

Curing Kinetics of UV-Initiated Cationic Photopolymerization of Divinyl Ether Photosensitized by Thioxanthone

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ABSTRACT: Photodifferential scanning calorimetry was used to investigate the photocuring kinetics of UV-initiated cationic photopolymerizations of 1,4-cyclohexane dimethanol divinyl ether (CHVE) monomer with and without a photosensitizer, 2,4-diethylthioxanthone (DETX), in the presence of a diaryliodonium-salt photoinitiator. Two kinetics parameters, the rate constant (k) and the order of the initiation reaction (m), were determined for the CHVE system with different amounts of added DETX photosensitizer (0–1 wt %) and at different isothermal temperatures (25–55°C) using an autocatalytic kinetics model. The photosensitized CHVE system exhibited much higher k and m values than did the nonphotosensitized system, which was attributable to the effects of photosensitization. Furthermore, the

values of k and m for both CHVE systems increased significantly with increasing isothermal temperature because of a thermal contribution toward increasing the mobility of active species. The addition of DETX lowered the activation energy for the UV-curable vinyl ether system. The collision factor for the system with DETX was higher than that obtained for the system without DETX, indicating that the reactivity of the former was greater than that of the latter because of the photosensitization effect. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1345–1351, 2005

Key words: photopolymerization; kinetics; calorimetry; photosensitizer; autocatalytic model

INTRODUCTION

UV-induced photopolymerizations have received considerable attention because of their rapid curing even at ambient temperatures, solvent-free curing of coating films, and lower energy consumption. Such photopolymerizations have been in constant development over the past few decades, because the above advantages lead to important industrial applications, including coatings, adhesives, varnishes, inks, dyes, and electronics.^{1,2}

Cationically UV-initiated photopolymerizations exhibit several advantages over free-radical photopolymerizations. The epoxides and vinyl ethers cured via a cationic mechanism are negligibly toxic, are not inhibited by oxygen, exhibit relatively low viscosities, have low shrinkage during curing, and exhibit dark-curing behavior in which the unreacted epoxides and vinyl ethers continue to slowly react upon storage of the sample in the dark after irradiation has ceased.^{3–7} However, despite all of these advantages, their market share remains small, probably because their reactivity

is lower than that of acrylates and methacrylates cured via free-radical mechanisms.^{1,3} Overcoming this disadvantage of the cationically UV-cured coatings has recently become an important part of the overall UV-cured industrial market. For this reason, several authors^{5–8} have reported the use of a photosensitizer for enhancing the low reactivity of UV-curable cationic systems.

However, to date there have been few detailed investigations into the curing kinetics of photosensitized cationic systems. An accurate kinetics model for these systems not only would help to predict cure behavior for process design and control, but also could be used to predict aging or degradation of photosensitized cationic systems and to compare the cure behavior of different systems or formulations with and without a photosensitizer.

With the aim of developing a method of kinetics analysis and obtaining good control over the photosensitizer content and curing rate in photosensitized cationic systems, in this study we used photodifferential scanning calorimetry (photo-DSC) to investigate the effect of a photosensitizer, 2,4-diethylthioxanthone (DETX), on the curing kinetics of 1,4-cyclohexane dimethanol divinyl ether (CHVE) systems.

