

Polymers Based on *N,N*-Diglycidylaniline. I. Investigations of the Curing Kinetics by Dynamic Differential Scanning Calorimetry Measurements

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ABSTRACT: *N,N*-Diglycidylaniline was reacted with aniline (yielding polymer EP-1) and the newly synthesized chromophore 4-(phenylazo)aniline (yielding polymer EP-2). The curing kinetics of these two epoxy resin systems was studied in dynamic experiments by means of differential scanning calorimetry. Kinetic parameters such as the activation energy and frequency factor were estimated with the Ozawa method [$E(O)$ and $A(O)$, respectively], the Kissinger method [$E(K)$ and $A(K)$, respectively], and the modified Avrami method [$E(A)$ and $A(A)$, respectively]. The activation energy and frequency factor of EP-1 were much lower than those of EP-2 estimated with the Ozawa, Kissinger, and Avrami methods. The activation energy and frequency factor for EP-1 determined with the Ozawa method [$E(O) = 55.8$ kJ/mol, $A(O) = 10 \times 10^3$ 1/s] and the Avrami method [$E(A) = 56.4$ kJ/mol, $A(A) = 9.2 \times 10^3$ 1/s] were higher

than those determined with the Kissinger method [$E(K) = 51.0$ kJ/mol, $A(K) = 2 \times 10^3$ 1/s]. In the case of EP-2, the kinetic parameters calculated with the Ozawa model [$E(O) = 140.4$ kJ/mol, $A(O) = 12.3 \times 10^{13}$ 1/s] and the Kissinger model [$E(K) = 139.9$ kJ/mol, $A(K) = 10.9 \times 10^{13}$ 1/s] were higher than those calculated with the Avrami model [$E(A) = 130.4$ kJ/mol, $A(A) = 7.9 \times 10^{12}$ 1/s]. The obtained polymers were characterized with Fourier transform infrared, $^1\text{H-NMR}$, differential scanning calorimetry, and ultraviolet-visible spectroscopy. The polymers exhibited low glass-transition temperatures in the range of 57–79°C and good solubility in common organic solvents. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3596–3604, 2009

Key words: activation energy; curing of polymers; differential scanning calorimetry (DSC)

INTRODUCTION

Epoxy resins constitute a class of important thermosetting polymers and are most often used in high-performance applications because of their unique properties and versatility in formulations. In general, the principal uses for epoxy resins are surface coatings, electrical/electronic components, composites, bonding and adhesives, construction materials, tooling, and casting.^{1–4} Over the last decade, epoxy-based polymers have attracted much attention as materials for optoelectronic applications. Epoxy polymers functionalized with azobenzene groups have been investigated for applications in holography^{5–9} and for second-order nonlinear optical processes.¹⁰ Epoxy compounds are characterized by the presence of a ring called the oxirane group, which consists of an oxygen atom bonded to two carbon atoms and is able to react with many compounds; chemical reactions can be used for curing, and many different

properties can result.¹¹ Furthermore, the curing conditions are the next factor determining epoxy resin properties. Knowledge of the curing kinetics permits controlling the degree of chemical conversion achieved after a cure schedule, which plays an important role in physical properties. Therefore, it is important to verify the cure kinetics for various applications of epoxy polymers. There are several techniques used to monitor the cure process, such as infrared spectroscopy, direct-current conductivity, and differential scanning calorimetry (DSC).^{12–19} The most powerful method is DSC because the curing reaction of epoxy resin is highly exothermic. There are two DSC methods for investigating the curing process, that is, isothermal and dynamic measurements. The advantage of isothermal experiments is that the rate constants at each temperature are better defined and the constants obtained at different temperatures permit the determination of the activation energy (E) associated with the cure reactions.^{20,21} On the other hand, the nature of the reactions and the final products may differ at different temperatures, and the kinetic parameters thus obtained are without ambiguity.²² Dynamic experiments conducted at a specified heating rate by means of DSC will yield

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conversion–time–temperature data that are comprehensive enough to permit direct evaluations of the kinetic parameters. In comparison with the isothermal method, the dynamic cure is theoretically more difficult because of the complex temperature dependence of the rate constant and the peculiar features of the cure, although it more closely simulates the process.²³ A single dynamic run gives more information than several isothermal runs. Dynamic measurements can provide kinetic information over a larger temperature range, and there are no precure problems, as is the case with isothermal experiments, in which the sample must first be heated to the isothermal hold temperature; during this time, cure reactions may take place. Dynamic measurement is valuable as an initial method for isothermal studies and is important for analyzing the cure kinetics of systems with multiple exotherms.²⁴

In this study, dynamic DSC experiments were carried out to investigate the reaction of *N,N*-diglycidylaniline (DGA) with aniline (A-1) and 4-(phenylazo)aniline (A-2). These monomers were chosen for investigation because of our interest in the synthesis of novel materials for optoelectronic applications.^{25–29} Polymers studied in this work could be treated as precursor materials for further functionalization, that is, for the introduction of azobenzene groups to obtain suitable materials for optoelectronics. Various chromophores may be introduced into polymer chains through the use of the post-azocoupling reaction between the polymer and diazonium salts because of the presence of *N,N*-dialkylaminophenylene units.^{30,31} The diazonium salt attacks the benzene ring pendent from the backbone at the position with higher electron density. Even though a polymer synthesized from DGA and A-2 already possesses azobenzene units and should exhibit nonlinear optical properties, it may be functionalized with other chromophores as well.

