

Copolymerization Behavior and Kinetics of an Epoxy Copolymer with Zero Shrinkage

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ABSTRACT: The copolymerization behavior and the apparent cure kinetics of epoxy resin E51 containing the expanding monomer 3,9-di(5-norbornene-2,2)-1,5,7,11-tetraoxaspiro [5,5] undecane (NSOC, norbornene spiro orthocarbonate), were investigated by using differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. Evidence for random copolymerization of the E51-NSOC system was obtained by dynamic mechanical analysis and electron microscopy. The ring-opening reaction of the epoxy resin was found to be first order with an activation energy of 62.0 kJ/mol and the reaction with the expanding monomer NSOC was second order with an activation energy of 121.3 kJ/mol. The comonomers were joined with an ether linkage. Longer copolymerization sequence lengths were obtained with higher NSOC contents in the copolymer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1457–1464, 2002; DOI 10.1002/app.10485

Key words: ring-opening; polymerization; copolymerization; kinetics

INTRODUCTION

The bicyclic spiro monomer, 3,9-di(5-norbornene-2,2)-1,5,7,11-tetraoxaspiro [5,5] undecane (NSOC, norbornene spiro orthocarbonate), increases in volume during ring-opening polymerizations^{1–7} similar to the freezing of water. A resin matrix with a controllable volume could thus be obtained by copolymerizing a generally available commercial resin, which contracts during curing, with the bicyclic expanding monomer. This kind of copolymerization is very significant for some special uses. In the previous work,^{8–10} we synthesized the norbornene spiro orthocarbonate and copolymerized it with epoxy resin E51 in varying proportions. By measuring the volume change in the epoxy copolymers with dilatometry, we found that the copolymer showed no volume change when the E51 : NSOC = 5.88 : 1 in equivalents. This epoxy copolymer with zero shrinkage was used as an adhesive for joining the optical parts of a large telescope.⁸ Measurements of

the thermal and mechanical properties of the copolymer have shown that both the change in the macromolecular chain structure of the resin and the expansion volume affect these physical properties.⁹ In the case of NSOC, the change in chain structure caused by NSOC's copolymerization with epoxy resin was dominant compared with the volume expansion arising from the ring opening of the bicyclic spiro group. The glass transition temperature, the thermal degradation temperature, and the fracture strength were found to decrease with the increasing NSOC content in the copolymer.⁹ In the present contribution, we discuss the copolymerization behavior and the cure kinetics of the epoxy-NSOC copolymer system.

EXPERIMENTAL

Materials

The bicyclic monomer, NSOC (norbornene spiro orthocarbonate), was synthesized in our lab. A detailed description of the synthesis can be found in ref.⁸ The obtained NSOC was a needle-shaped

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white crystalline solid with a melting point of 233°C and a molecular weight of 316, which was ground into powder (< 200 mesh) before use. The epoxy resin used was bisphenol-A E51 with an epoxy equivalent of 196, produced by the Wuxi Resin Factory (China). The hardener was boron trifluoride monoethyl amine (imported from U.S.A.).

Dilatometry experiments have shown that pure epoxy sample (N_{00}) showed a greater volume decrease during curing than the copolymer sample containing 10 wt % NSOC (N_{10}). Copolymers containing 25 wt % NSOC (N_{25}) even showed some expansion upon curing. It was found that N_{21} , the sample containing 21 wt % NSOC, showed no volume change during copolymerization.⁸ These results verified the expansion effect of the spiro orthocarbonate compounds.

Instrument Analysis

Infrared spectra were obtained with a Nicolet 170SX FTIR spectrometer. A Perkin-Elmer DSC-2C was used in the differential scanning calorimetry (DSC) experiments and a rheograph solid viscoelastometer, made by Toyo Seiki (Japan), was used in dynamic mechanics analysis (DMA). Nuclear magnetic resonance (NMR) was carried out on FX-90Q spectrometry.

