Characterization of the Cure of Some Epoxides and Their Sulphur-Containing Analogues with Hexahydrophthalic Anhydride by DSC and TGA

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ABSTRACT: A series of curing reactions of epoxides and different substituted (1,3-oxothiolane-2-thione)s with hexahydrophthalic anhydride in the presence of 2,4,6-tri(dimethylaminomethyl)phenol have been characterized by nonisothermal and isothermal differential scanning calorimetry (DSC). The DSC method was employed to investigate the thermal behavior of the systems cured and to evaluate the short-term stability of one-pot compositions. It was found that the cure processes of novel sulphur analogues of epoxides were generally described through lower (absolute) values of enthalpy of curing; on the other hand, the cure onset and the peak maximum temperatures were considerably higher. To evaluate the thermal stability of the networks obtained, thermogravimetric analysis (TGA) was applied. Its use allowed us to observe that derivatives of (1,3-oxothiolane-2-thione)s were thermally more stable that their analogue epoxides (up to 25°C) and the degradation profiles depended on the steric hindrances and interactions introduced by the substituents used. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 451–460, 1998

Key words: epoxy–anhydride cure; (1,3-oxothiolane-2-thione)s; differential scanning calorimetry; thermogravimetric analysis

INTRODUCTION

Epoxides are widely used due to their extreme versatility. They can be cured with a number of nucleophilic and electrophilic reagents. Amongst the curing agents of greatest technological importance are polycarboxylic acid anhydrites, amines, and imidazoles.[1] The curing reactions have been investigated by various techniques, such as differential scanning calorimetry (DSC),[2–19] Fourier transform infrared (FTIR) spectroscopy,[20–24] high-performance liquid chromatography (HPLC),[25,26] and nuclear magnetic resonance (NMR)[12,13,15,20] and the main mechanism is believed to be known. It comprises formation of ester linkages via an ionic reaction (Scheme 1).[27] If tertiary amine is used as catalyst, the curing reaction proceeds also via an ionic route (Scheme 2).[27]

Relatively less work has been carried out on sulphur-containing compounds. There is a series of articles by Charmas and Podkościelny[28–34] on thioetherglycidyl resins, which were synthesized by condensation of di(mercaptomethyl)naphthalenes with epichlorohydrin. It was found that the thioderivatives can be cured by means of common curatives used for epoxy resins, yielding products with often better properties in comparison to those of the cured resins from Bisphenol A. The cure process itself has not, however, been a subject of detailed investigation.

Derivatives of (1,3-oxothiolane-2-thione) are of interest as initial compounds; they can be further cured to give novel resins with some valuable properties (for example, high reactivity in subambient temperatures[35–39]), which are known as a
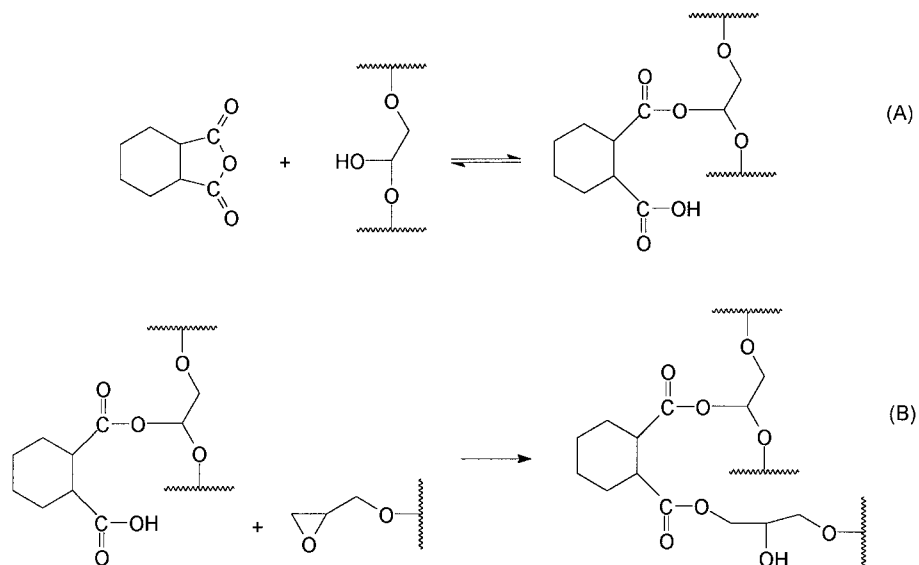
Scheme 1

result of the thio-structures introduction into the polymer chain.

