Polymer Bulletin 48, 111–118 (2002)

Polymer Bulletin

Synthesis and curing of rod-like epoxies with alkoxy groups as flexible side chain

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Received: 15 January 2002 / Accepted: 4 March 2002

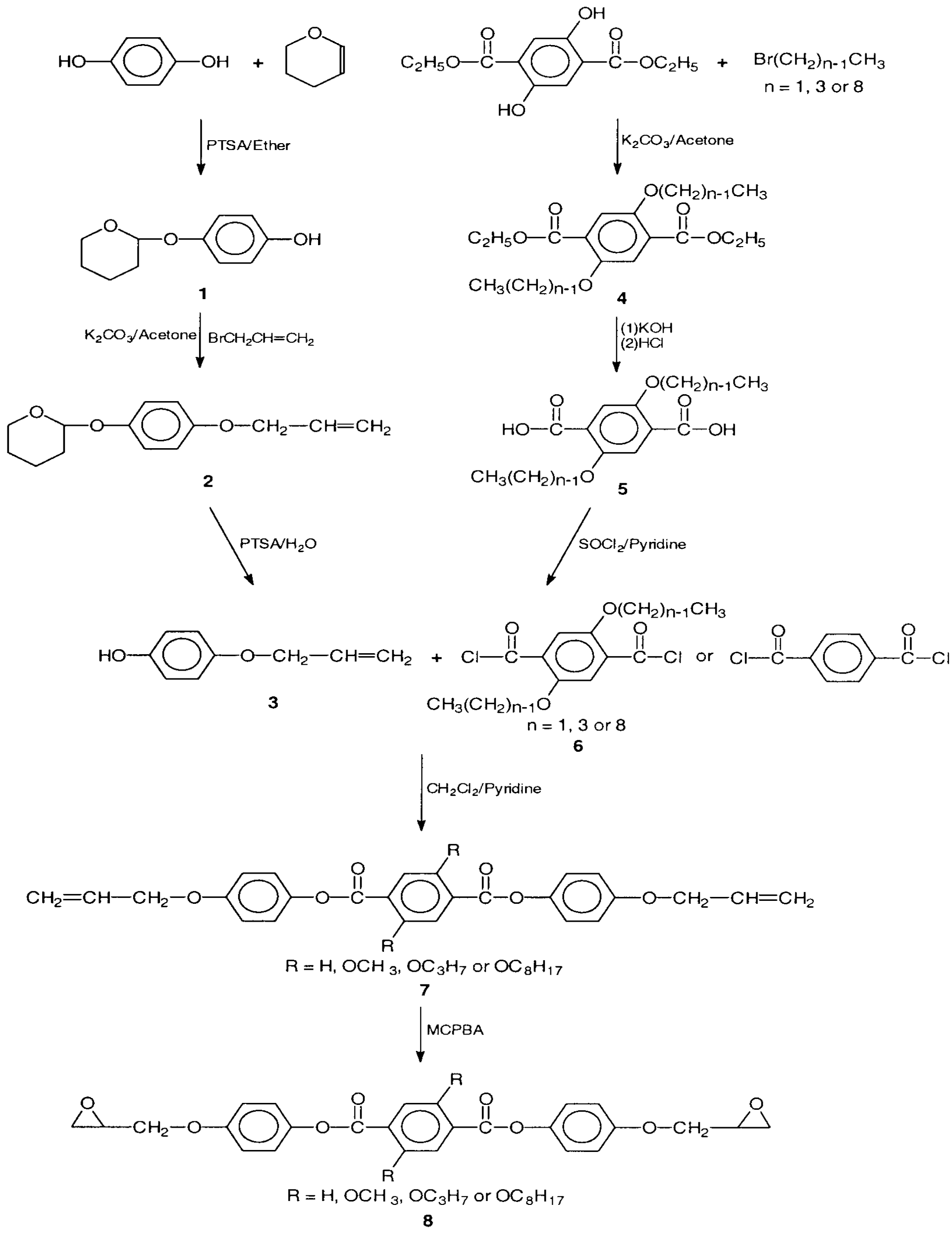
Summary

A series of aromatic diepoxides consisting of rigid ester unit with different lengths of flexible alkoxy side groups (R = H, OCH_3, OC_3H_7, and OC_8H_{17}) were synthesized, and their thermal and cure behavior with aromatic diamine were investigated by using a DSC. The values of melting temperatures for the epoxy monomers ranged from 65 to 221°C depending upon the length of side groups. Cure kinetics of an epoxy/4,4'-diaminodiphenylmethane (DDM) system with two different side groups (R = OC_3H_7 and OC_8H_{17}) forming homogeneous mixture was examined using a multi-temperature scan method, developed by Ozawa and Kissinger, in order to determine the activation energy (E) and the frequency factor (A). The epoxy monomer having longer side group showed smaller E and larger A, indicating that the introduction of the long flexible side group could accelerate the cure reaction of rod-like epoxy.

Introduction

During the past decade, a large number of aromatic epoxy resins have been reported such as aromatic diepoxides with substituents in a central aromatic unit [1, 2], and with flexible spacers in the main chain [3-6]. Incorporating rigid rod-like structure into epoxy network could induce unique properties such as anisotropic orientation, high modulus and tensile strength, and low coefficient of thermal expansion [7]. However, rod-like epoxy monomers have too high melting temperature to conduct thermal curing due to their structural rigidity [8]. In principle the structure of stiff-chain polymers can be modified by the two ways: insertions of flexible spacer such as polyalkylene unit in the main chain, and appending of flexible side chains onto the stiff main chains. Especially, the flexible side chains, which may act like a bound solvent, could be improved solubility and lower melting temperature without reducing