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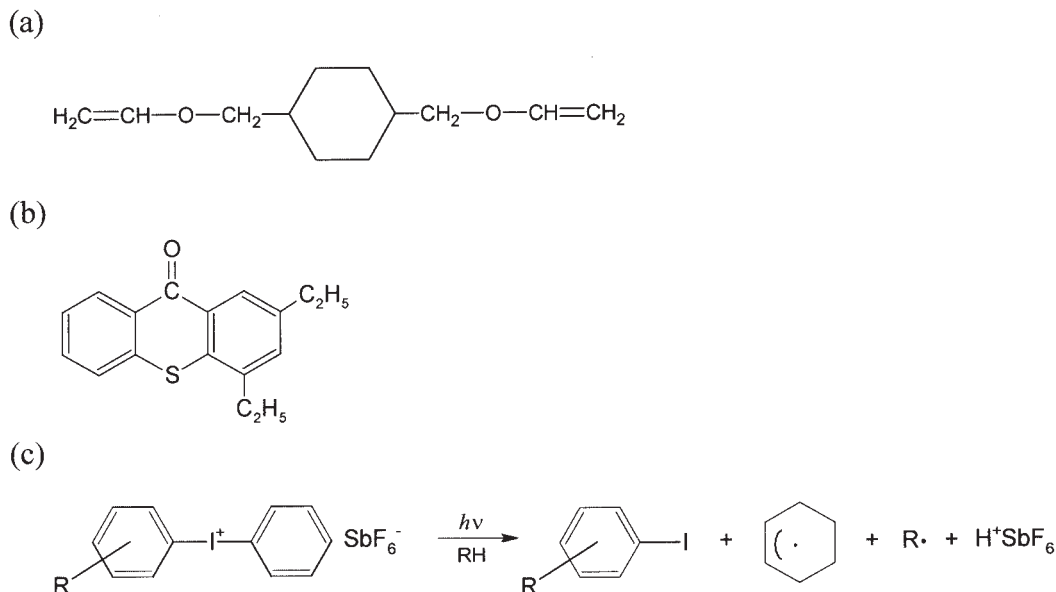


Figure 1 The chemical structures of (a) CHVE and (b) DETX photosensitizer and (c) the photochemical decomposition of the cationic photoinitiator; RH, hydrogen donor molecule.

EXPERIMENTAL

Materials

CHVE (RAPI-CURE, ISP) was used as a monomer, diaryliodonium hexafluoroantimonate (DAI, CD-1012, Sartomer) was used as a cationic photoinitiator, and DETX was used as a photosensitizer (Kayacure DETX-S, Nippon Kayaku). The structures of the three chemicals are shown in Figure 1, all of which were used as received. It should be noted that the photolysis of the cationic photoinitiator (CD-1012) in the presence of a hydrogen donor molecule produces both protonic species (Brønsted acid) and free radicals, of which protonic acid initiates the cationic polymerization as shown in Figure 1.^{1,5}

Photo-DSC

The photo-DSC experiments were conducted using a DSC calorimeter equipped with a photocalorimetric accessory (TA 5000/DPC system). The initiation light source was a 200-W high-pressure mercury lamp, which gave a UV light intensity at the sample of 35 mW/cm² over a wavelength range of 200–440 nm. Samples weighing 4.0 ± 0.1 mg (mean ± SD) were placed in uncovered aluminum pans at a thickness of ~500 μm, and the reference aluminum pan was empty. Isothermal photocure experiments were performed at four temperatures: 25, 35, 45, and 55°C. The highest value achieved for the four isothermal photocuring temperatures was then chosen as the total heat (ΔH_{total}) for the fully cured CHVE, and it was used for subsequent analysis. TA Instruments soft-

ware was employed to obtain the results from the photo-DSC experiments.

UV-visible spectroscopy

The absorption spectra of the photoinitiator (CD-1012) and photosensitizer (DETX) were obtained using a Cary 3 Bio UV-visible spectrophotometer. Dilutions of 0.02 g/L in methylene chloride were prepared, and 1.0-cm pathlength quartz cells were used in the analysis.

RESULTS AND DISCUSSION

Effect of photosensitizer concentration

The photo-DSC method assumes that in a curing process the measured heat flow is proportional to the conversion rate. This assumption is valid for materials exhibiting a single reaction and no other enthalpic events, such as the evaporation of solvent or volatile components, enthalpy relaxation, or significant changes in heat capacity with conversion. The rate of change in the conversion can therefore be defined as follows^{9–11}:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{\text{total}}} \left(\frac{dH}{dt} \right)_T \quad (1)$$

where $d\alpha/dt$ is the conversion rate or the polymerization rate, ΔH_{total} is the total exothermic heat of reaction, and $(dH/dt)_T$ is the measured heat flow at a

TABLE I
Formulations of Cationic Systems with Varying Amounts of Photosensitizer

Component	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)
CHVE (vinyl ether monomer) ^a	100	100	100	100	100	100
DAI (photoinitiator) ^b	3	3	3	3	3	3
DETX (photosensitizer) ^c	—	0.1	0.25	0.5	0.75	1.0

The data values are weight percentages.