The reaction mechanism and kinetics of DGA with A-1 have been investigated.^{32–39} These studies have been carried out with model systems and with high-performance liquid chromatography (HPLC), gel permeation chromatography, NMR, and Fourier transform infrared (FTIR) spectroscopy.^{28–32,35} However, to the best of our knowledge, *E* has not been estimated by the DSC technique previously.

In this work, experimental DSC results were analyzed with the Ozawa and Kissinger methods^{24,40–47} and with the modified Avrami equation.^{44,48,49} These methods, in which the system is cured at various heating rates, are simple and valuable for the study of cure kinetics.

The objectives of this work were (1) the determination of *E* and the frequency factor (*A*) of the reaction of DGA with A-1 and novel compound A-2 and (2) a comparison of the kinetic parameters estimated with the different

models. The reaction conditions established with the DSC method in this work were applied then to obtain novel polymers capable of further modifications.

EXPERIMENTAL

Materials

A-1 (99%) was purchased from Aldrich (Sigma-Aldrich Co., Poland Trade, Poznan), and was purified by distillation before use. DGA and *N*-methyl-2-pyrrolidone (NMP; 99.5%) were purchased from Aldrich Chemical and were used as received.

Synthesis

Synthesis of A-2

A-2 was synthesized according to the published procedure [Fig. 1(a)].⁵⁰

Yield: 77%. ¹H-NMR [hexadeuterated dimethyl sulfoxide (DMSO-*d*₆), δ, ppm]: 6.95–7.05 (m, 2H), 7.2–7.5 (m, 6H), 7.5–7.6 (m, H), 12.43 (s, NH₂). FTIR (KBr, cm⁻¹): 3199 (NH₂), 1603, 1503 (Ar). ANAL. Calcd for C₁₂H₁₁N₃: C, 73.07%; N, 21.30%; H, 5.62%. Found: C, 73.63%; N, 21.56%; H, 5.69%. Ultraviolet–visible (UV–vis; NMP): λ_{max} = 358, 296 nm (ε₃₅₈ = 8.2 × 10⁴ L mol⁻¹ cm⁻¹). DSC: melting temperature = 103°C.

Synthesis of the polymers

Synthesis of the polymer from DGA and A-1 (EP-1). Polymer EP-1 was prepared according to the modified method.^{51,52}

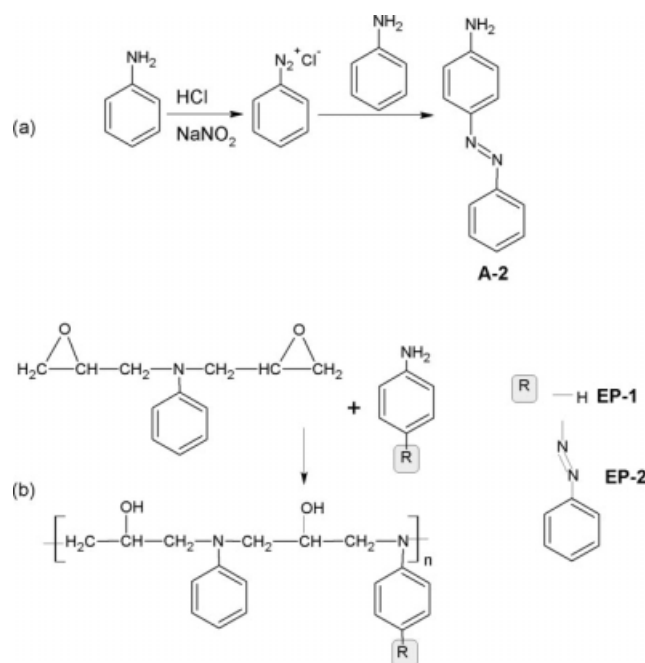


Figure 1 (a) Chemical structure and synthetic route for chromophore A-2 and (b) reaction scheme for polymers EP-1 and EP-2.

DGA (4.1052 g, 0.02 mol) and A-1 (1.82 mL, 0.02 mol) were homogeneously mixed under slow heating and polymerized at 110°C for 26 h. The solid product was dissolved in 50 mL of chloroform and methanol (4 : 1 v/v) and dropped in 500 mL of acetone under stirring. This product was soluble in these solvents, and the solvent were evaporated under reduced pressure. Then, the epoxy polymer was dried at 100°C *in vacuo* for 24 h.