the rigidity of the main chain due to substantial gain in entropy on dissolving or melting [9]. Similarly, as in aromatic epoxy monomer, the stiff-chain with the rod-like nature experiences lack of versatility in its conformation, whereas introduction of flexible side chain may assume a vast number of conformations in the melt or solution.

In this study, we have synthesized and characterized the diepoxy monomers consisting of rigid triad aromatic ester unit having alkoxy groups as the flexible side chain. In addition, cure kinetics of the newly synthesized epoxy monomers with diamines was investigated to understand the curing process of the rigid epoxy monomers having the flexible side groups.



Scheme 1. Synthetic route to aromatic diepoxides with flexible side groups

Experimental

Synthetic route to epoxy monomers is shown in Scheme 1. Since the synthetic procedures used to prepare the epoxy monomers were essentially same, one representative epoxy with R=OC_8H_{17} is given in the following.

Synthesis of 4-Allyloxyphenol (3)

Compound **3** was prepared using a modification of a literature procedure [10]. Yield was 98%. IR (KBr pellet, cm^{-1}): 3081 (aromatic =C-H, st), 2984 (aliphatic C-H, st), 1660, 1600 (aromatic C=C, st), 1425 (aliphatic CH_2, bend), 1230, 1025, 1005 (C-O, st). ^{1}H NMR ($CDCl_3$, δ in ppm): 7.06 (1H, s, OH), 6.77 (4H, s, Ar-CH), 5.93-6.07 (1H, m, $C\underline{H}=CH_2$), 5.19-5.40 (2H, t, $CH=C\underline{H}_2$), 4.44 (2H, d, $OC\underline{H}_2CH=$).

Synthesis of 2,5-Dioctyloxyterephthalic acid (5)

Compound **5** was prepared according to details given in the literature [11]. Yield was 99%. IR (KBr pellet, cm^{-1}): 3100 (O-H, st), 3050 (aromatic =C-H, st), 2930, 2918 (aliphatic C-H, st), 1680 (C=O, st), 1504 (aromatic C=C, st), 1450 (aliphatic CH_2 or CH_3, bend) 1379 (aliphatic CH_3, bend), 1249, 1220, 1033 (C-O, st). ^{1}H NMR ($CDCl_3$, δ in ppm): 7.92 (2H, s, Ar-CH), 4.13 (4H, t, $OC\underline{H}_2$), 1.90-1.76 (4H, m, $OCH_2C\underline{H}_2$), 1.53-1.42 (2H, m, $C\underline{H}_2CH_3$), 1.19 (16H, s, $(C\underline{H}_2)_5$), 0.86-0.79 (6H, t, $C\underline{H}_3$).