^a International Specialty Products (RAPI-CURE).

^b Sartomer (CD-1012).

^c Nippon Kayaku (Kayacure DETX-S).

constant temperature T . The degree of conversion is obtained by integrating eq. (1):

$$\alpha = \frac{1}{\Delta H_{\text{total}}} \int_0^t \left(\frac{dH}{dt} \right)_T dt \quad (2)$$

where α is the degree of conversion. Note that according to the above definition of α , the monomer is considered to be uncured when $\alpha = 0$ and completely cured when $\alpha = 1$.

In an autocatalyzed curing reaction it is generally assumed that at least one of the reaction products is also involved in the propagating reaction, and thus the reaction is characterized by an accelerating isothermal conversion rate that typically reaches its maximum after the initial stage of conversion. The cure kinetics of an autocatalyzed reaction is described by the following equation^{9–11}:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (3)$$

where k is the Arrhenius-type reaction rate constant, m is the order of the initiation reaction, and n is the order of the propagation reaction.

Using this numerical methodology, the autocatalytic model for cure kinetics was successfully applied to the estimation of the curing behavior of epoxide systems, although in most cases, to simplify the analysis and to enable comparisons between more complex systems, it was necessary to assume that m is calculated with the value of n fixed at 1.5, even for nonlinear regression analysis. This approximation is realistic to the extent that the formulation of the reactants did not change, and the range of considered temperatures varied only from 25 to 55°C.^{10–12}

The formulations of the cationic systems with varying amounts of photosensitizer are given in Table I. The concentration of cationic photoinitiator (DAI) was fixed at 3 wt % for the resin, which is generally known to be optimal in cationic UV-curable clear formulations.² Therefore, in this study we varied the concentration of photosensitizer from 0 to 1.0 wt % for the

resin to investigate the effect of a photosensitizer (DETX) on the curing kinetics of CHVE systems. Figure 2 shows the photo-DSC exotherms for the photopolymerization of the CHVE systems containing different concentrations of DETX. Figure 3 plots the percentage of conversion versus the irradiation time derived from Figure 2 for the photopolymerization of the above systems. Figure 3 indicates that, for all the studied formulations, the recorded percentage of conversion versus the time kinetics curves are indicative of the autoaccelerated processes that are a typical feature of an autocatalytic reaction mechanism.

The kinetics analysis data derived from Figures 2 and 3 are collected in Table II. The photosensitized cationic systems (formulations B–F) exhibited much higher exotherms and ultimate percentages of conversions as well as much faster polymerization reactivity than did the nonphotosensitized cationic system (formulation A). This tendency is attributable to the pho-

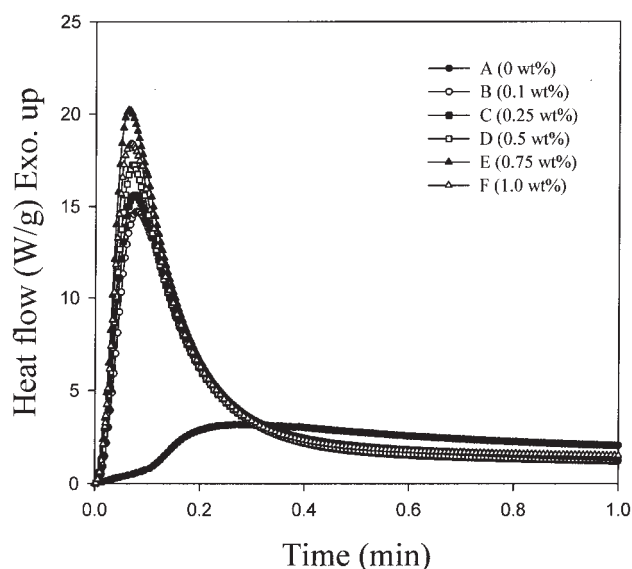


Figure 2 Photo-DSC exotherms for the photopolymerization of formulations A–F with the following conditions: isothermal curing temperature = 25°C, sample weight = 4.0 mg, sample thickness = ~500 μm , light intensity = 35 mW/cm^2 .