RESULTS AND DISCUSSION

Random Copolymerization

Figures 1 and 2 show DSC and DMA results of epoxy copolymers containing various amounts of NSOC, respectively. It can be seen that only one glass transition exists for both pure epoxy resin

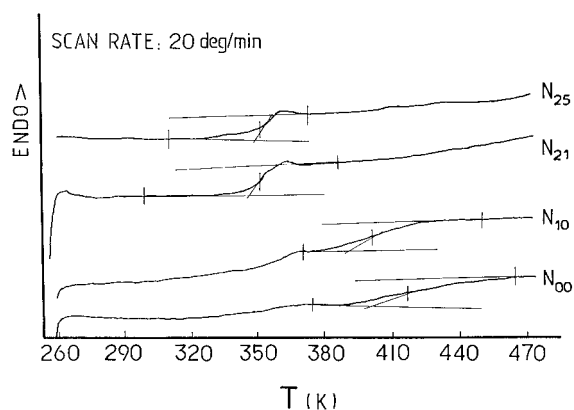


Figure 1 DSC temperature spectrum of the pure epoxy N_{00} and epoxy copolymers N_{10} , N_{21} , N_{25} .

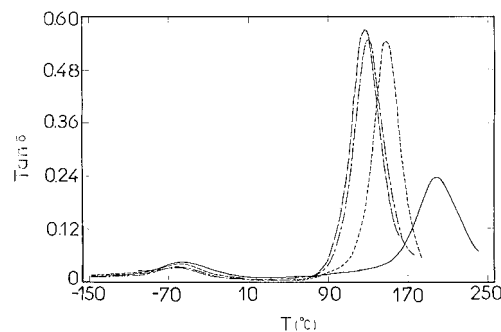


Figure 2 Dynamic mechanical properties (loss tangent) of the pure epoxy resin N_{00} (—) and epoxy copolymers N_{10} (- - -), N_{21} (- · - ·), and N_{25} (- · - ·).

(N_{00}) and other three copolymers of N_{10} , N_{21} , and N_{25} . The glass transition temperatures decrease as the content of NSOC increases, because NSOC molecules introduce long flexible chains into the copolymers. Considering that the catalyst $\text{BF}_3\text{NH}_2\text{C}_2\text{H}_5$ is nonselective and cannot produce an alternating copolymer, we assume that the E51-NSOC copolymers initiating with $\text{BF}_3\text{NH}_2\text{C}_2\text{H}_5$ should be random, because graft and block copolymers are nonhomogeneous and should show two or more glass transition changes. The scanning electron micrograph of the fractural surface of sample N_{21} (not shown here) also proves a homogeneous microphase structure.

NMR is one of the best means for determining the type of copolymerization, in which the spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_2) may reflect the structural properties. T_1 and T_2 for these samples are listed in Table I. The results indicate that (1) the spin lattice relaxation is a single relaxation; and (2) for the epoxy copolymers, the NMR attenuation is of Lorentz line shape (L); for pure epoxy resin, the attenuation is of Gaussian line shape (G) and for the pure NSOC polymer, G/L is 39/61. All the epoxy copolymers show similar values for the spin-spin relaxation time, suggesting that

Table I Spin-Lattice Relaxation time T_1 and Spin-Spin Relaxation Time T_2 of the Samples

