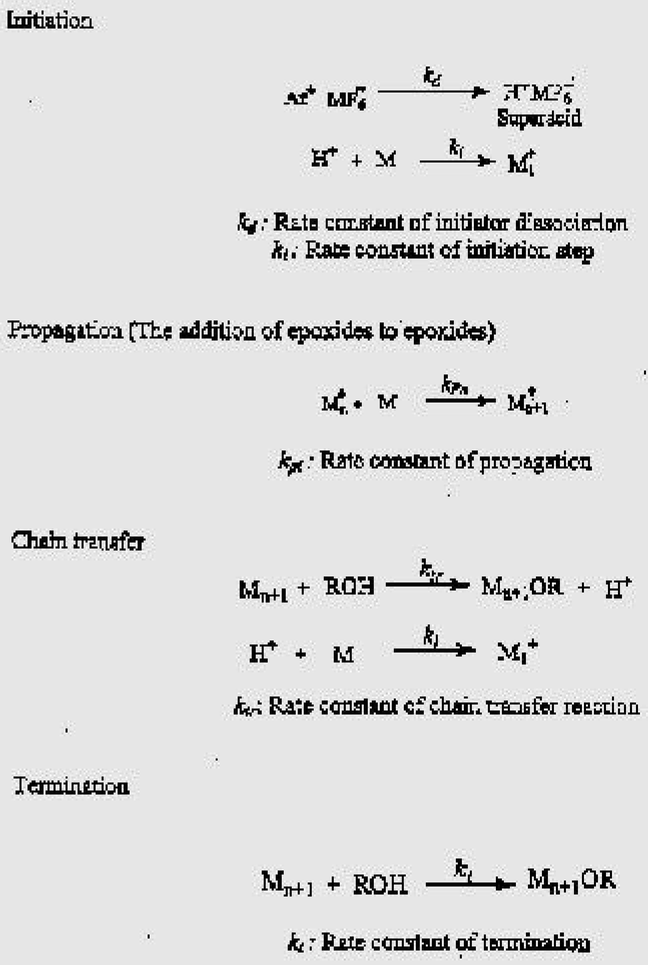


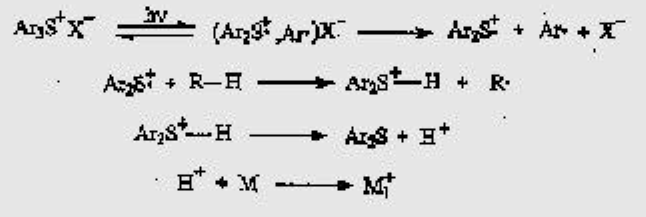
Scheme 1—Sequence of steps of the UV-curing reaction.

found that trace quantities of water could be used as a co-catalyst in the cationic polymerization using BF_3, $AlCl_3$, or $TiCl_4$ as an initiator. However, when water was in excess, it was found to inhibit the polymerization.[9] The effect of water on the photopolymerization of cationic UV-curable cyclohexyl coatings was investigated by Brann[10] and Hanrahan.[11] Brann found that at higher relative humidity a higher irradiation dose was required to reach the same state of cure at humidity levels less than 35%, and at 70% relative humidity the extent of cure was reduced by 25%. Hanrahan and coworkers found that relative humidity has a dramatic effect on surface cure, but little effect on through-cure. It was also found that the effect of water on the UV-curing reaction was highly dependent upon the chemical and physical properties of the cationic system.[12] For example, in the epoxy systems, the role of water was shown to be concentration dependent and participated in both chain transfer and chain termination.

The superacid catalyzed UV-curing reaction of cycloaliphatic epoxide and polyol is a chain reaction consisting of four steps: initiation, propagation, chain transfer, and chain termination, as shown in *Scheme* 1. The initiation of photopolymerization was first studied by McEwen and co-worker.[13] They performed photolysis experiments in the methanol and proposed that the initiation step involves three chemical processes (*Scheme* 2). The formation of diarylsulfonium radical-cation, aryl radical, and anion is followed by the subsequent reaction of the diarylsulfonium radical-cation with a hydrogen donor to generate the superacid. Then the superacid protonates the monomer, producing the chain initiating species M_1^+ known as the activated monomer (AM).

The chain propagation can occur via Active Monomer (AM) mechanism or Active Chain End (ACE) mechanism.[14-16] When the ring-opening reaction is conducted in the presence of a sufficiently high concentration of nucleophilic groups such as alcohols and water, propagation takes place through the AM and chain transfer mechanism.[17-19] The more nucleophilic groups react with the protonated monomer (AM), instead of another epoxide monomer or water which would form new vicinal hydroxyl groups. It was found that the major reaction pathway for the formation of cyclohexyl epoxide oligomers was via an ACE mechanism followed by the termination of the ACE complex by a nucleophile attack, as shown in *Scheme* 3.[20] The reaction of the AM with the secondary hydroxyl groups on the cyclohexyl ring was not observed. The lack of reactivity was attributed to the steric hindrance of the secondary hydroxyl groups.[21]

Although the effect of water on the cationic polymerization has been reported,[9] the previous studies have not presented a complete model. It is our goal to develop a more complete model of the effects of relative humidity on the UV-curing of cyclohexyl epoxide coatings. Real-time FTIR spectroscopy was used to investigate the curing kinetics of cyclohexyl epoxide coatings. The relative humidity investigated ranged from 6-75%. The curing kinetics were studied with and without a polyol. For formulations with a polyol, the curing kinetics were investigated as a function of hydroxyl equilvalent weight (HEW), and epoxide to polyol ratio.