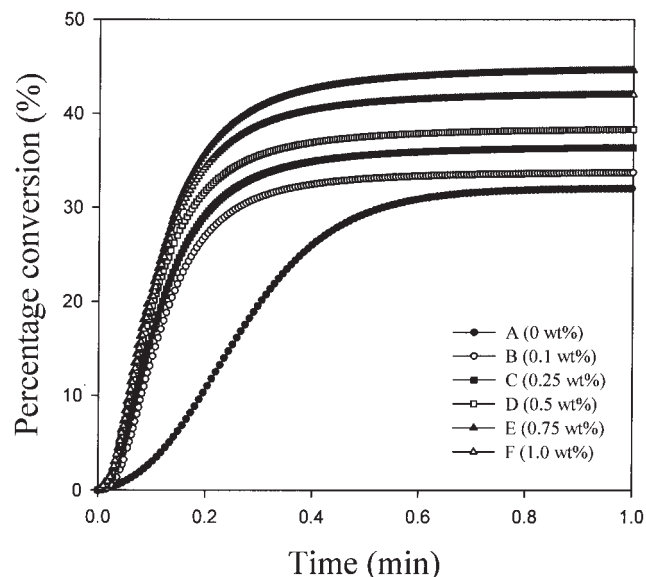


Figure 3 Percentage of conversion profiles for the photopolymerization of formulations A–F with the following conditions: isothermal curing temperature = 25°C, sample weight = 4.0 mg, sample thickness = ~500 μm , light intensity = 35 mW/cm^2 .

tosensitization effect, in which the efficiency of the photoinitiator was improved to produce more active species.^{6–8} Further experiments were designed to determine the above hypothesis by using a UV–visible spectrophotometer. Figure 4 shows the absorption spectra for the photoinitiator and photosensitizer. The photoinitiator exhibits an absorption that is maximal at 230 nm with a secondary local maximum at 260 nm and then decreases rapidly to near zero at 350 nm. The DETX photosensitizer exhibits strong absorption in the 225–400 nm regions. Because of this strong absorption by the photosensitizer, the initiating wavelength for the photopolymerization may be enlarged to these regions by including DETX.

Generally, DAI and triarylsulfonium salts of cationic photoinitiators are most effective for initiating wavelengths between 210 and 350 nm.^{6–8} Therefore, one disadvantage of the onium salt initiators is their

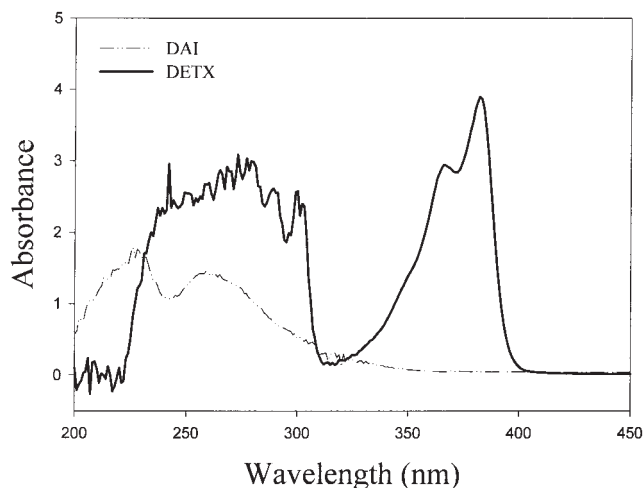


Figure 4 Absorption spectra for the photoinitiator (DAI) and photosensitizer (DETX).