Synthesis of Di(4-allyloxyphenylene) 2,5-dioctyloxyterephthalate (7)

Into 30 mL of $SOCl_2$ was dissolved compound **5** (0.42 g, 1.0 mmol). After addition of a drop of pyridine, the solution was refluxed with stirring for 4 hrs. The excess $SOCl_2$ was removed by distillation under a reduced pressure. Without further purification, the obtained diacid dichloride **6** was dissolved into a mixture of 30 mL of dichloromethane with a drop of pyridine. To this solution was added dropwise a solution of compound **3** (0.33 g, 2.2 mmol) in 3 mL of dichloroethane at 0°C for 2 hrs with a vigorous stirring. The reaction mixture was then poured into a large excess of 0.2 M HCl. The precipitate formed was washed thoroughly with water. The crude product was further purified by means of column chromatography using silica gel as the stationary phase and a mixture of ethylacetate and hexane (9:1 v/v) as an eluent. Yield was 73%. IR (KBr pellet, cm^{-1}): 3020 (aromatic =C-H), 2840 (aliphatic C-H, st), 1740, 1681 (C=O, st), 1605, 1505 (aromatic C=C, st), 1450 (aliphatic CH_2, bend), 1245, 1195, 1110, 1025 (C-O, st). ^{1}H NMR ($CDCl_3$, δ in ppm): 7.47 (2H, s, Ar-CH), 7.05-7.09 (4H, d, Ar-CH), 6.86-6.90 (4H, d, Ar-CH), 5.93-6.08 (1H, m, $C\underline{H}=CH_2$), 5.20-5.41 ($CH=C\underline{H}_2$), 4.48 (2H, d, $OC\underline{H}_2CH=$), 4.01 (4H, t, $OC\underline{H}_2CH_2$), 1.71-1.79 (4H, m, $OCH_2C\underline{H}_2$), 1.36-1.44 (2H, m, $C\underline{H}_2CH_3$), 1.17 (20H, s, $(C\underline{H}_2)_5$), 0.75-0.82 (6H, t, $C\underline{H}_3$).

Synthesis of Di[4-(2,3-epoxypropoxy)phenylene] 2,5-dioctyloxyterephthalate (8)

Into a solution of compound **7** (0.14 g, 0.20 mmol) in 5 mL of chloroform was added a solution of m-chloroperoxybenzoic acid (MCPBA) (0.14 g, 0.80 mmol) in 5 mL of chloroform with continuous stirring. The mixture was then refluxed 48 hrs. After cooling and subsequent addition of 10 mL of petroleum ether, the mixture was filtered. The filtrate was sequentially washed with a 5% aqueous solution of $NaHSO_4$, a 5% aqueous solution of $NaHCO_3$, and a 30% aqueous solution of NaCl. The solution was dried over $MgSO_4$, filtered and evaporated. The crude product was recrystallized from cyclohexane. Yield was 92%. IR (KBr pellet, cm^{-1}): 3410 (O-H, st), 3025 (aromatic =C-H, st), 2825 (aliphatic C-H, st), 1720, 1681 (C=O, st), 1610, 1505 (aromatic C=C, st), 1450 (aliphatic CH_2, bend), 1250, 1210, 1110, 1020 (C-O, st), 910 (epoxy C-O, st). ^1H NMR ($CDCl_3$, δ in ppm): 7.54 (2H, s, Ar-CH), 7.14 (4H, d, Ar-CH), 6.98 (4H, d, Ar-CH), 4.24 (2H, d, epoxy-$OC\underline{H}_aCH_b$), 3.96 (4H, t, $OC\underline{H}_2CH_2$), 3.93 (2H, m, epoxy-$OCH_aC\underline{H}_b$), 3.38 (2H, m, epoxy-$OC\underline{H}$), 2.93 (2H, t, $CHC\underline{H}_aH_bO$), 2.77 (21H, t, $CHCH_a\underline{H}_bO$), 1.76-1.86 (4H, m, $OCH_2C\underline{H}_2$), 1.11-1.44 (20H, m, $(C\underline{H}_2)_5$), 0.86 (6H, t, CH_3).