Yield: 90%. ¹H-NMR (DMSO-*d*₆, δ, ppm): 2.9–3.3 (m, CH₂, 4H), 3.5–4.0 (m, CH, H), 5.31 (t, OH, H), 6.5 (t, H), 6.6 (d, 2H), 7.0 (t, 2H). FTIR (KBr, cm⁻¹): 3376 (OH), 2914 (CH₂), 1600, 1504 (Ar). UV-vis (NMP): λ_{max} = 303, 263 nm. DSC: glass-transition temperature (*T*_g) = 57°C. Final heat of cure: 489.45 J/g or 134.21 kJ/mol of epoxy equivalent. Weight-average molecular weight (*M*_w): 1500 g/mol. Weight-average molecular weight/number-average molecular weight (*M*_w/*M*_n): 2.4.

Synthesis of the polymer from DGA and A-2 (EP-2). EP-2 was prepared according to the modified method.^{51,52}

DGA (0.4105 g, 2 mmol) and A-2 (0.3945 g, 2 mmol) in 2 mL of methanol were mixed under slow heating and polymerized at 110°C for 3 h, at 120°C for 21 h, and at 130°C for 20 h. The product was solid.

¹H-NMR (DMSO-*d*₆, δ, ppm): 2.9–3.2 (m, CH₂, 8H), 3.6–4.0 (m, CH, 2H), 4.74 (t, OH, H), 5.15 (t, OH, H), 6.53 (t, H), 6.7 (t, 4H), 6.85 (t, 2H), 7.03 (d, 2H), 7.2 (t, 2H), 7.4 (t, 2H), 7.7 (t, H). FTIR (KBr, cm⁻¹): 3372 (OH), 2923 (CH₂), 1602, 1510 (Ar). UV-vis (NMP): λ_{max} = 420, 305, 262 nm. Yield: 90%. DSC: *T*_g = 79°C. Final heat of cure: 1171 J/g or 411.52 kJ/mol of epoxy equivalent. *M*_w for the soluble fraction: 3000 g/mol. *M*_w/*M*_n for the soluble fraction: 3.0.

Measurements

FTIR spectra were recorded on a Bio-Rad FTS 40 A spectrometer (Krefeld, Germany) with KBr pellets. ¹H-NMR spectroscopy was carried out on a Varian 300 spectrometer (Walnut, Creek, CA) with DMSO-*d*₆ as the solvent and tetramethylsilane as the internal standard. UV-vis spectra were recorded in NMP solutions of the polymers with a Jasco V570 UV-V-NIR spectrometer (instrumental corporation, Tokyo, Japan). The X-ray diffraction patterns on solid samples were recorded with Cu Kα radiation on a wide-angle HZG-4 diffractometer working in the typical Bragg geometry. The *M*_w and molecular weight distribution (*M*_w/*M*_n) values of the polymers were determined by size exclusion chromatography measurements conducted in tetrahydrofuran (THF) at 35°C with a flow rate of 1 mL/min with a set of two PLgel 5-μm, mixed-C, ultrahigh-efficiency columns. A Spectra Physics 8800 isocratic pump as a solvent delivery system, a VE3580 differential refractive-

index detector (Viscotek, Houston, TX), and a 270 dual detector array viscometer detector (viscometer only; Viscotek) were applied. A volume of 100 μL of a sample solution in THF (concentration = 2% w/v) was injected. Polystyrene standards with narrow molecular weight distributions were used to generate a calibration curve.

DSC measurements

DSC measurements were taken with a TA DSC 2010 apparatus (TA Instruments, New Castle, DE). Curing experiments were performed at heating rates of 2.5, 5, 10, and 20°C/min and in the temperature range of 20–300°C. The *T*_g values of amorphous samples were determined at a heating rate of 20°C/min. In this study, *T*_g was taken as the midpoint of the step transition. Samples of 10–15 mg in crimped aluminum cells were heated in the DSC apparatus under a nitrogen atmosphere (flow = 50 mL/min). An empty cell was used as the reference. The instrument was calibrated with high-purity indium.

RESULTS AND DISCUSSION

In this work, the kinetics of the curing reaction of DGA with A-1 and synthesized A-2 [cf. Fig. 1(a)] was studied with dynamic DSC measurements. A scheme of the curing reactions and structures of the obtained polymers are presented in Figure 1.

DSC was performed with A-1 and A-2 at various heating rates. Three different methods, that is, the Ozawa, Kissinger, and modified Avrami methods, were chosen to analyze the experimental results of the cure reaction. The advantages of these methods include simplicity and accuracy for estimating *E* and *A* in various types of cure reactions.^{40,42}