This study investigates the curing reactions of several epoxides and their sulphur analogues with hexahydrophthalic anhydride (HHPA) as curing agent, and the thermal stability of some of the products. In this way, it is hoped to demonstrate that (1,3-oxothiolane-2-thione)s can be cured, giving products with some superior properties over commonly used epoxides.

EXPERIMENTAL

Materials

Initial epoxy compounds, carbon disulphide, diethyl ether, and Al_2O_3 were commercial products

from Merck. Carbon disulphide was purified by distillation prior to use. Sulphur-containing derivatives have been obtained by the reaction of epoxides with carbon disulphide[40] (Scheme 3).

The reaction has been carried out at the boiling temperature of diethyl ether used as solvent and in the presence of Al_2O_3 as catalyst. (1,3-Oxothiolane-2-thione) as a main product, and the oligomer can be then easy separated on short silicagel column. A series of differently substituted (1,3-oxothiolane-2-thione)s, as presented in Table I, have been obtained.

Technique

Molecular weight was determined by gel permeation chromatography (GPC) performed at 25°C on
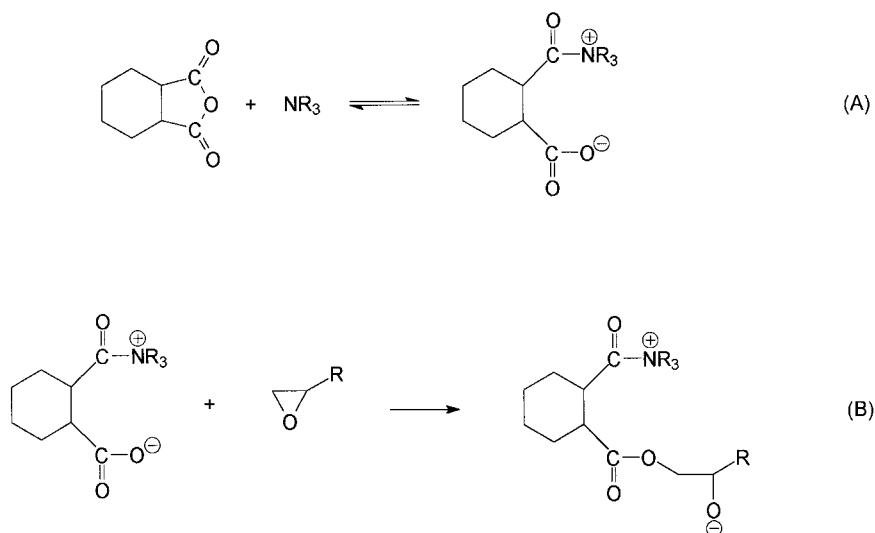
Scheme 2

Scheme 3
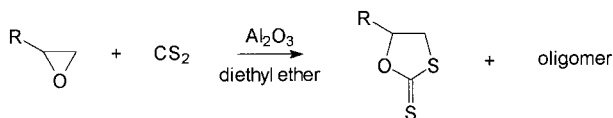
a Knauer GPC System with a ultraviolet (UV) detector, with a column system for oligomers as follows: $2 \times$ PL-gel (300×7.5 mm) with a grain size of 3 mm and a MIXED-E pore. Tetrahydrofuran dried over metalic sodium was used as eluent at a flow rate of 0.8 cm³/min; the sample concentration was ~1 mg/cm³. Polystyrene standards (Waters) were used to construct a calibration curve. GPC data were processed on a CHROMA data processor to calculate average molecular weights, M_n and M_w, as well as polydispersity, M_w/M_n.