poor absorption at wavelengths above 350 nm, which is where medium- and high-pressure mercury lamps emit much of their radiation. Using photosensitizers represents one of the methods for overcoming this limitation by expanding the spectral region over which onium salts are effective. Photosensitizers make it possible to initiate polymerization in the near-UV or visible parts of the electromagnetic spectrum as a result of a direct interaction between an excited state of a photosensitizer and the photoinitiator. In the excited-state complex (exciplex), this photosensitization reaction proceeds by an energy- or electron-transfer mechanism to form a radical cation that is capable of initiating free-radical and cationic photopolymerizations.^{6,7,13}

Examination of Figures 2 and 3 and Table II reveals that as the concentration of DETX was increased to 0.75 wt %, the exotherm and percentage of conversion (which are both related to the crosslink density) also increased but the induction time (the time to attain 1% conversion, related to the efficiency of the photoinitiator) and the peak maximum (the time to attain the exotherm maximum) decreased. The addition of a

TABLE II
Kinetics Analysis Results for Photopolymerization of Cationic Formulations in Table I

Formulation	ΔH (J/g)	Induction time (s)	Peak max (min)	Conversion (%)	k (min^{-1})	m^a
A (0 wt %)	159	4.54	0.250	32	8.0	0.512
B (0.1 wt %)	172	1.56	0.078	34	13.0	0.564
C (0.25 wt %)	180	1.49	0.073	36	13.9	0.569
D (0.5 wt %)	192	1.41	0.065	38	14.5	0.576
E (0.75 wt %)	218	1.33	0.060	44	16.3	0.588
F (1.0 wt %)	203	1.37	0.062	41	15.4	0.581

The conditions are described in the legend of Figure 2.

^a For the value of n fixed at 1.5.

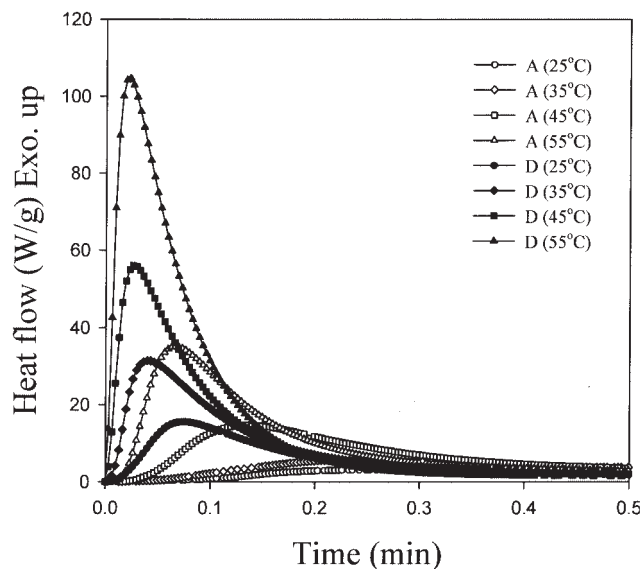


Figure 5 Isothermal photo-DSC traces of formulations A and D photocured at 25, 35, 45, and 55°C with the following conditions: sample weight = 4.0 mg, sample thickness = $\sim 500 \mu\text{m}$, light intensity = $35 \text{ mW}/\text{cm}^2$.

larger amount of DETX resulted in a gradual decrease in the exotherms and percentage of conversion and a gradual increase in the induction time and the peak maximum. This result may be explained by a UV-filter effect, in which a higher DETX concentration leads to faster surface curing of the sample by the aforementioned photosensitization, which limits the penetration of light into the sample. This radiation attenuation effect prevents the excitation of many of the photosensitizer molecules near the bottom of the sample such that they are unable to produce active cationic centers formed by the interaction between an excited state of a photosensitizer and the photoinitiator. This interpretation is supported by the absence of the crosslinking reaction near the bottom of the sample.^{6–8}

In addition, the values of kinetics parameters k and m are consistent with higher exotherms and percent-

ages of conversion as well a faster curing rate for the photosensitized cationic systems (Table II). The k for formulation E (with 0.75 wt % DETX) at 16.3 min^{-1} is about twofold higher than the value obtained for formulation A (without DETX). Moreover, the m value is about 15% higher for formulation E than for formulation A.