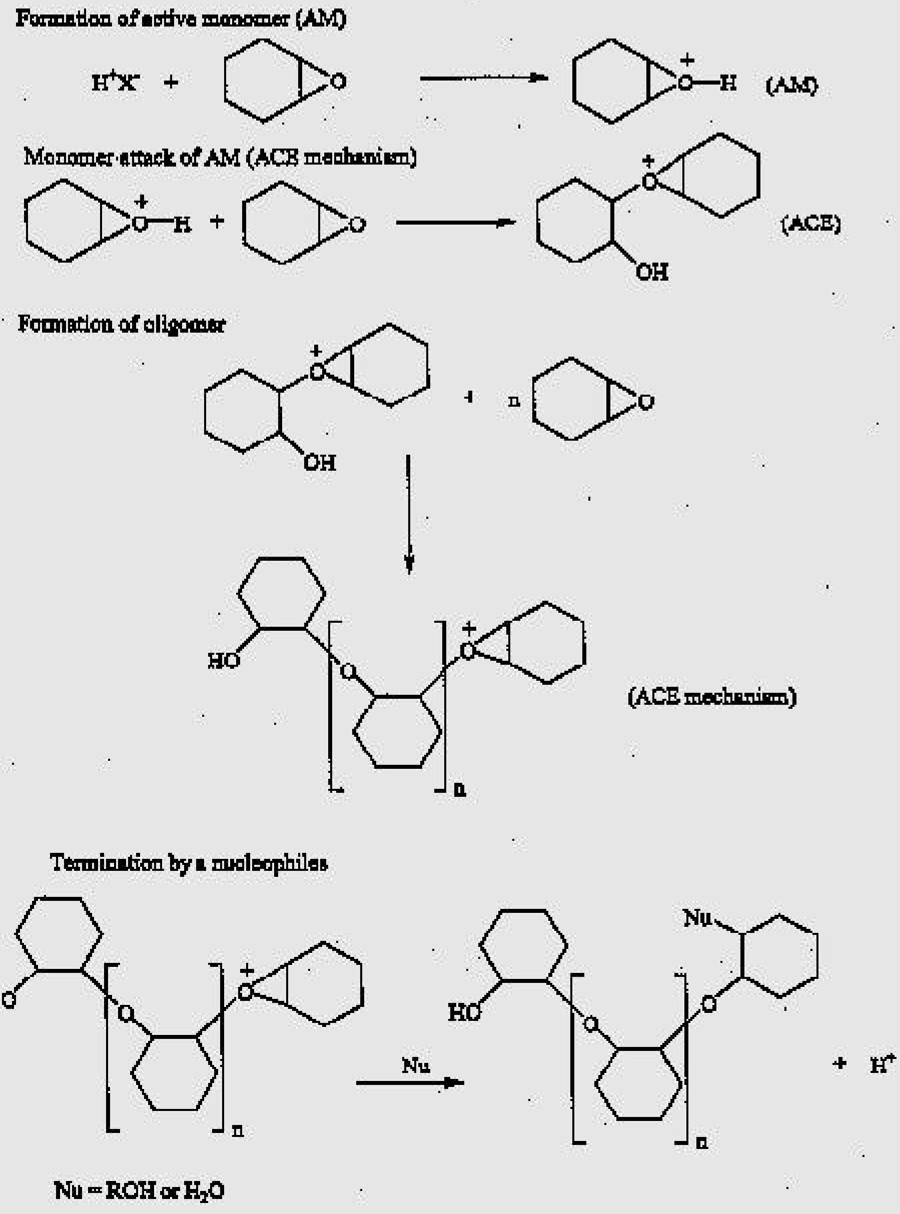


Scheme 2—Mechanism of cationic photoinitiation.

EXPERIMENTAL

Materials

Cyclohexyl epoxides UVR-6110, polyols TONE 0301, TONE 0305, and photoinitiator UVI-6974 were supplied by (Dow) Union Carbide Chemicals and Plastics Company Inc. Wetting agent (Silwet L-7604) was provided by Witco Corp. The $NaOH{\cdot}H_2O$, $CaBr_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $NaI{\cdot}2H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, NH_4NO_3, NH_4Cl, and KNO_3 were purchased from



Scheme 3—Propagation mechanism of cycloaliphatic epoxide in the presence of hydroxyl groups.

Aldrich Chemical Co. All the materials were used as received.

Formulations

A typical formulation consists of cyclohexyl epoxide, polyol, cationic photoinitiator, and Silwet L-7604 wetting agent. The cyclohexyl epoxide, polyols, and photoinitiators used in this study are shown in *Tables* 1 and 2, respectively. For a typical formulation, the desired amounts of polyols, as shown in *Table* 3, were added to cyclohexyl diepoxide (R-value 2.0 to 4), with 4.0 wt% of photoinitiator solution, and 0.5 wt% of Silwet L-7604. Please note that the photoinitiator is added as a 50 wt% solution, and thus 4.0 wt% of the solution is only 2.0 wt% photoinitiator. The mixture was thoroughly mixed on a roller mill for 10 hr. The coating was then cast onto a KBr crystal for the kinetics study. The R-value is defined by equation (1)

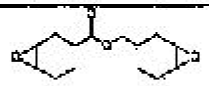
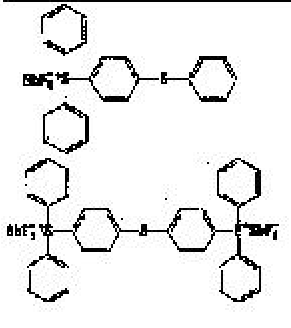
$$\text{R} - \text{value} = \frac{\text{g epoxy / epoxy equivalent weight (EEW)}}{\text{g polyol / hydroxyl equivalent weight (HEW)}} \quad (1)$$

where EEW and HEW represent the epoxide equivalent weight and hydroxyl equivalent weight, respectively.

Real-Time FTIR Spectroscopic Measurements

Real-time FTIR spectroscopic measurements were performed on a Nicolet Magna-IR® 850 spectrometer equipped with a LESCO Super Spot MK II UV-curing system. The experimental setup is shown in *Figure* 1. The relative humidity was controlled by using constant

Table 1—Structures and Typical Properties of the Cycloaliphatic Epoxides and Photoinitiator

	Structure
UVR-6110	 3,4-Epoxycyclohexyl-3,4-epoxycyclohexane carboxylate EEW: 131-143 Viscosity (at 25°C, cP): 350-450
UVI-6974	 Mixed triarylsulfonium hexafluoroantimonate salts

humidity solutions (*Table* 4).[22] The humidity chamber was fitted into the FTIR spectrometer sample chamber. The UV-radiation was introduced from a 100 Watt DC mercury vapor short-arc lamp into the humidity chamber by a flexible optical fiber. The end of the optical fiber was positioned at a distance of 5 mm from the KBr crystal to insure the full crystal irradiation. A UVX digital radiometer was used to measure the radiation (9.2 mw/cm^2). The formulations were coated onto the KBr crystal. Data acquisitions and spectra calculations were performed using Omnic FTIR software (Nicolet). UV-curing was conducted at temperature 23±2°C with 6-75% relative humidity. Spectra were collected at resolution 4 cm^{-1}, and at the rate of 2 spectra/sec. The consumption of the epoxy groups at any time can be calculated from the IR spectra by the following equation:

Table 2—Structures and Typical Properties of Polyols

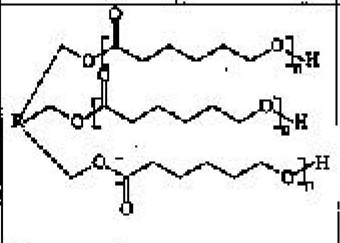
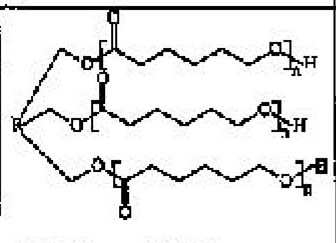
	Structure	Hydroxyl Equivalent Weight	Viscosity at 25°C, cP
TONE® 0301		98-103 (M.W.: 294-309)	2250
TONE® 0305		174-188 (M.W.: 522-564)	2050

Table 3—Formulations[a] for the Study of the Effect of Relative Humidity on the Curing Reactions

	UVR-6110 (g)	Polyol (g)		R-value
		TONE 0301	TONE 0305	
A1	95.50	—	—	∞
B1	69.87	25.63	—	2.0
B2	80.70	14.80	—	4.0
C1	57.51	—	37.99	2.0
C2	71.79	—	23.71	4.0

(a) The amount of photoinitator UVI-6974 used was 4.0 g for all formulations. The amount of Silwet L-7604 used was 0.5 g for all formulations. "—" means none of this component.

$$\text{Conversion}\,(\%) = \frac{[A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_0 - [A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_t}{[A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_0} x100\% \quad (2)$$

where $[A_{(789\text{cm}^{-1}+746\text{ cm}^{-1})}]_0$ and $[A_{(789\text{ cm}^{-1}+746\text{ cm}^{-1})}]_t$ represent the peak area under 789 and 746 cm^{-1} bands at the beginning of the reaction and at time t, respectively. The actual rate of polymerization at time t can be calculated from the IR data by the following equation:

$$R_p = [M]_0 \frac{[A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_{t1} - [A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_{t2}}{t_2 - t_1} \quad (3)$$

where $[M]_0$ is the original concentration of epoxy groups.

RESULTS AND DISCUSSION

While the role of water in UV-initiated cationic curing has been acknowledged by all, it has not been separately investigated. The paradigm is that water is deleterious to UV-curing, and a preheating can solve the problem. Several researchers have acknowledged that the effect of water is more complex, but offered no explanation as to why. Part of the complexity is in the observation that too little water inhibits the cure. Also, the polyol has an effect upon the curing process.[23] It has been previously reported that there is an optimal R-value for each polyol. Since the curing of cycloaliphatic epoxide coatings consists of competitive reactions, which are interdependent, a complete model of the reactivity is a difficult prospect.

Figures 2a and 2b show the effect of relative humidity on the curing reaction of formulation UVR-6110/UVI-6974 (4.0%) without polyol. *Figure* 2a shows the effect of relative humidity

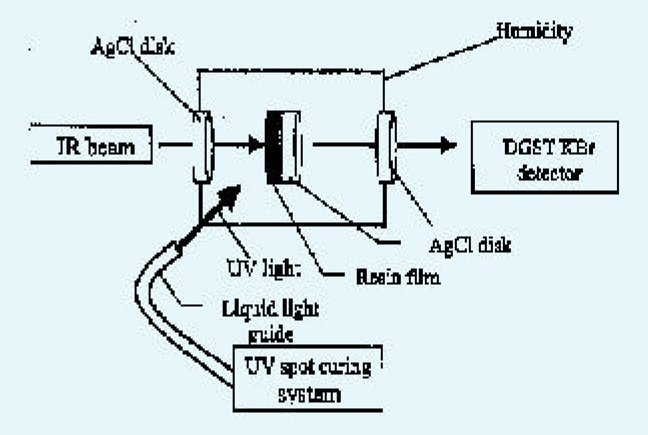


Figure 1—Real-time FTIR experimental set-up.

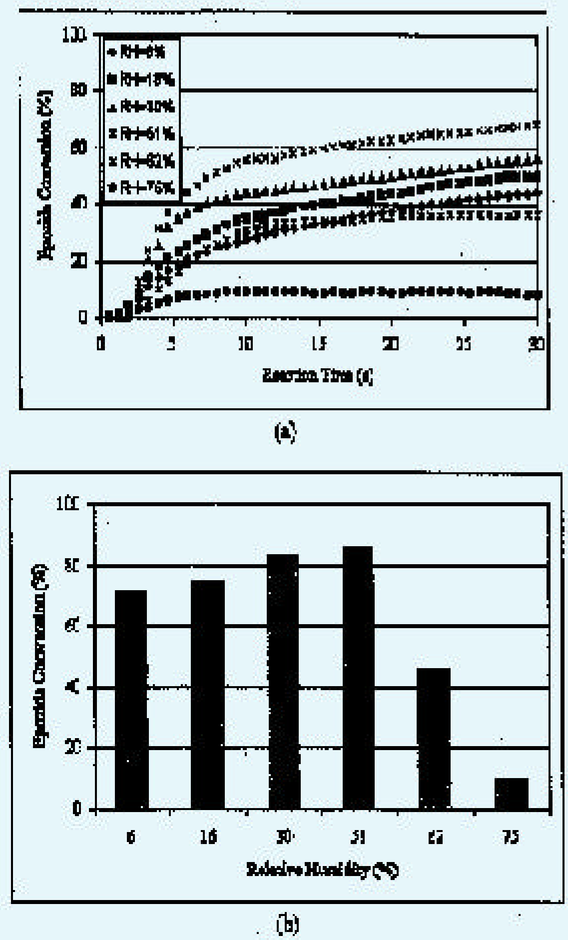


Figure 2—Effect of RH on the curing reaction of formulation UVR-6110/UVI-6974 (4.0 wt%) (without polyol) with 3.5 sec exposure time: (a) t = 0 – 30 sec; (b) overall conversion at t = 600 sec.