Analysis of the DSC results with the Ozawa and Kissinger methods

In the first stage of this work, kinetic parameters were studied with the Ozawa and Kissinger methods. With these methods, the relationships between the heating rate (ϕ) values and the peak exotherm temperature (*T*_p) values were used to determine the reaction kinetics. Under the assumption that the chemical conversion was constant at *T*_p and independent of ϕ , *E* was calculated on the basis of the Ozawa equation:^{42,43}

$$E = -R/1.052 \times \Delta \ln \phi / \Delta(1/T_p) \quad (1)$$

where *R* is the universal gas constant. The equations derived by Kissinger for *E* and *A* are as follows:^{40,45}

$$-E/R = d[\ln(\phi/T_p^2)]/d(1/T_p) \quad (2)$$

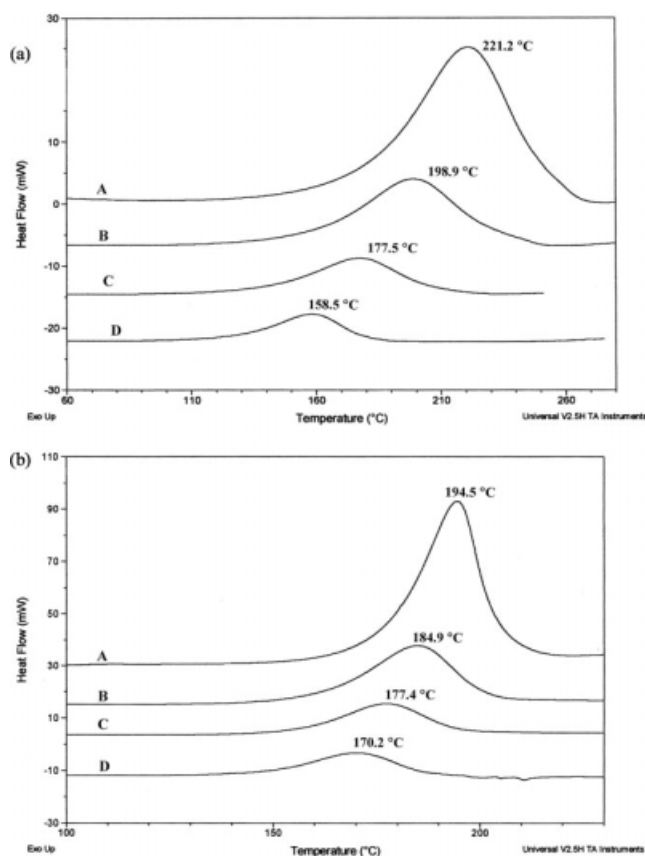


Figure 2 DSC curves at different heating rates for (a) EP-1 and (b) EP-2: (A) 20, (B) 10, (C) 5, and (D) 2.5 °C/min.

$$A = \phi E \exp(E/RT_p) / RT_p^2 \quad (3)$$

These methods are simple and convenient in comparison with the cut-and-weigh method and spectroscopic method,⁴⁶ and the Ozawa and Kissinger methods are independent of the sample size.⁴⁷

Typical dynamic DSC curves at four heating rates for the EP-1 and EP-2 epoxy systems are shown in Figure 2.

The cure exothermic temperature peaks shift to higher temperatures with the heating rate increasing in both systems. At the same heating rates, the maximum of the exothermic peak is shifted to a higher temperature for the EP-1 epoxy system.

A plot of $1/T_p$ versus $\ln \phi$ according to eq. (1) (Ozawa method) for each polymer is presented in Figure 3(a). The calculated slope is -0.0563 for EP-2 and -0.1417 for EP-1.

Figure 3(b) shows plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ obtained according to eq. (2) (Kissinger method) for each polymer. In this case, the slope is -6.1345 for EP-1 and -16.831 for EP-2.

Figure 4 illustrates a plot for eq. (3) with E values estimated by the Ozawa and Kissinger methods for EP-1 and EP-2.

The calculated kinetic parameters, that is, E and A , for EP-1 and EP-2 estimated by the Ozawa and Kissinger methods are collected in Table I.

E and A for EP-2 are much higher than those for EP-1 by both methods. It can be suggested that EP-2 needs to be cured at a higher temperature than EP-1.

The values of E and A for EP-1 determined with the Ozawa method are higher than those determined with the Kissinger method. In the case of EP-2, the kinetic parameters calculated with the Ozawa and Kissinger methods are similar.

It can be also inferred that A has more influence than E because the T_p values for EP-2 are lower than those for EP-1.

Analysis of the DSC results with the Avrami method

In the next step of our research, the Avrami method was applied for the determination of the reaction kinetics, and the obtained parameters were compared with those estimated previously with the Ozawa and Kissinger methods. In this method, the kinetic parameters were determined from the heat of the curing process, which was carried at various