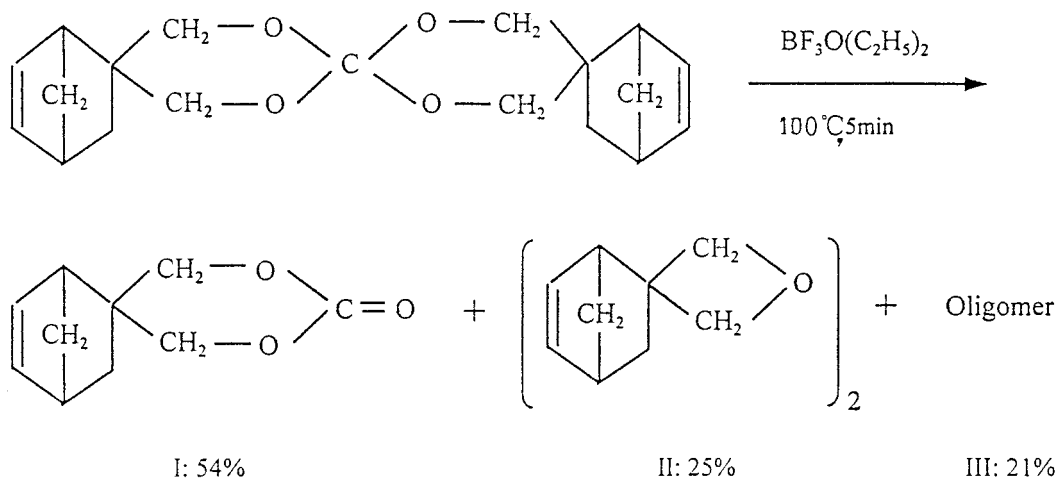
	T_1 (s)	T_2 (s)	$I(G)/I(L)$
N_{00}	0.55	10.6	94/6
N_{10}	0.79	10.6	8/96
N_{21}	0.84	10.5	3/97
N_{25}	0.80	10.3	14/86
NSOC	1.53	7.9	39/61

the samples contain homogeneous domains in the size range of several nanometers.

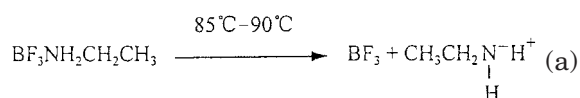
Ring-Opening Mechanism

Generally, the cationic polymerizations of cyclic ethers are carried out through a tertiary oxonium ion,¹¹ and so are the cases of most spiro orthocarbonates (SOC). However, NSOC is unique; it undergoes quite a different mecha-

nism from other SOC and is more complex.^{3,4} When initiated with BF₃OEt₂, the NSOC first decomposed to form some smaller cyclic compounds quickly.³ The main decomposition component is compound I (54%), which is still a spirocyclic carbonate and can further polymerize when catalyzed by Lewis acid through the breakage of the double bonds and the ring-opening process. Compound III is an oligomeric mixture which contains 72% olefin.



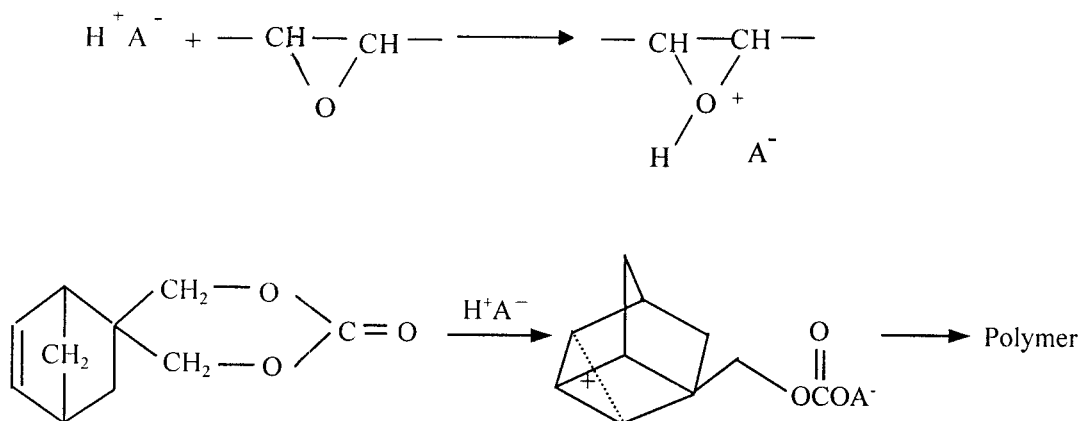
In this article, the catalyst is boron trifluoride monoethyl amine (BF₃NH₂C₂H₅), a similar catalyst to BF₃O(C₂H₅), which is a stable complex and only decomposes above a certain temperature:



if water is present:



Both the active centers in eqs. (a) and (b) can initiate the polymerization of epoxy E-51 and spiro orthocarbonate (compound I). If the active centers are denoted as H⁺ A⁻, the copolymerization of epoxy and NSOC can be expressed as follows:



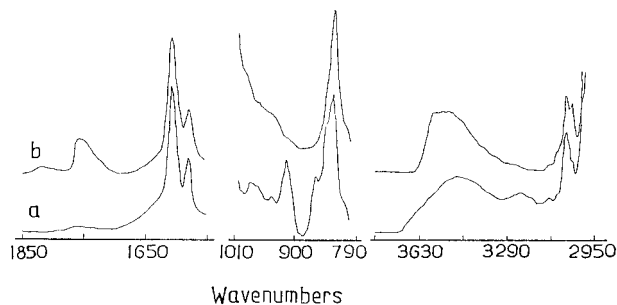
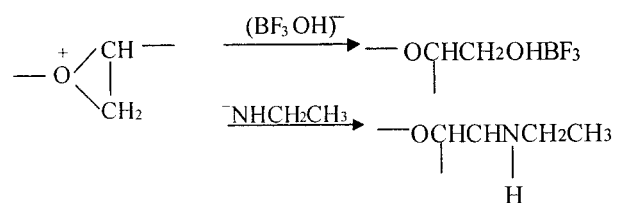


Figure 3 IR spectrum of sample N_{10} before (a) and after (b) 2.3 h polymerization.

Then the chain propagation process begins. The molecules of epoxy E-51 and SOC (compound I) are initiated randomly to form copolymer. At lower temperatures, the propagating chain may terminate:



Chains ending with SOC I units terminate similarly. Chain termination may take place just after chain initiation or in the chain propagation process. Because chain transfer does not reduce the number of active centers, the only effect is to lead different end groups; therefore, this kind of reaction can be neglected in chain termination. The hydrogen on the secondary amine produced in the termination reaction is less active than that on the primary amine. However, an increase in temperature will activate this hydrogen and allow it to initiate polymerization as an active center again. This is the reason the curing of epoxy resins using amine as catalysts must pass through a postcure procedure.

Because of the emergence of the group, ---O---C(=O)--- generated from SOC (I) in the copolymer product, the copolymerization reaction could be detected on the basis of the appearance of the corresponding absorption peak in the infrared spectrum. Figure 3 shows an infrared spectrum of the epoxy copolymer N_{10} before and after 2.3 h of polymerization. The appearance of the peak at 1754 cm^{-1} , which does not exist in the sample before polymerization, indicates that the ring-

opening reactions have occurred in the E51-NSOC system.

Comparing the spectra of the E51-NSOC system before and after polymerization, we found that an absorption peak at 915 cm^{-1} , ascribed to

$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{---CH---CH}_2 \end{array}$ in the pure epoxy resin (N_{00}) before curing, diminished with the proceeding of the ring-opening reactions in the E51-NSOC system; whereas the peak at 1754 cm^{-1} , due to the

$\begin{array}{c} \text{O} \\ || \\ \text{---O---C---O---} \end{array}$ groups in the copolymer product, increased in intensity. After full cure, the peak at 915 cm^{-1} disappeared completely and the peak at 1754 cm^{-1} reached a maximum height. According to the ring-opening process of NSOC,³ it first decomposes mainly to SOC I, then SOC I continues reacting to generate $\begin{array}{c} \text{O} \\ || \\ \text{---O---C---O---} \end{array}$ group. This process is nearly quantitatively; also, the group $\begin{array}{c} \text{O} \\ || \\ \text{---O---C---O---} \end{array}$ only comes from SOC. Therefore, the extent of the cure reaction in the epoxy resin