The DSC data were recorded on a Netzsch DSC 200, operating in a dynamic or isothermal mode, with the following conditions: sample weight, ~4 mg; heating rate, 10 K/min or $T_{iso} = T_{onset} + 30\%$; atmosphere, argon (30 cm³/min); sealed aluminum pan. The heating rate of 10 K/min was chosen as the best possibility to ensure high resolution of the DSC curves. The calorimeter was

Table I   Description of the Samples Used in the Course of This Work

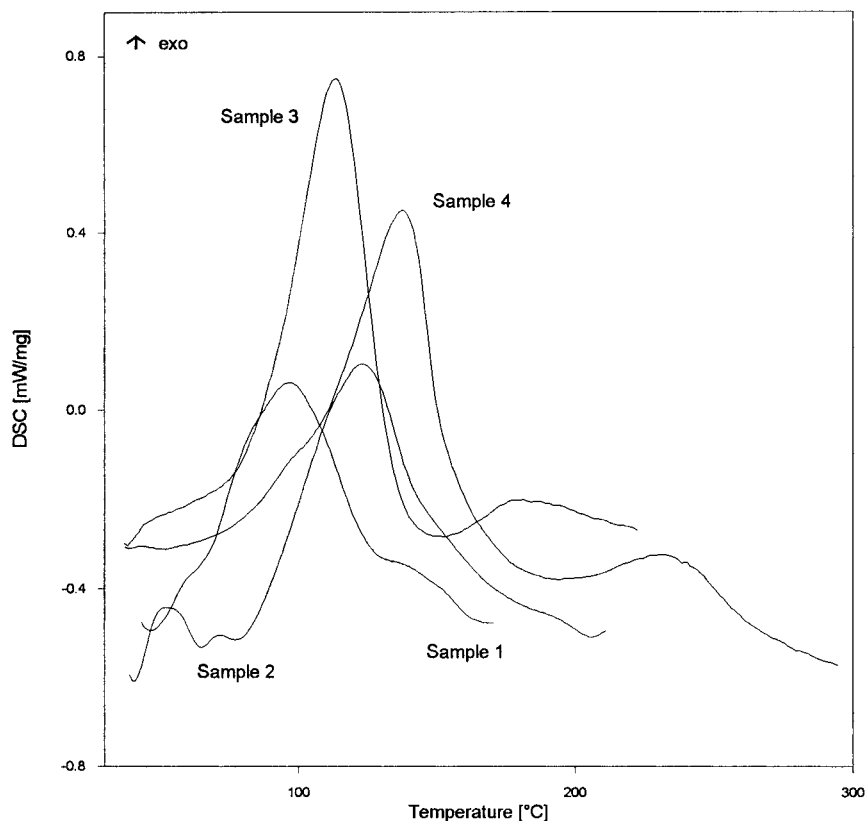|			R
1	1A		CH₃
2	2A		CH₂CH₃
3	3A	3B	CH₂Cl
4	4A		epoxycyclohexane
5	5A	5B	
6	6A		
7	7A		
8	8A		

Figure 1   DSC scans at 10 K/min of samples 1–4.

Table II   DSC Data of the Curing Reaction of Epoxy Compounds

No.	ΔH_c (J/g)	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)
1	171.9	46.1	97.5	163.6
2	195.6	78.1	122.3	205.8
3	215.7	45.0	113.5	221.2
4	241.5	51.4	137.5	293.7
5	306.2	39.5	123.5	256.1
6	152.5	40.2	98.5	153.5
7	324.8	41.2	102.9	160.1
8	360.3	42.2	101.8	263.9

calibrated with an indium standard; an empty aluminium pan was used as a reference.

For thermogravimetric analysis (TGA), a Derivatograph-C thermal analyzer was employed, operating in a dynamic mode at a heating rate of 10 K/min. The conditions were: sample weight, $\sim$ 10 mg; atmosphere, argon; and temperature range, 25–500°C.