on the curing reaction in the first 30 sec. The slope at each point is proportional to the curing speed. At each humidity, the curing speed passes through a maximum and then falls off rapidly. The deceleration of the curing speed was due to gelation.[24] When the relative humidity was increased from 6 to 75%, the curing speed increased with an increase in relative humidity until it reached a maximum at 51% relative humidity, after which the curing speed decreased very quickly. The overall conversion at 600 sec after UV-irradiation shows the same trend (*Figure* 2b). The results are intriguing since most researchers have reported that higher relative humidity resulted in lower curing speed.[10,11]

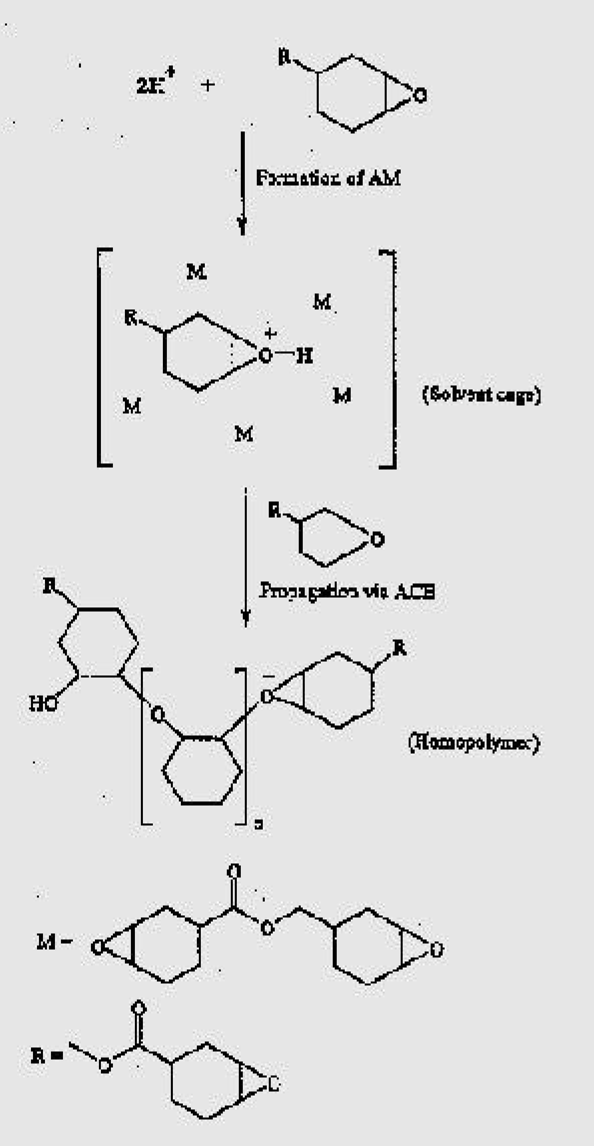
When there was no polyol present in the formulation, the cyclohexyl epoxides showed a maximum in consumption of epoxide group at 51% relative humidity. At very low relative humidity, such as 6% RH, the water content in the formulation was 0.11 wt%. It is proposed that there is not enough water to transport the proton to the oxirane oxygen to form the AM. The water may also be the actual protonating entity. Once formed, the AM is highly solvated by monomer molecules, and homopolymerization proceeds via ACE mechanism, as depicted in *Scheme* 4. As the relative humidity was increased to 51%, the water concentration in the formulation increased concurrently and a change in curing rate was observed. The proposed role of water at an intermediate relative humidity is shown in *Scheme* 5. Due to the higher basicity of water than the monomer, the water participates in the solvation of the AM or ACE. The AM can react with either another nonprotonated epoxide or water molecule. The reaction pathway appeared to be more dependent on the relative concentration of reactant than on the relative nucleophilicity. Excess of cyclohexyl epoxides led to the formation of oligomer or polymer, whereas the presence of stronger nucleophiles should suppress the oligomerization.[20] This, however, does not appear to be the case for intermediate (30-51% RH) concentrations of water.

For the intermediate relative humidity, the relatively low water concentration would result in homopolymerization (ACE mechanism) followed by a chain termination via water and regenerating a proton, as shown in *Scheme* 5a. The diol terminated chain end derived from the AM would also be available to react with another AM via a step-growth mechanism generating a proton for transfer, and regenerating the chain process (*Scheme* 5b). This is a slow reaction due to the steric hinder-

Table 4—Constant Humidity Solution Used for the Relative Humidity Study

Compound	Temperature Range (°C)	RH (25°C)[a]	A	B
$NaOH{\cdot}H_2O$	15-60	6	5.48	27
$CaBr_2{\cdot}6H_2O$	11-22	16	0.17	1360
$CaCl_2{\cdot}6H_2O$	15-25	29	0.11	1653
$NaI{\cdot}2H_2O$	5-45	38	3.62	702
$Ca(NO_3)_2{\cdot}4H_2O$	10-30	51	1.89	981
NH_4NO_3	10-40	62	3.54	853
NH_4Cl	10-40	79	35.6	235
KNO_3	0-50	92	43.22	225

(a) RH=Aexp(B/T), where RH is the percentage relative humidity, T is the temperature in kelvin, and A and B are constants.