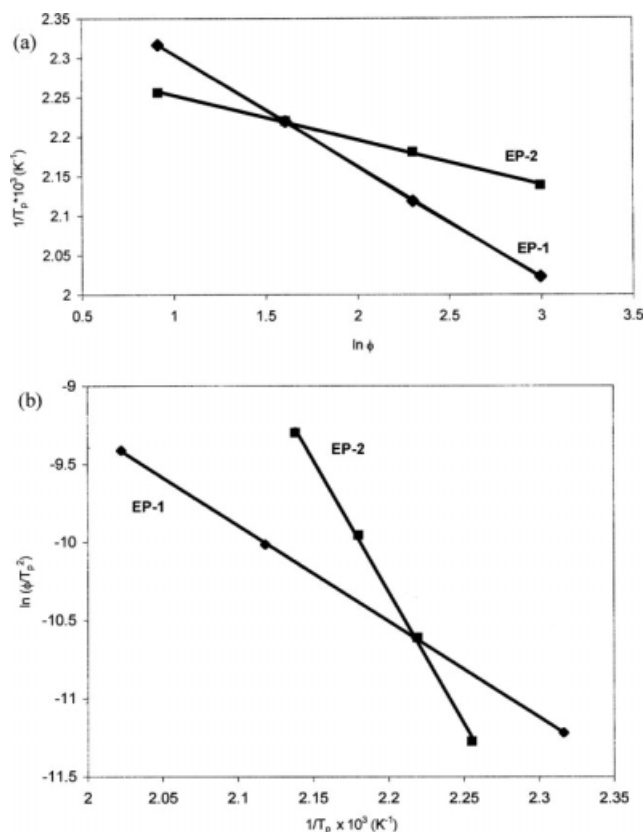


Figure 3 Plots for the determination of E in the curing reaction of EP-1 and EP-2 by (a) the Ozawa method and (b) the Kissinger method.

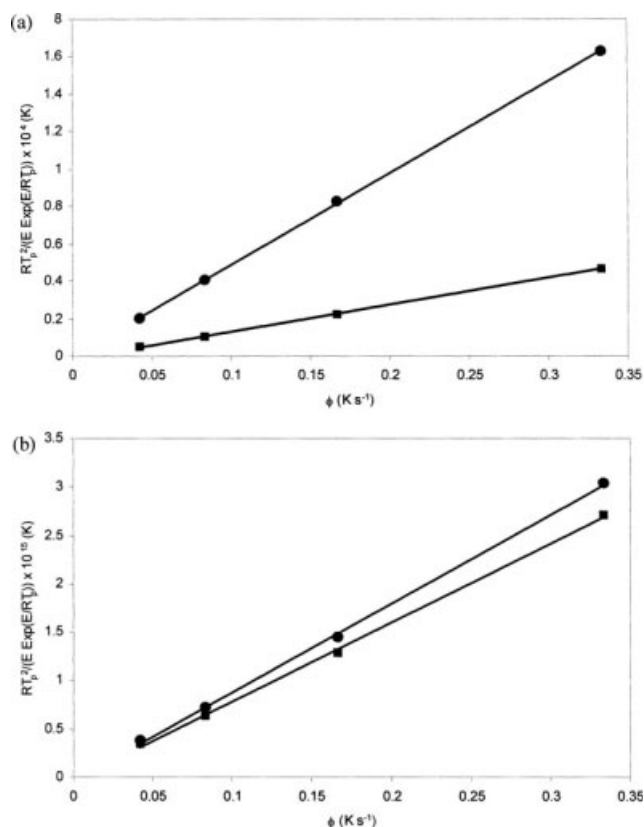


Figure 4 Plots for the determination of A by (■) the Ozawa method and (●) the Kissinger method in the curing reaction of (a) EP-1 and (b) EP-2.

heating rates. In this method, the DSC curves were analyzed on the basis of the following assumptions:

- The area under the exotherm dynamic DSC curves in Figure 2 is proportional to the extent of reaction.
- The extent of reaction during the mixing of the epoxy monomers can be neglected.

The extent of cure at any time (α) is defined as follows:

$$\alpha = \Delta H / \Delta H_0 \quad (4)$$

where ΔH is the heat of reaction determined from the partial area under the DSC curve up to the point of interest and ΔH_0 is the final heat of cure. α can be calculated from the heat of cure. Figure 5 reveals that α decreases correspondingly at the given cure

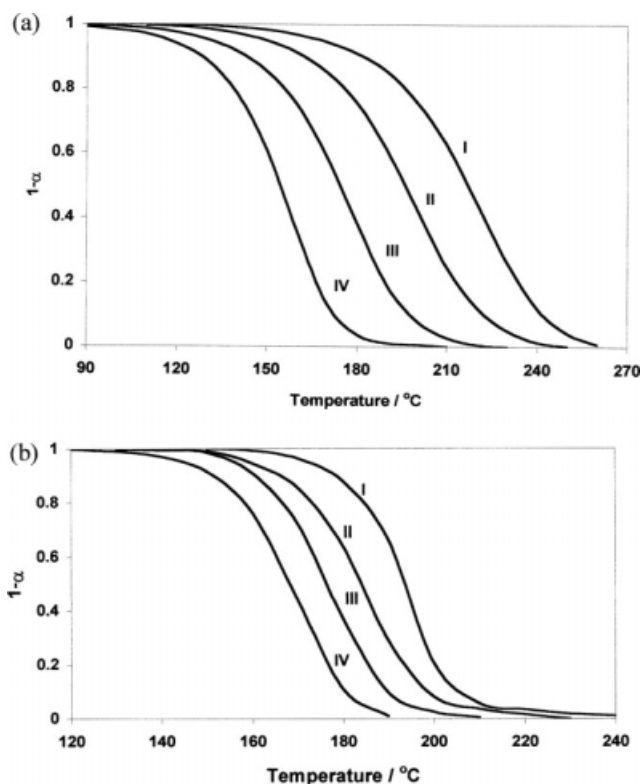


Figure 5 Temperature dependence of the unreacted fraction at different heating rates for (a) EP-1 and (b) EP-2: (I) 20, (II) 10, (III) 5, and (IV) 2.5°C/min.

temperature when the heating rates are increased for these two systems. An examination of Figure 5 demonstrates that there is a higher α value at the same cure temperature for EP-2.