Gas chromatography–mass spectroscopy (GC–MS) data of the products of the reaction were collected on a Hewlett-Packard 5890 II gas chromatograph with an MS spectrometer MSD 5971 and a capillary column HP-5 MSD (length, 30 m; diameter, 0.25 mm; and film size, 0.25 mm.

RESULTS AND DISCUSSION

Dynamic Curing DSC

DSC curves of samples 1, 2, 3, and 4 are presented in Figure 1. The thermograms are complex, often displaying several exothermic peaks. Each transition represents partial curing reaction of a certain segment of the system. It can be assumed that curing proceeds first through a scission of bonds, which are easy accessible (that is, there is no steric hindrance in the surrounding area). Then comes the regions of difficult geometrical access. Another factor seriously affecting the process of curing is probably located on the higher architectural levels of the system and may be associated with any difficulties of mass transport (diffusion).

Several interesting dependences have been found on the basis of DSC analysis. All the data are summarized in Table II. The heat of curing (ΔH_c) is increasing with an increase of the molecular weight and the molar volume of the R substit-
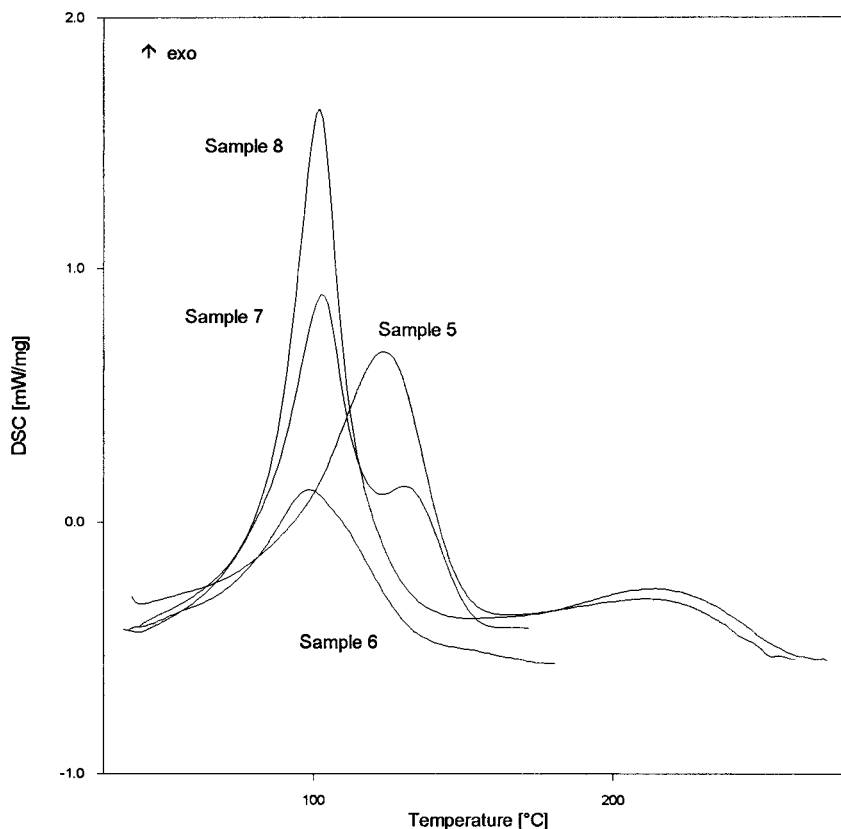

Figure 2   DSC scans at 10 K/min of samples 5–8.

Table III DSC Data of the Curing Reaction of Substituted (1,3-Oxothiolane–2 thione)s

| No.	ΔH_c (J/g)	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)
1A	80.2	78.0	171.2	195.5
2A	101.6	58.4	171.0	198.5
3A/3B	83.9/62.2	57.8/42.2	146.6/85.8	259.7/151.0
4A	192.7	65.7	189.3	215.1
5A/5B	68.9/22.4	44.5/105.5	144.8/151.3	189.0/188.2
6A	131.1	68.1	185.4	249.6
7A	30.9	102.2	194.8	209.8
8A	63.3	140.1	175.8	210.1

uents. Temperature of the peak maximum (T_{max}) is getting higher also in such a way. When $R = C$L, T_{max} lies in between (Fig. 1).