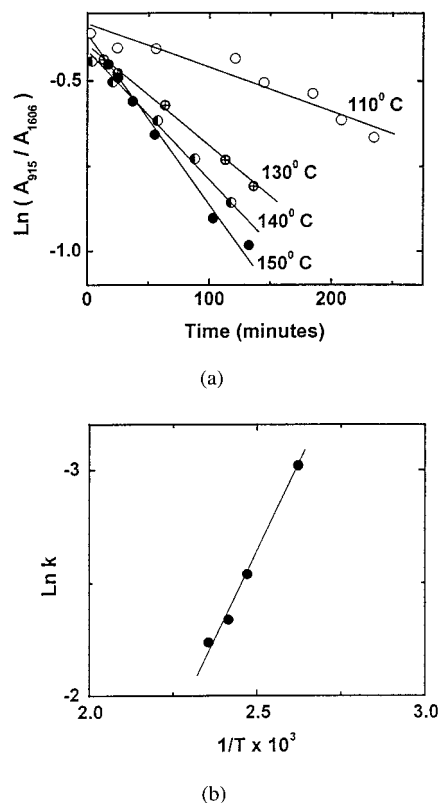


Figure 4 The kinetic curves of pure epoxy resin N_{00} . (a) $\ln(A_{915}/A_{1606})-t$ plot; (b) $\ln k-1/T$ plot.

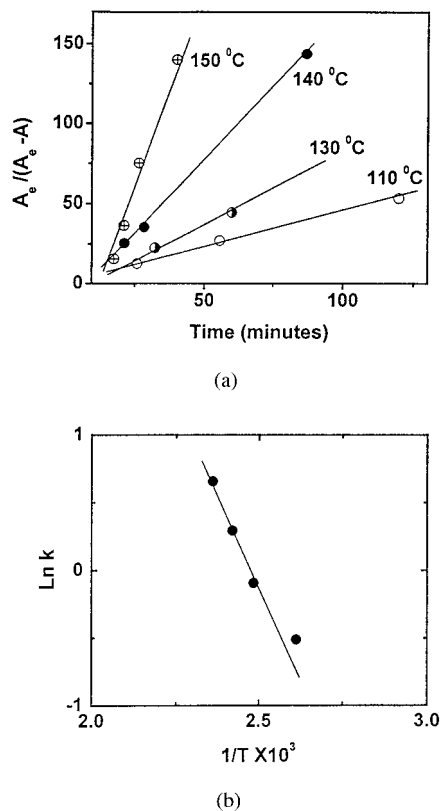


Figure 5 The kinetic curves of pure expanding monomer NSOC. (a) $A_e/(A_e - A) - t$ plot; (b) $\ln k - 1/T$ plot.

and the extent of the ring opening reaction in NSOC could be determined by the change in the intensities of the two peaks. According to Beer's law: $A = \beta C$;¹² if the reaction is first order, then

$$\ln C = -2.303k_1t + \ln C_0 \quad \text{or} \\ \ln A = -2.303k_1t + \ln A_0 \quad (1)$$

where C and C_0 are the concentrations of reactants at any time t and at the starting time, respectively, A and A_0 are the corresponding absorbance strengths, respectively, and β is the absorbance coefficient. If the reaction is second order,

$$1/C - 1/C_0 = k_2t \quad \text{or} \quad A_e/(A_e - A) = k_2t + \text{const} \quad (2)$$

where the A and A_e represent the absorbance strength of the 1754 cm^{-1} at any time t and after full cure, respectively. Thus, $(A_e - A)/A_e$ can indirectly represent the concentration of NSOC at time t , k_1 and k_2 are both rate constants.

To minimize the possible errors arising from different extents of contraction of the copolymers with different compositions and other factors, the absorption peak of the benzene ring at 1606 cm^{-1} in epoxy E-51, which remains unchanged during the reaction, is used as a reference. In this way, kinetic curves of the reactions occurring in the pure epoxy resin and in pure NSOC can be obtained and are shown in Figures 4 and 5, respectively. Although the number of plots in Figure 5(a) is somewhat small, we think it can clearly show the relationship between concentrations of reactants and the reaction time. Also, the activation energy is an approximate value due to the complexity of the polymerization reaction of NSOC. It can be seen that curing of the pure epoxy resin proceeds via a first-order reaction with an activation energy of 62.0 kJ/mol , whereas the reaction in pure NSOC is second order with an activation energy of 121.3 kJ/mol . The difference of the reaction orders can be explained by the above discussion of the polymerization mechanisms. The polymerization of NSOC is more complex than that of pure epoxy resin. The latter