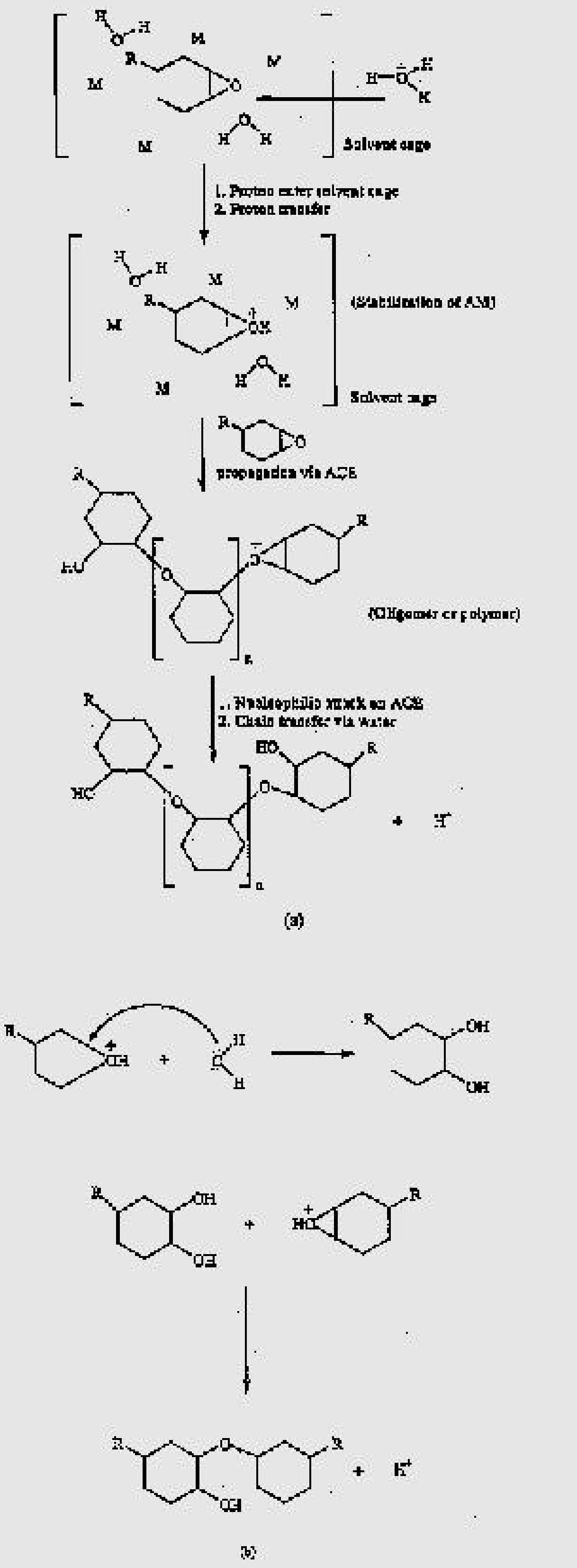


Scheme 4—Proposed UV-curing mechanism of cycloaliphatic epoxide (without polyol) at low relative humidity.

ance of a secondary hydroxyl (diol) on a cyclohexyl ring attacking a cyclohexyl AM.

From previous model compound study,[20] it was found that after ring-opening the ACE, the resultant secondary hydroxyl group was not reactive. In the case where water attacks the ACE, the hydroxyl groups formed are most likely to sterically hinder an attack on AM. The AM generated diol, however, is located on the chain end and has considerably less steric hindrance. Although the increase of the concentration of the chain initiation species and chain transfer reaction will lower the molecular weight, the combination of chain transfer and step growth results in an increase in both the curing speed and overall conversion.

Increasing the relative humidity to above 51% lowered the curing speed and overall conversion of epoxy groups due to the excess of water in the formulation. At



Scheme 5—Proposed UV-curing mechanism of cycloaliphatic epoxide (without polyol) at intermediate relative humidity.

Table 5—Relative Basicities

Base	pK_a ^{a,b}	ΔG_{BH^+} ^{b} (kcal/mol)	K_b ^{c}
H_2O	–2.0	–102	38 ± 0.4
CH_3OH	–3.0	–81	5.8 ± 1.0
PGE	–8.57^{d}		

(a) pK_a for the equilibrium

$$BH^{\oplus} \xrightleftharpoons{H_2O} B + H^{\oplus}$$

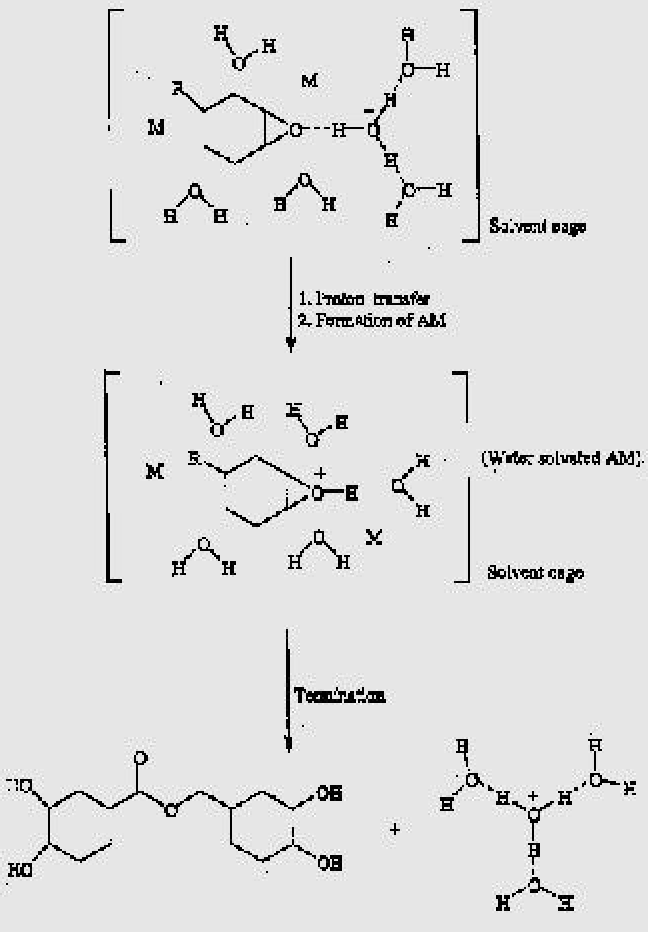
(b) Reference 31.
(c) K_B for the equilibrium

$$B + HClO_4 \rightleftharpoons BH^{\oplus}ClO_4^{\ominus}$$

(d) Reference 32

75% relative humidity, the curing speed and overall conversion of epoxy group was very low, even at 600 sec after UV-irradiation. This indicated that at 75% RH, the growing polymer chain is prematurely terminated and a proton is regenerated. Water is most probably the termination agent. The termination effect of excess water is due to two factors. First, there is a leveling effect on acid strength. *Table* 5 shows that the pKa value of water (pKa: –2.0)[25] is much higher than that of epoxide (pKa: ~ –8.0),[26] which indicates that epoxide is a much weaker base than water. Therefore, the regenerated proton will be mainly solvated by H_2O clusters due to the higher basicity and solvating effect of water, which in turn lowers the acid strength of the once super-acid. If the acid strength of the super-acid is lowered too much, the proton will lose its ability to initiate the polymerization reaction. Second, once the AM is solvated predominately by a solvent cage of water, it results in preferential formation of diol due to a high local concentration of water within the solvent cage, as shown in *Scheme* 6.