For analogous compounds with the (1,3-oxothiolane-2-thione) group one can observe a complex curing behavior, as shown in Figure 2. There is no distinct correlation between R and ΔH_c (Table III). The peak maximum temperatures changes, being the lowest for the curing reaction of sample 3A. This CL-containing derivative has the lowest ΔH_c and T_{max} among methyl-substituted compounds.

Epoxides with ester linkages (Fig. 3) exhibit a larger heat of cure, except sample 6. T_{max} raises from 97.5°C for sample 1, through 101.8°C for sample 8, up to 137.5°C for sample 4 (epoxycyclohexane). (1,3-Oxothiolane-2-thione) derivatives exhibit clear dependences of ΔH_c and T_{max} during cure. ΔH_c decreases from 192.7 J/g (sample 4A) to 30.9 for sample 7A (Fig. 4). In the same way, T_{max} is getting lower from 194.8°C (sample 7A) to 144.8°C (sample 5A).

In general, derivatives of (1,3-oxothiolane-2-thione)s are characterized through lower ΔH_c than their epoxy precursors. It is connected with lower stress in a five-membered ring, which is
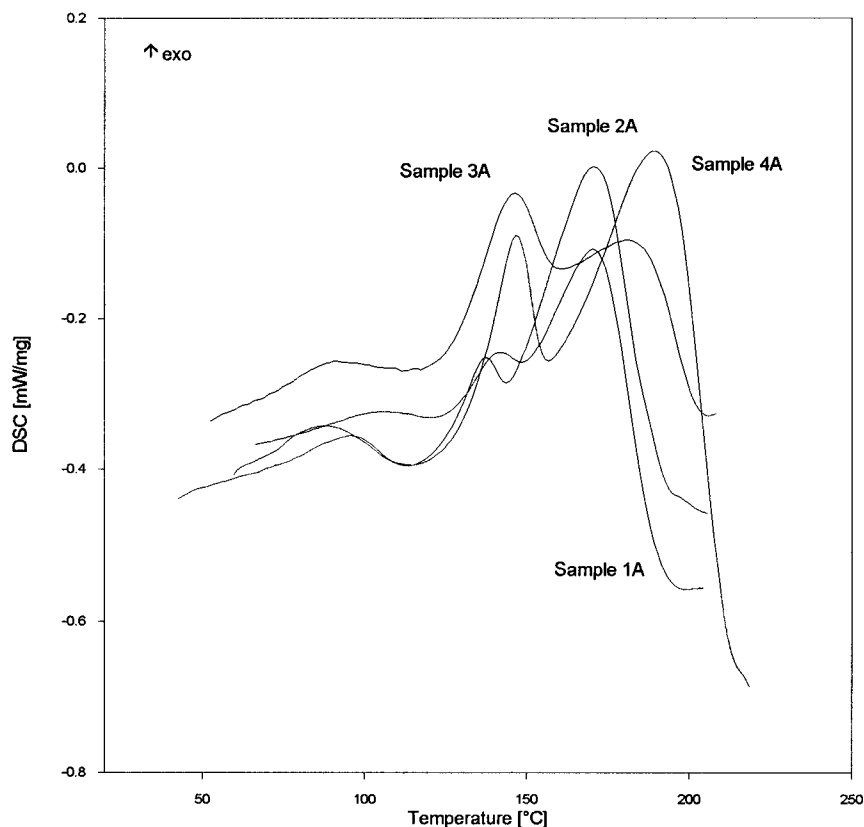
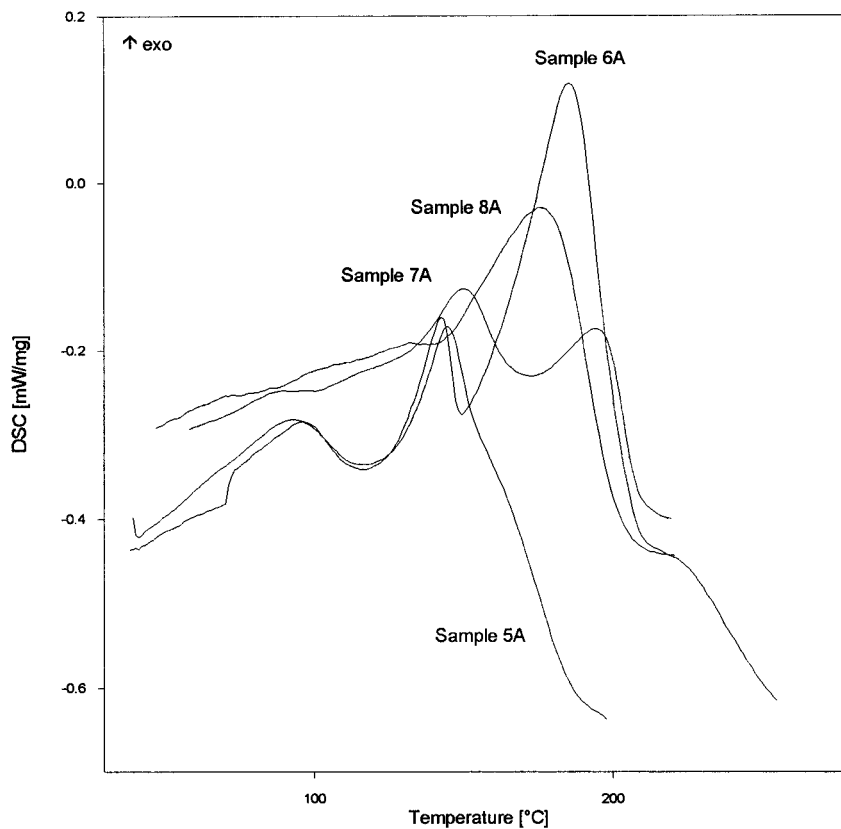**Figure 3** DSC scans at 10 K/min of samples 1A–4A.