Table II Kinetic Parameters from IR Spectrum

	Temp (°C)			
	110	130	140	150
k				
E51 min^{-1}	9.45×10^{-4}	2.91×10^{-3}	4.57×10^{-3}	5.82×10^{-3}
NSOC $\text{mol}^{-1}\text{min}^{-1}$	0.31	0.80	1.88	4.45
E_a				
E51		62.0 kJ/mol		
NSOC		121.3 kJ/mol		
k_0				
E51		$4.01 \times 10^5 \text{ mol}^{-1}\text{min}^{-1}$		
NSOC		$4.09 \times 10^{15} \text{ mol}^{-1}\text{min}^{-1}$		
n				
E51		1		
NSOC		2		

Table III Data of IR Absorption Peak of Samples N_{00} , N_{10} , and N_{21}

N_{00}				N_{10}				N_{21}			
Before Polymerization		After Polymerization		Before Polymerization		After Polymerization		Before Polymerization		After Polymerization	
Wavenumber (cm^{-1})	Absorption Degree	Wavenumber (cm^{-1})	Absorption Degree	Wavenumber (cm^{-1})	Absorption Degree	Wavenumber (cm^{-1})	Absorption Degree	Wavenumber (cm^{-1})	Absorption Degree	Wavenumber (cm^{-1})	Absorption Degree
915	1.50			915	1.25			915	1.77		
938	1.04			937	1.02			939	1.27		
1035	2.19	1033	1.08	1035	1.52	1034	1.23	1033	3.10	1033	2.29
										1014	2.28
1108	1.19	1105	0.77	1108	1.20	1104	0.93	1112	1.82	1103	2.19
				1146	1.18	1144	0.86	1146	1.78	1142	2.05
1182	2.15	1183	1.08	1184	1.54	1183	1.22	1184	2.83	1183	2.42
										1232	2.64
1298	1.72	1293	0.82	1297	1.39	1294	0.87	1298	2.03	1293	1.74
1608	1.74	1606	0.80	1607	1.41	1606	0.86	1608	1.94	1606	1.46
						1754	0.78			1739	0.73
						1819	0.58			1821	0.50
3123				3125				3234			
≈ 3216	0.74			≈ 3230	0.71			≈ 3249	0.79		
3489	0.76	3515	0.57	3491	0.77	3530	0.64	3477	0.90	3516	0.75

reacts through a simple ring-opening polymerization and is a first-order reaction, whereas the former does not polymerize directly; it decomposed first before further polymerization (of SOC I) take places. The whole reaction depends on the decomposition reaction and polymerization of SOC I and some potential unknown factors, so it is reasonable that it undergoes via second order.

If it is assumed that the apparent activation energy of the copolymerization reaction can be estimated from the activation energies of each of the individual reactions, then the activation energy of the reaction of the epoxy copolymers should be greater than that of the pure epoxy resin. However, the experimental results showed that the activation energies were in the order: $N_{10} > N_{00} > N_{21} > N_{25}$. This may be due to the shrinkage in volume during curing. The shrinkage in volume during curing would freeze a portion of the volume, leading to more holes or free volume within the resin. In contrast, if the volume of the resin expands during curing, there would be less free volume. With increasing amounts of NSOC in the copolymer, the free volume would decrease, thus increasing the probability of collisions between active centers and cyclic monomers and resulting in lower activation energy.