To describe the cure process of an epoxy resin at a constant heating rate, the Avrami equation can be applied:

$$\alpha(t) = 1 - \exp(-kt^n) \quad (5)$$

where $\alpha(t)$ is the extent of cure at time t ; k is the Avrami rate constant; and n is the Avrami exponent, which can be extended to the nonisothermal process with the Ozawa method.^{44,49} At a given temperature, n is a constant, and the untransformed volume fraction can be written as follows:

$$1 - \alpha = \exp(-k'\phi^{-n}) \quad (6)$$

where α is a function of temperature. ϕ is equivalent to dT/dt . k' is a function of the temperature of the process.

TABLE I
 E and A Values for the Polymers from DSC

Polymer	Ozawa method		Kissinger method		Avrami method	
	E (kJ/mol)	A (1/s)	E (kJ/mol)	A (1/s)	E (kJ/mol)	A (1/s)
EP-1	55.773	10.00×10^3	51.000	2.05×10^3	56.360	9.18×10^3
EP-2	140.373	12.25×10^{13}	139.932	10.91×10^{13}	130.438	7.94×10^{12}

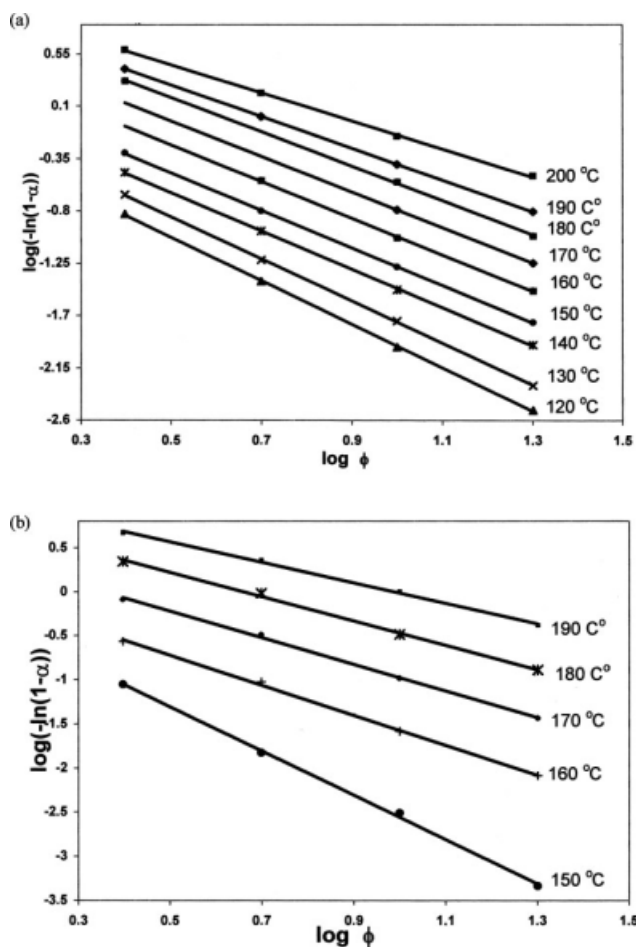


Figure 6 Avrami plots of dynamic curing at various temperatures for (a) EP-1 and (b) EP-2.

Equation (6) can be rewritten in a linear form:

$$\log[-\ln(1-\alpha)] = \log k' - n \log \phi \quad (7)$$

Equation (7) was used to obtain the kinetic parameters from observations of the cure process at different heating rates. A plot of $\log[-\ln(1-\alpha)]$ versus $\log \phi$ at a given temperature should yield a straight line with a slope of $-n$ and an intercept of $\log k'$.

A plot of this equation for the dynamic cure behavior of EP-1 and EP-2 is shown in Figure 6. The values of the rate constant and exponent at different temperatures are listed in Table II.

The unit of the rate constant, corresponding to the unit for the isothermal result (min^{-1}), is $\text{min}^n \text{K}^{-n}$. The plots in Figure 6 exhibit good linear relationships for the whole cure temperature range. It has been found that the rate constant is sensitive to temperature and increases with rising temperature.

The values of E (here the overall activation energy) and A (here the overall frequency factor)

were next obtained from an Arrhenius temperature dependence:

$$k = A \exp[(-E)/(R_0T)] \quad (8)$$

where R_0 is the universal gas constant. E and A were calculated from the slope and intercept, respectively, of the best fit line. Figure 7 shows a plot of $\ln k$ versus $1/T$. The estimated E values are reported in Table I, and they are in good agreement with those obtained with the Ozawa and Kissinger methods for both investigated epoxy systems.