Overall, water has three roles in the photopolymerization of cyclohexyl epoxide without polyol. First, water is needed as a proton carrier or chain transfer agent at low water concentration. Without water, the super-acid once formed will most likely be associated with the ester functionality, not the oxirane. The water essentially solvates the proton in a small cluster, perhaps even one water molecule. Second, once the propagating cation is formed, the presence of excess water may terminate the growing polymer chain to form one of two hydroxyl groups, depending on whether the water attacks the AM or ACE. Both result in a chain



Scheme 6—Proposed UV-curing mechanism of cycloaliphatic epoxide (without polyol) at high relative humidity.

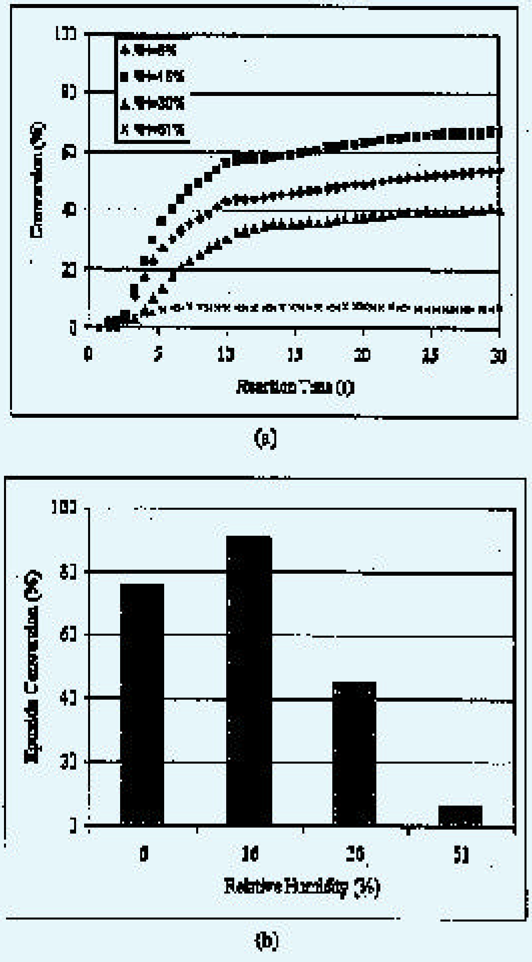


Figure 3—Effect of RH on curing reaction of formulation UVI-6974 (4.0 wt%)/UVR-6110/TONE 0301(R=4.0), with 3.5 sec exposure time: (a) t=0–30 sec (b) overall conversion at t=600 sec.

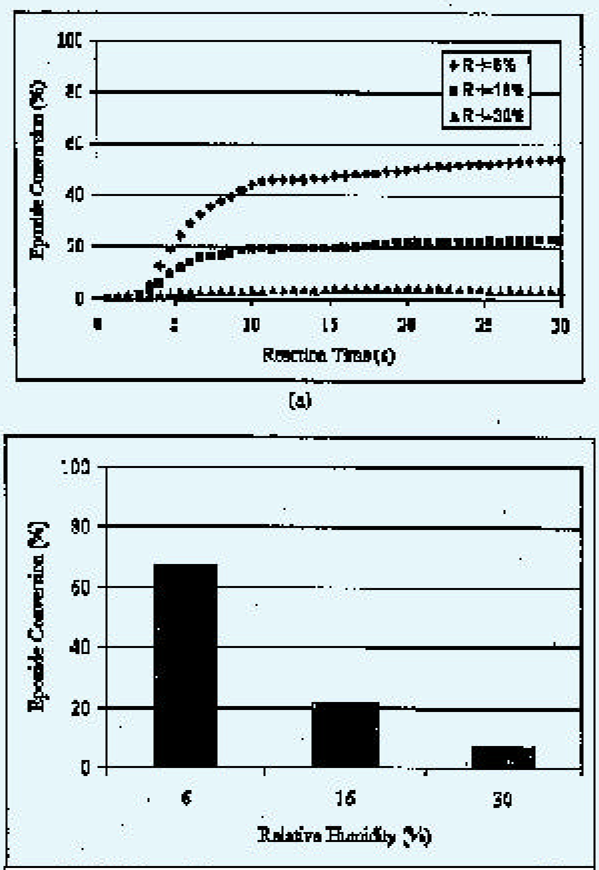


Figure 4—Effect of RH on curing reaction of formulation UVI-6974 (4.0 wt%)/UVR-6110/TONE 0301(R=2.0) with 3.5 sec exposure time: (a) t = 0 – 30 sec; (b) overall conversion at t = 600 sec.