Molecular Structure of Epoxy Copolymer

In the infrared spectra (detailed data is shown in Table III), an absorption peak at 3300–3500 cm^{-1} is observed, which is ascribed to the lipid amine but not the tertiary amine. In this copolymerization reaction, $\text{BF}_3\text{NH}_2\text{C}_2\text{H}_5$ catalyzes the polymerization in the form $\text{C}_2\text{H}_5\text{NH}_2$, $\text{H}(\text{BF}_3\text{NHC}_2\text{H}_5)$, or $\text{H}(\text{BF}_3\text{OH})$ (in the presence of water). For sample N_{21} , before copolymerization, a peak is present at 3234–3249 cm^{-1} ; after reac-

tion, the amine becomes $\begin{array}{c} \text{—N—} \\ | \\ \text{C}_2\text{H}_5 \end{array}$ or $\begin{array}{c} \text{—NH—} \\ | \\ \text{C}_2\text{H}_5 \end{array}$.

The peak at 3234–3249 cm^{-1} disappears, showing that the amine is tertiary with a few secondary amines contained in the copolymer network.

Comparison between the infrared spectra of samples with different polymerization times suggests that hydrogen bonds decompose during copolymerization: the positions of the —OH vibration peaks of samples N_{00} , N_{10} , and N_{21} before and after copolymerization were at 3488–3515 and 3476–3516 cm^{-1} , respectively. Because of steric effects, the formation of hydrogen bonds is not possible in the copolymers.

Ether bonds form the joints in the E51-NSOC copolymers. The peak at 1244 cm^{-1} corresponds to the absorption of benzene ether and the peak at

1033 cm^{-1} corresponds to the absorption of lipid C—O in the pure epoxy resin. Peaks at 1183 and 1293 cm^{-1} are characteristic of the pure epoxy resin.

It is possible to estimate the length of a copolymer sequence from the intensity of the peak at 1142 cm^{-1} , which corresponds to the joint bond in the copolymer. As this peak increases in intensity, the joints in the E51-NSOC copolymer become more and the copolymer sequences decrease in length. Taking the peak at 1606 cm^{-1} as a reference, ratios of the peak at 1142 cm^{-1} can be calculated to produce values of the relative sequence lengths for copolymers of different compositions. For example, for N_{21} and N_{10} , the ratio is calculated to be 1.3 : 1, which is much lower than the theoretical value of 2.08 : 1, indicating that N_{21} with a high content of NSOC has a longer copolymerization sequence than N_{10} .

Apparent Kinetics of Copolymerization

The rate equation for the ring-opening copolymerization reaction can be expressed as

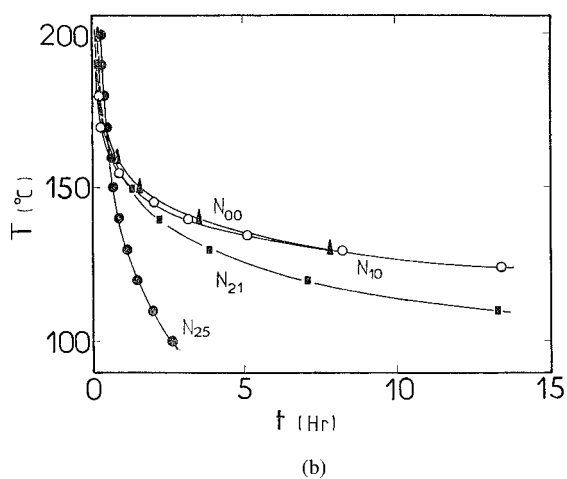
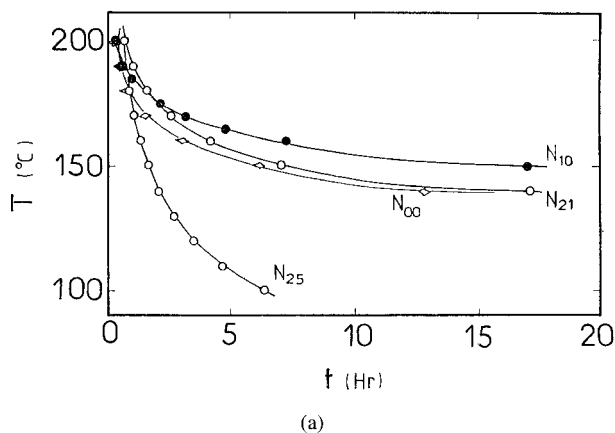