E for DGA reacted with A-1 is more than 2 times lower than E for DGA cured with A-2. The E value of DGA cured with A-1 (obtained in this study) is in good agreement with the theoretical value (60 kJ/mol) determined from a model reaction.³⁴ The polymers prepared from DGA and difunctional amine were rather linear polymers. However, E for the reaction between DGA and A-2 (64.1 kJ/mol) is higher than E for the reaction of DGA cured with the tetrafunctional curing agent 2,4-diamino-4'-methylazobenzene (56.2 kJ/mol), as estimated from DSC isothermal experiments.²⁹ Taking into account similar DGA epoxy compounds, that is, diglycidyl benzene and diepoxy propyl phthalate cured with A-1, we found that E values calculated from HPLC and NMR measurements were in the range of 62.7–102.8 kJ/mol.³⁷ Typical thermosetting epoxy resins obtained from diglycidyl ether of bisphenol A and 4,4'-methylene dianiline exhibited an E value, calculated from dynamic DSC measurements, of about 55.1 kJ/mol.⁴⁹ Data published for similar diglycidyl ether of bisphenol A/4,4'-methylene dianiline epoxy systems were in the same range, that is, 58.57 kJ/mol, as reported by Gough and Smith⁵³ from gel time measurements, and 50–58 kJ/mol, as reported by Prime⁵⁴ and Horie et al.⁵⁵ from reaction rates measured by DSC. A higher E value (i.e., 148.8 kJ/mol) was obtained for diglycidyl ether of 4,4'-biphenyl cured with *p*-phenylenediamine.⁵⁶

TABLE II
Kinetic Parameters Obtained with Eq. (7) at Different Temperatures Under Dynamic Conditions for Two Epoxy Systems: EP-1 and EP-2

Temperature (°C)	EP-1		EP-2	
	k' (min^n/K^n)	n	k' (min^n/K^n)	n
120	0.81	1.86	—	—
130	1.13	1.80	—	—
140	1.51	1.64	—	—
150	2.14	1.61	0.58	2.50
160	3.51	1.60	1.34	1.69
170	5.41	1.53	3.42	1.50
180	8.123	1.47	8.17	1.38
190	9.16	1.36	14.89	1.16
200	11.43	1.21	—	—

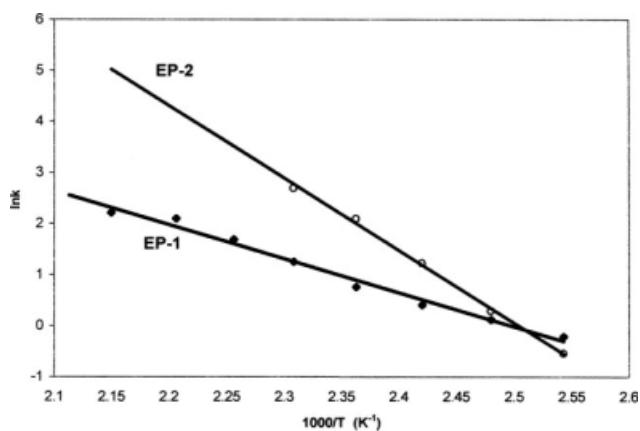


Figure 7 Temperature dependence of k for EP-1 and EP-2.

Polymer characterization

In the last part of our work, polymers based on DGA (EP-1 and EP-2) were synthesized by a polyaddition reaction and characterized. The reaction conditions were established from DSC investigations. Instrumental techniques including FTIR and $^1\text{H-NMR}$ spectroscopy were used for characterization of the polymer molecular structure. In FTIR spectra, the absence of absorption band characteristics for oxirane rings at 915 cm^{-1} and the appearance of bands at approximately 3376 cm^{-1} , typical for hydroxyl groups, were observed. The $^1\text{H-NMR}$ spectra of EP-1 and EP-2 showed a peak at about 5.0 ppm corresponding to a phenolic hydroxyl proton and peaks in the range of 3.5–4.0 ppm due to CH groups. The results obtained for the polymers are in accordance with the proposed structures.

The ideal material for many end-use applications should be highly amorphous as crystallites introduce unwanted light scattering. Thus, the structure of the polymer films structure was evaluated with wide-angle X-ray diffraction experiments. X-ray patterns obtained from these measurements are shown in Figure 8. One broad diffraction peak of the diffusion type, centered at 20° (2θ), was observed for the studied samples (Fig. 8). Both polymers showed the same diffraction patterns typical of perfectly amorphous materials.