Characterization

The structures of epoxy monomers were determined using a Jasco 300E FT/IR and a Bruker AMX 200 MHz NMR spectrometer. Thermal analyses were performed by a du Pont TA910 DSC at heating rates of 5, 10, 20, 30 and 40°C/min under a nitrogen atmosphere. Optical texture was examined by a polarized microscope (Zeiss, Jenapol) equipped with a heating stage (Mettler FP82H).

Results and discussion

Synthesis and thermal properties of diepoxy monomers

The molecular structures of the diepoxy monomers were evaluated by means of FT/IR and NMR techniques. The results from IR and NMR spectroscopies are consistent with the expected structure as shown in Figure 1.

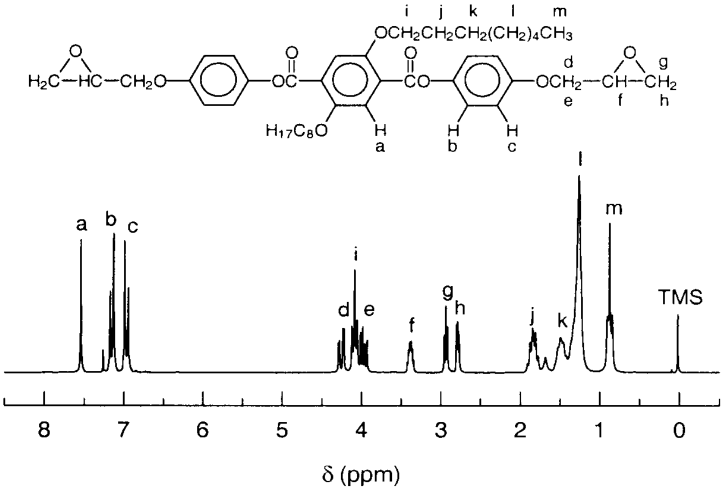


Figure 1. ^1H NMR spectrum of diepoxy monomer with R = OC_8H_{17}.

Since compounds **7** as well as compounds **8** having triad aromatic ester mesogenic unit can be used as the monomer of liquid crystalline thermosets, thermal and mesomorphic properties of the divinyl and diepoxy monomers with different lengths of flexible side chain were compared. In Figure 2, DSC thermograms of the monomers are displayed. On the DSC heating scan, the divinyl monomer with R = H and the diepoxy monomer with R = OC_8H_{17} showed melting and isotropization peaks, whereas the rest of monomers showed only the melting transition. The diepoxy monomer with R = H also could form a mesophase, but its isotropization temperature (T_i) could not determined due to thermal degradation occurred below T_i. Note that the value of T_i for the divinyl monomer with R = H was of 235°C. The mesomorphic regions were confirmed by the optical microscopic observation of birefringence in melt state. These results mean that the formation of mesophase for the monomers is greatly influenced by the length of flexible side groups.

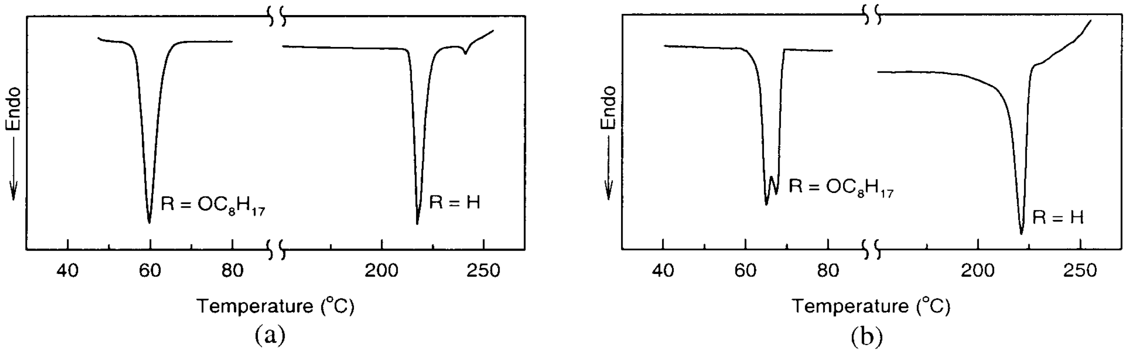


Figure 2. DSC thermograms for divinyl (a) and diepoxy (b) compounds (heating rate: 2°C/min).