Figure 6 The relationship between curing temperature and time requiring 99% (a) and 90% (b) curing degree of epoxy resin copolymer system.

$$\ln(d\alpha/dt) = \ln k_0 - E_a/RT + n \ln(1 - \alpha)^n \quad (3)$$

where α is the extent of the reaction, k_0 is the frequency factor, n is the order of the reaction, E_a is the activation energy, t is the time, and R is the gas constant. The parameter α can be calculated from the relationship $\alpha = -H_{\text{part}}/H$ and k_0 , E_a , and n can be obtained from linear regression analysis of DSC measurements. Table II lists the results obtained from DSC measurements at a heating rate of 5°C/min. Figure 6 shows the relationship between curing temperature and the time required to produce 99 and 90% cure in the epoxy copolymers. Figure 7 shows the relationship between storage temperature and the time required to reach 1 and 5% cure. The results indicate that if the resin needs to be fully cured within 2 h, the curing temperatures for samples N_{00} , N_{10} , N_{21} , and N_{25} must be greater than 174, 176, 166, and 144°C, respectively. To store a mixture of epoxy resin, NSOC, and hardener for at least 100 h with only 1% reaction, the storage temperature must be below 35.5, 51, and 14.5°C for samples N_{00} , N_{10} , and N_{21} , respectively. However, sample N_{25} would reach an extent of 1% reaction after only 1 h, even under refrigeration.

For isothermal processes, a kinetic equation can be obtained from the integral of eq. (3):

$$1/(1 - \alpha)^{n-1} - 1 = (n - 1)[k_0 \exp(E_a/RT)]t \quad (4)$$

Specifically,

$$\begin{aligned} \text{for } N_{00} \quad & 1/(1 - \alpha)^{0.85} - 1 = 4.19 \\ & \times 10^{10} \exp(-12,647/T)t \quad (5) \end{aligned}$$

$$\begin{aligned} \text{for } N_{10} \quad & 1/(1 - \alpha)^{1.08} - 1 = 3.04 \\ & \times 10^{13} \exp(-15,351/T)t \quad (6) \end{aligned}$$

$$\begin{aligned} \text{for } N_{21} \quad & 1/(1 - \alpha)^{0.65} - 1 = 3.91 \\ & \times 10^6 \exp(-9259/T)t \quad (7) \end{aligned}$$

$$\begin{aligned} \text{for } N_{25} \quad & 1/(1 - \alpha)^{0.16} - 1 = 4.71 \\ & \times 10^0 \exp(-4152/T)t \quad (8) \end{aligned}$$

Thus for N_{21} to obtain a 20% degree of cure in 2 h, a minimum reaction temperature of 133°C is needed.

In conclusion, the copolymerization behavior and the apparent cure kinetics of epoxy resin E51 containing the expanding monomer NSOC was investigated. The copolymerization process was analyzed on the basis of the former studies, and some kinetic relationships are obtained, which we believe are useful for the preparation, storage, and application of the copolymer system.

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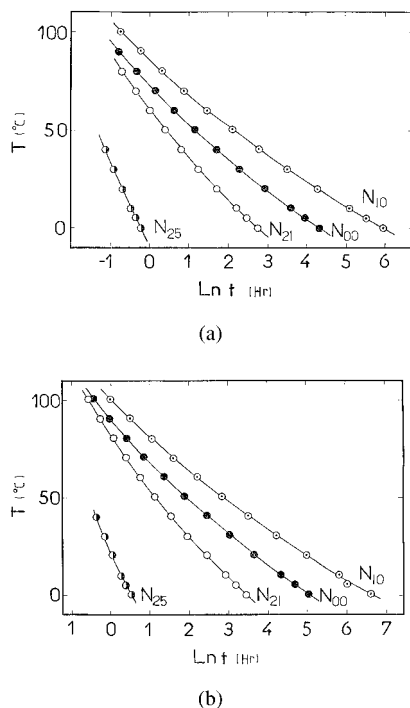


Figure 7 The relationship of storage temperature and time to reach 1% (a) and 5% (b) curing degree.