The solubility of the synthesized polymers was determined (by visual observation) for powdered

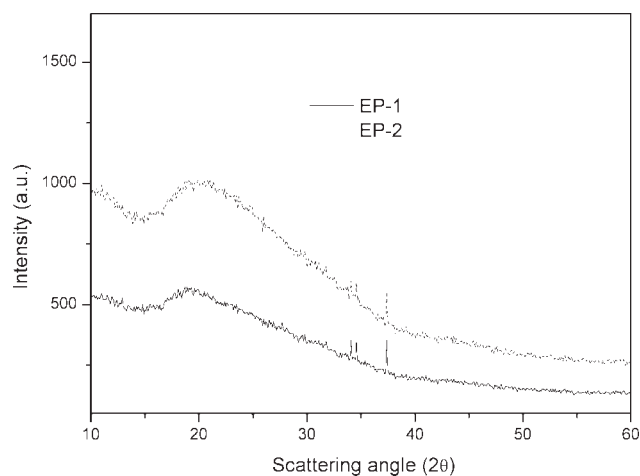


Figure 8 X-ray diffraction patterns of the prepared polymers (EP-1 and EP-2).

samples with excesses of various solvents. These results along with the reduced viscosities of the polymers are listed in Table III. Both polymers are soluble in strong polar organic solvents such as NMP, *N,N*-dimethylformamide (DMF), and DMSO. Polymer EP-1 is also soluble in THF, chloroform, and acetonitrile, but polymer EP-2 is only partially soluble in these solvents. The molecular weight of EP-1 is rather modest. M_w (with respect to polystyrene standards) is 1500 g/mol. The molecular weight of the soluble fraction of EP-2 is 2 times higher than that of EP-1. The insoluble residue is expected to have a much higher average molecular weight. Polymers with moderate molecular weights are desirable for applications in holography.⁵⁷

The polymers have low T_g values. Polymer EP-2 has a higher T_g value (79°C) than EP-1 (57°C).

The optical properties of the epoxy-based polymer were analyzed with UV-vis absorption spectroscopy. The UV-vis spectra of the polymers were acquired both in NMP solutions and in polymer films on glass. The range of UV-vis measurements was limited by the transparency of the solvent and substrate. Figure 9 shows UV-vis spectra for polymers EP-1 and EP-2. The absorption spectra of polymer EP-1 show intense absorption bands in the UV region with maxima (λ_{max}) located at 263 and 303 nm. In the case of polymer EP-2, besides peaks

TABLE III
Solubility and Reduced Viscosity of the Synthesized Polymers

Polymer	Solubility						Reduced viscosity (dL/g) ^a
	NMP	DMF	DMSO	THF	CHCl ₃	CH ₃ CN	
EP-1	+	+	+	+	+	++	0.033
EP-2	+	+	+	±	±	±	0.067

+ = soluble at room temperature; ++ = soluble on heating; ± = partially soluble on heating.

^a Measured in NMP at a concentration of 0.2 g/100 mL at 25°C .

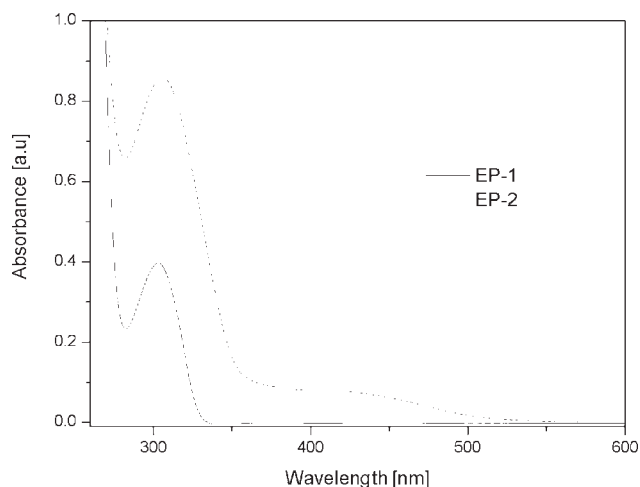


Figure 9 UV-vis spectra of EP-1 and EP-2 in NMP solutions (concentration = 1×10^{-5} mol/L).

attributed to a transition within the polymer backbone, an additional absorption band at a lower energy, that is, at 420 nm, can be detected. The third peak is assigned to the vibronic coupling between the $\pi-\pi^*$ and $n-\pi^*$ electronic transitions of the *trans*-isomer of the azobenzene moiety.²³

The positions of the azobenzene absorption band of polymer EP-2 changed in comparison with those of the A-2 compound. A redshift (ca. 62 nm) of the azobenzene transition between polymer EP-2 and chromophore A-2 was observed. The polymers exhibited the same position of λ_{\max} in solution and in the solid state as in film on glass.

Further study of the functionalization of EP-1 and EP-2 with various chromophores is in progress and will be described in a forthcoming article.

CONCLUSIONS

The kinetics of DGA reacted with A-1 and A-2 was studied with dynamic DSC measurements. The main advantage of this method is that the measurements can be conducted over a wide temperature range and precure problems can be avoided. The kinetic parameters can be estimated quickly and with high precision in a single heating run; this is important for establishing the reaction conditions. *E* and *A* of the epoxy resins cured with A-1 (EP-1) are much higher than those of EP-2. The value of *E* obtained from the slope from the Avrami method closely agrees with the values obtained with the Ozawa and Kissinger methods for both investigated polymers.

Amorphous, soluble polymers from DGA were synthesized, and they can be considered parent materials for further functionalization.

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