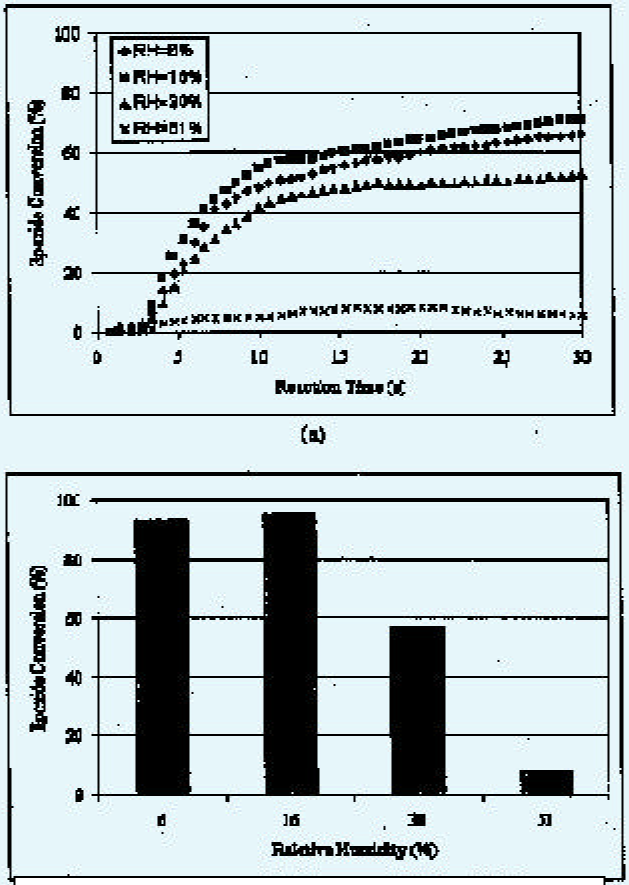


Figure 5—Effect of RH on curing reaction of formulation UVI-6974 (4.0 wt%)/UVR-6110/TONE 0305 (R=4.0) with 3.5 sec exposure time: (a) t = 0 – 30 sec; (b) overall conversion at t = 600 sec.

transfer to initiate another polymer chain. The former results in a mechanism transfer from chain growth to step growth and the latter results in the termination of that chain end. As the size of the water clusters increases enough to lower the pH and flood the solvent cage of the reactive species with a very high concentration of water, the homopolymerization reaction is retarded to a point where only the step-growth process is operating. As the size of the water clusters continues to increase to the point of fully stabilizing the proton, protonation of the oxirane group is unlikely. This model which has been proposed for cycloaliphatic epoxide without polyol takes into account the observed results with respect to the observed maxima.

The effect of relative humidity on the curing reaction of coatings with polyol at different R-values are shown in *Figures* 3-6. A similar trend was obtained when TONE 0301 was added to the epoxide at an R-value of 4.0 (*Figure* 3). But in this case, the conversion of the epoxy groups or the curing speed reached the maximum at 16% relative humidity and the overall conversion of the epoxy group became very low (6.7% at 51% RH). Due to the presence of polyol, the curing speed and overall conversion reached the maximum at a much lower water content (0.38% at 16% RH) than that in the formulation without polyol (0.75% at 51% RH). If the amount of TONE 0301 was increased to an R-value of 2.0, no maximum value was detected at humidity as low as 6% (*Figure* 4). The conversion of the epoxy group decreased all the way with the increase of the relative humidity. However, it is possible that if the relative humidity was further lowered the curing speed or the overall conversion may decrease. Similar data were obtained when TONE 0305 was added to the formulation. When R = 4.0, a maximum was observed at 16% relative humidity (*Figure* 5), however, when R = 2.0, no maximum was detected (*Figure* 6).

Polyol has a similar effect on the curing reaction as water (*Figures* 3-6). The polyol functions as a proton donor for both initiation and proton transfer. In addition, the primary hydroxyl groups at the end of long flexible chains enhanced the reactivity of either the AM or ACE. The polyol also provided a better medium than water for crossover from chain to step growth and transfer to chain growth again. The curing mechanism of the UV-curing reaction with polyol at intermediate relative humidity is shown in *Scheme* 7. In comparison with water, the protonated polyol is a better proton source due to its lower basicity. Both water and polyol can be chain transfer agents. The relative reaction is dependent on both nucleophilicity and stoichiometry. At a low R-value and low relative humidity, the polyol

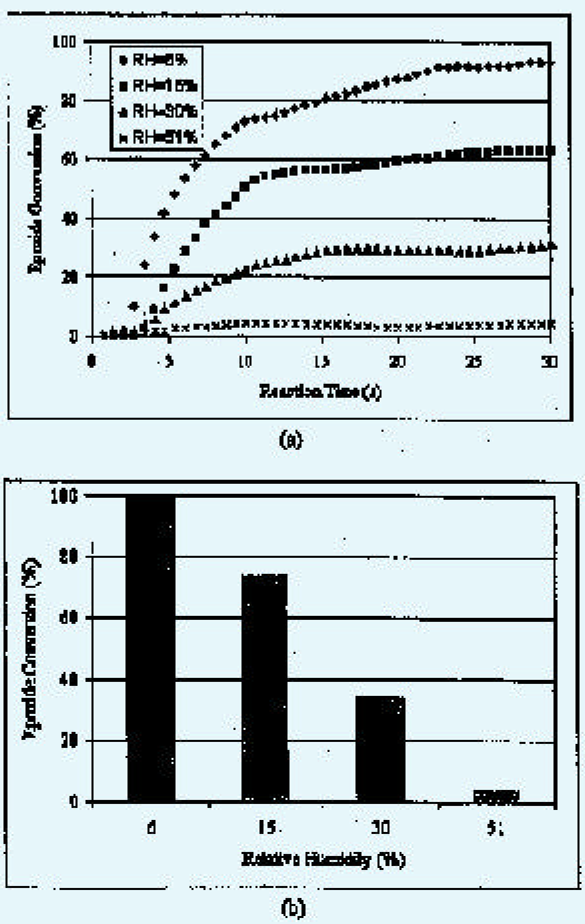
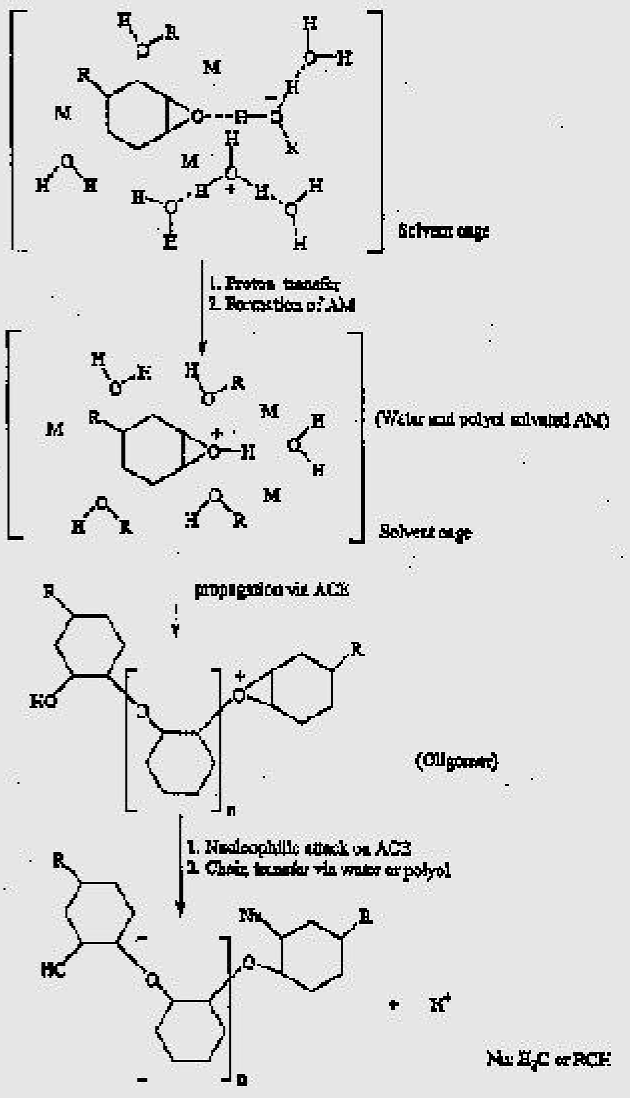