Effect of photopolymerization temperature

In this study, isothermal photopolymerization experiments were performed with formulation A (without DETX) and formulation D (with 0.5 wt % DETX) at temperatures ranging from 25 to 55°C (Fig. 5). The kinetics data values obtained at each isothermal temperature are summarized in Table III. On the basis of the kinetic results, it was quite reasonable to deduce that the exotherm, percentage of conversion, and cure rate of both systems increased as the isothermal cure temperature was raised. At least two factors could be responsible for this behavior: a thermal contribution toward the photocationic polymerization of the vinyl ethers or raising the temperature increases the mobility of the unreacted initiating and propagating species remaining in the network, thereby increasing their effectiveness on the initiation or propagation reaction.

Figure 6 plots $d\alpha/dt$ versus the degree of conversion for the experimentally obtained data and for the autocatalytic model [eq. (3)] for formulation D with the model parameters values determined above. Excellent agreement is observed, with the degree of fit (R^2) at 0.9958. The other formulation systems behave almost the same as that shown in Figure 6. Thus, the autocatalytic model [eq. (3)] can be used to calculate $d\alpha/dt$ and α with reasonable accuracy and the cure process of the vinyl ether system containing photosensitizer was perfectly described by the proposed model, as shown in Figure 6. However, it should be noted here that the autocatalytic model used in this study is essentially empirical and does not provide any mechanistic insight.

TABLE III
Kinetics Analysis Results for Photopolymerization of Formulations A and D at Different Isothermal Temperatures

Formulation	Temperature (°C)	ΔH (J/g)	Induction time (s)	Peak max (min)	Conversion (%)	k (min^{-1})	m^a
A (0 wt %)	25	159	4.54	0.250	32	8.0	0.512
	35	185	4.12	0.223	37	9.5	0.525
	45	298	3.23	0.137	60	11.8	0.537
	55	363	1.21	0.063	73	15.2	0.590
D (0.5 wt %)	25	192	1.41	0.065	38	14.5	0.576
	35	294	1.15	0.039	59	18.8	0.591
	45	374	0.97	0.030	75	22.3	0.595
	55	496	0.86	0.026	99	26.5	0.599

The conditions are described in the legend of Figure 4.

^a For the value of n fixed at 1.5.

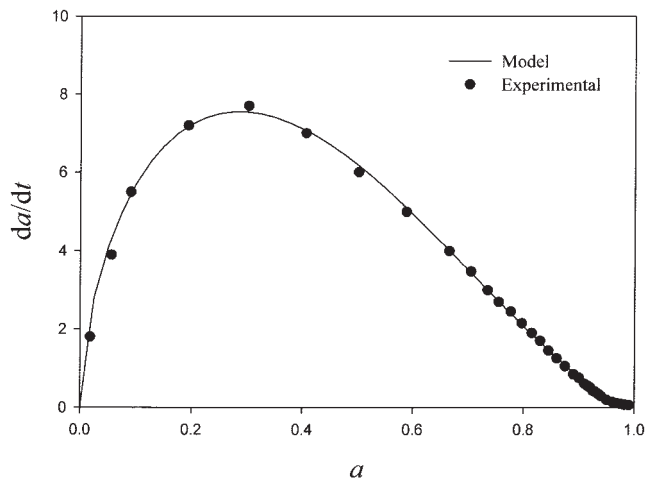


Figure 6 Plots of the conversion rate ($d\alpha/dt$) versus the degree of conversion (α) for experimental data and the autocatalytic model for formulation D at an isothermal temperature of 55°C.