Table 1 contains the melting temperatures (T_m) and the changes of enthalpy (ΔH_m) and entropy (ΔS_m) for melting obtained from DSC thermograms. In the table, T_ms of diepoxy monomers decreased as the length of side chain increased, whereas ΔH_m and ΔS_m increased until the carbon number is not quite high. Taking into account of the trend of T_m for monomers, increase in the length of side chain leads to large increase in entropy due to versatility in its conformation overcoming some increase in enthalpy.

Table 1. Thermal transition temperatures of diepoxy compounds

R	T_m(°C)	ΔH_m (kJ/mol)	ΔS_m (J/mol·K)	T_i(°C)
H	221	12.0	24.4	a
OCH_3	201	47.6	101	b
OC_3H_7	145	51.4	123	b
OC_8H_{17}	65.0	33.0	97.2	67.4

[a]Thermal degradation occurred before isotropization. [b]The diepoxy compound was non-liquid crystalline.

Reaction between epoxy monomer and aromatic diamine

An epoxy monomer with R = OC_8H_{17} showed good solubility in $CHCl_3$ and the lowest melting temperature among the epoxy monomers obtained. Thus, reactivity of the epoxy monomer with R = OC_8H_{17} was examined with three different aromatic diamines; 4,4'-diaminodiphenylmethane (DDM), 1,4-phenylenediaminine (PDA), and 4,4'-diamino-diphenylsulfone (DDS). Mixtures for curing were obtained by dissolving stoichiometric amounts of the epoxy monomer and curing agent in $CHCl_3$, and removing the solvent under reduced pressure at room temperature. Figure 3 displays DSC thermograms of unreacted mixtures during heating. The mixture of the epoxy monomer shows a single melting with DDM but a double melting with DDS and PDA. The single melting transition implies that the mixture is considered to be homogeneous. Therefore, DDM was taken as curing agent to study the cure of the epoxy monomer.

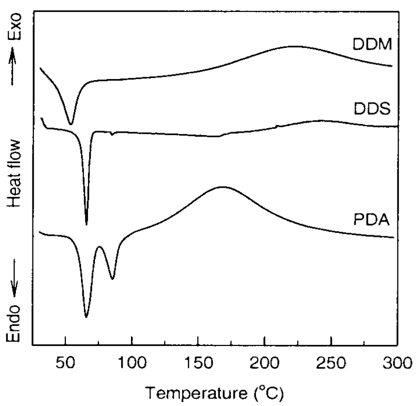


Figure 3. DSC thermograms for mixtures of epoxy monomer with R = OC_8H_{17} and different diamines (heating rate: 10°C/min).

Curing kinetics of epoxy monomers with DDM

Cure kinetics of epoxy monomers with flexible side chains was investigated to understand the cure process by means of the DSC technique [12-17]. We have used a common muti-temperature scan method, namely Ozawa and Kissinger method, which allows estimation of the activation energy (E) and the frequency factor (A). Advantages of these methods include simplicity and accuracy for various types of cure reactions [18].

Under the assumption that chemical conversion at the peak exotherm temperature is constant and independent of heating rates, the following relationship between the activation energy, the heating rate, and the peak exotherm temperature were derived on the basis of the work of Ozawa [19]. The equation for the activation energy (E) obtained is

$$E = -\frac{R}{1.502}\frac{\Delta \ln q}{\Delta(1/T_p)} \qquad (1)$$

where q is the heating rate and T_p is the peak temperature. The expressions derived by Kissinger [20] for the activation energy (E) and frequency factor (A) are