Figure 6—Effect of RH on curing reaction of formulation UVI-6974 (4.0 wt%)/UVR-6110/TONE 0305 (R=2.0) with 3.5 sec exposure time: (a) t = 0 – 30 sec; (b) overall conversion at t = 600 sec.

concentration is much higher than the concentration of water. In this case, polyol functions as the main chain transfer agent. However, at a high R-value, water can be the chain transfer agent due to its relative concentration and higher nucleophilicity.

The conversion of the epoxy groups with polyol reached a maximum at lower relative humidity than that of formulations without polyol. This is attributed to the synergistic effect of water and polyol on the curing reaction. At the same relative humidity the addition of polyol into the formulation increased the water concentration due to the hydrophilicity of the polyol (*Table* 6). In addition, in the presence of polyol, the proton may have solvated by both water and polyol. However, it is reasonable to assume that the proton is solvated by a cluster of water not a combination of polyol and water. This would, in turn, result in a leveling of the acid strength to the super-acid. As a consequence, the acid strength would decrease, resulting in slow formation of AM followed by hydrolysis.

Unlike the scenario without polyol, the polyol is a participant in the crosslinked network. After the reaction of one or two of the triol hydroxyl groups, the remaining hydroxyl group is effectively tethered, restricting the mobility of any proton stabilized by the hydroxyl group. Fortunately, the ε-caprolactone polyols have exceptional flexibility. This does not appear to be a problem until the water concentration reaches a critical concentration, after which the proton with water cluster could be tethered effectively, thus ending the polymerization. It would be of interest to expand this work into other more rigid polyesters to test this hypothesis.



Scheme 7—Proposed UV-curing mechanism of cycloaliphatic epoxide with polyol at intermediate relative humidity.

What is implied by the proposed model is the notion that sequential reactivity is driven by local concentrations. If the model is valid for the polyol formulations, it would follow that especially at higher polyol ratios (lower R), the polyols would preferentially react with AM. As a consequence, the chain oligomerization of the epoxide would follow as the concentration of the polyol was depleted. At the optimal R-value there would be enough excess of the epoxide (local concentration) to compete with greater nucleophilicity of the polyol. As the threshold of concentration driven competitive reactions is surpassed, the polyols will react first, then the

Table 6—Water Content in the Formulations

	Relative Humidity (%)						
	6	16	20	30	51	62	75
UVR-6110/TON 0301 (R=2)/UVI-6974 (4%)	0.39	0.48	0.64	1.06	1.52	—	—
UVR-6110/TON 0301 (R=4)/UVI-6974 (4%)	0.31	0.38	0.46	0.83	1.29	1.58	—
UVR-6110/TON 0305 (R=2)/UVI-6974 (4%)	0.26	0.35	0.51	0.86	1.31	1.69	—
UVR-6110/TON 0305 (R=4)/UVI-6974 (4%)	0.18	0.30	0.39	0.76	1.25	1.45	—
UVR-6110/UVI-6974 (4%)	0.11	0.23	0.28	0.51	0.75	0.94	1.30

homopolymerization. The homopolymerization would be controlled again by water concentration. This would result in different polyols having optimum coatings properties and cure speeds at different R-values and relative humidity. This is what was observed.

Although a cumulative effect of water and polyol exists, it does not appear to be straightforward. Weight percentage or moles of hydroxy groups are cumulatively proportional to epoxide reactivity and maxima; however, from system to system there is only a trend and not a direct correlation. The mole ratios of epoxide monomer to polyol and water afford a similar trend and again no direct correlation. The difficulty is that the moles or weight percent of the polyol is at least an order of magnitude larger than the concentration of water. Therefore, there is a synergistic effect between the water concentration and polyol. An empirical expression could be derived by utilizing constants as measures of relative proton stabilization and nucleophilicity; unfortunately it is not within the scope of this article. However, it may be the subject of future research.

It is important to note that water does not always lower the reaction rate of a cationic system. For the cyclohexyl epoxide coating system, it was found that there is a critical concentration of water at which the rate of UV-curing is a maximum and the initiation and propagation proceed through different mechanism at low and high water content. The role of water in the UV-initiated cationically cured coatings is complex. It is postulated that, at low concentration, water facilitates proton transfer, and stabilizes the reactive intermediate within the solvent cage. However, if the formulation is saturated with water, a leveling effect of acid strength is observed, resulting in a termination of cure.

CONCLUSIONS

It was found that the lack of water had a deleterious effect of the UV-initiated homopolymerization of cycloaliphatic epoxides. The curing speed increased with increasing water concentration until a maximum was reached, after which the curing speed was again retarded. It was found that water also has a synergistic effect with polyols on the UV-curing kinetics of cycloaliphatic epoxide coating formulation. A quantitative description of the model, however, was not straightforward. It is proposed that both water and polyol participate in the proton transport, stabilize the reactive intermediate (AM or ACE), and mediate a transition between chain growth and step growth polymerization.

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