With the calculation of k , which is temperature dependent, we can obtain the activation energy and frequency factor for the cure process. The value of k is given by the Arrhenius relationship^{10,11}:

$$k = A \exp(-E_a/RT) \quad (4)$$

where E_a is the overall activation energy, A is the overall frequency factor, R is the ideal gas constant, and T is the absolute temperature (K). This is a common analysis method when samples are cured isothermally. If the Arrhenius relation is obeyed, the activation energy and frequency factor can be determined from the slope and intercept, respectively, of the Arrhenius plot in eq. (4) of the best-line fit of $\ln(k)$ versus $1/T$.¹¹ Figure 7 plots the obtained relationship between $\ln(k)$ and $1/T$ to determine the values of E_a and A for the systems with and without photosensitizer using a regression analysis approach. The good linear correlation that was obtained supports the above assumption. The values of E_a and A that were obtained are listed in Table IV. This result clearly shows that the addition of DETX photosensitizer lowered the activation energy for the UV-curable vinyl ether system because of the photosensitization effect by which the autocatalytic reaction is more accelerated, which reflects the effectiveness of the photosensitizer, as described above.

The frequency factor is generally referred to as the collision factor, and normally an increase in the speed of the reaction should be reflected in an increase in the collision factor.¹² Our observations are in accordance with this expectation. We can see from Table IV that the frequency factor for the system with photosensitizer is about 1.15-fold higher than that for the system without photosensitizer, indicating that the reactivity

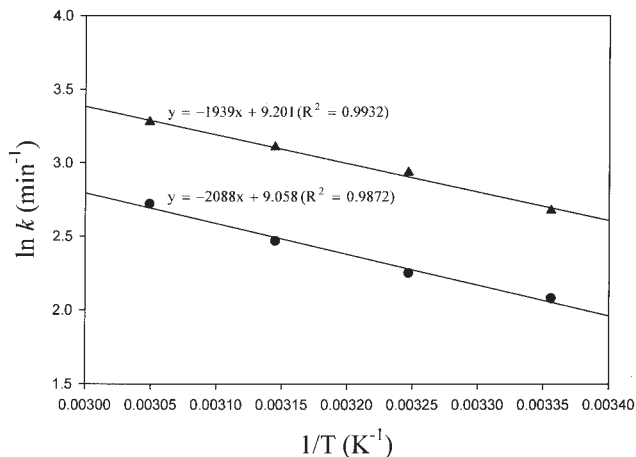


Figure 7 Typical Arrhenius plots of $\ln(k)$ versus $1/T$ for formulations (●) A and (▲) D.

of the former is greater than that of the latter because of the aforementioned photosensitization effect.

CONCLUSIONS

This study used photo-DSC to investigate the cure kinetics for UV-initiated cationic polymerizations of CHVE systems with and without the DETX photosensitizer in the presence of a DAI-salt photoinitiator. Two kinetics parameters (k and m) were successfully determined for CHVE systems with different amounts of added DETX photosensitizer (0–1 wt %) and at different isothermal temperatures (25–55°C) using an autocatalytic kinetics model. The photosensitized CHVE system exhibited much higher k and m values than did the nonphotosensitized system, which was attributable to the effects of photosensitization. Moreover, the values of k and m for both CHVE systems increased significantly with increasing isothermal temperature because of a thermal contribution toward increasing the mobility of active species. We also observed that the addition of DETX lowered the activation energy for the UV-curable vinyl ether system; the collision factor for the photosensitized system was higher than that obtained for the nonphotosensitized system, indicating that the reactivity of the former was much greater than that of the latter. It was concluded that, although the autocatalytic model used in this study was essentially empirical and did not give any

TABLE IV
Activation Energies and Frequency Factors for UV-Curable Vinyl Ether Systems with and Without Photosensitizer

Formulation	E_a (kJ/mol)	A (min ⁻¹)
A (0 wt %)	17.36	8587
D (0.5 wt %)	16.12	9907

mechanistic insight, photocuring kinetics analysis using photo-DSC provided a utilization to elucidate key cure-process parameters for obtaining good control over the photosensitizer content and cure rate in the photosensitized vinyl ether system.

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