$$E = -R\frac{d[\ln(q/T_p^{\,2})]}{d(1/T_p)} \tag{2}$$

and

$$A = \frac{qE\exp(E/RT_p)}{RT_p^{\,2}} \tag{3}$$

DSC scans of mixtures were made for two different lengths of side chains (R = OC_3H_7, and OC_8H_{17}) at different heating rates (5, 10, 20, 30, and 40°C/min) and presented in Figures 4 and 5. In the figures the epoxy monomers with R = OC_3H_7 and OC_8H_{17} show a single melting transition at ~130°C and ~50°C, respectively. The exothermic cure reaction was followed by the melting transition, and the exothermic peak temperature increases from ~150°C to ~210°C for R = OC_3H_7 and from ~150°C to ~220°C for R = OC_8H_{17}, with increase of the heating rate.

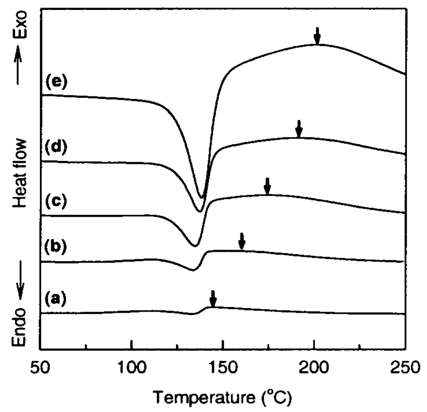


Figure 4. DSC thermograms for a mixture of epoxy with R = OC_3H_7 and DDM at different DSC heating rates: (a) 5, (b) 10, (c) 20, (d) 30, and (e) 40 °C/min.

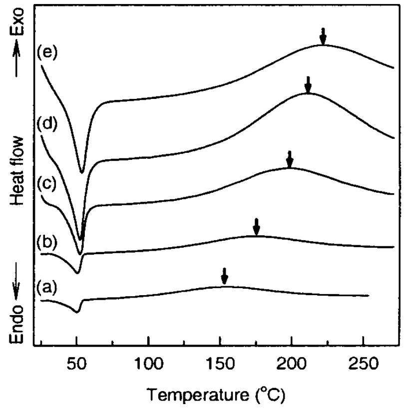


Figure 5. DSC thermograms for a mixture of epoxy with R = OC_8H_{17} and DDM at different DSC heating rates: (a) 5, (b) 10, (c) 20, (d) 30, and (e) 40 °C/min.

Table 2. Results of dynamic DSC studies for the epoxy/DDM system at different heating rates

DSC heating rate (°C/min)	R = OC_3H_7		R = OC_8H_{17}	
	T_{endo} (°C)	T_{exo} (°C)	T_{endo} (°C)	T_{exo} (°C)
5	134	145	50.1	151
10	134	159	50.6	173
20	135	176	52.5	199
30	137	198	52.2	210
40	138	205	53.6	219

In Table 2, transition temperatures obtained from the dynamic DSC scans are summarized. On the base of experimental results from the dynamic DSC study at multiple heating rates, the activation energy (E) and the frequency factor (A) were obtained by using Equations 1-3. In case of Ozawa method, a plot for $1/T_p \times 10^3$ *vs.* $Ln\ q$ was used to determine E from the slope [Equation 1] and A [Equation 3]. For Kissinger method, a plot for $-ln(q/T_p^2)$ *vs.* $1/T_p \times 10^3$ was used to estimate E from the slope [Equation 1] and A [Equation 3]. Table 3 has all the kinetic values obtained. Interestingly, E decreases and A increases as the side chain length becomes longer. This means that the curing reaction might occur more readily when the epoxy has the longer side chain.

Table 3. The activation energy and the frequency factor for the epoxy/DDM system from DSC experiments

R	Ozawa method		Kissinger method	
	E ($kJ \cdot mol^{-1}$)	A (s^{-1})	E ($kJ \cdot mol^{-1}$)	A (s^{-1})
OC_3H_7	53.4	2.97×10^3	47.5	2.65×10^3
OC_8H_{17}	50.7	8.87×10^2	44.7	7.69×10^2

Acknowledgements.

This paper was supported in 2000 by Research Fund, Kumoh National University of Technology.

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