Figure 4   DSC scans at 10 K/min of samples 5A–8A.

more stable than the epoxy group with the ring number of 3. The differences are from 1.3 times (sample 4 and 4A) up to nearly 11 times (sample 7 and 7A). On the contrary, the maximum peak temperatures are higher for thio-derivatives, with the greatest discrepancies for samples 7 and 7A (approximately 92°C) and for samples 6 and 6A (approximately 87°C). The thio-systems need a higher cure temperature, as reflected in a shift of the exothermic peak to higher and broader temperature range. The ΔH_c for samples 5, 7, and 8 is considerably higher than for other compounds
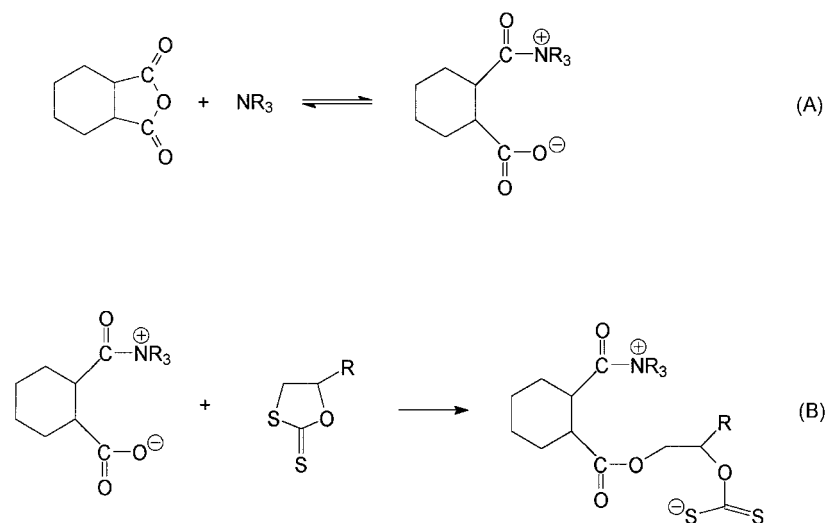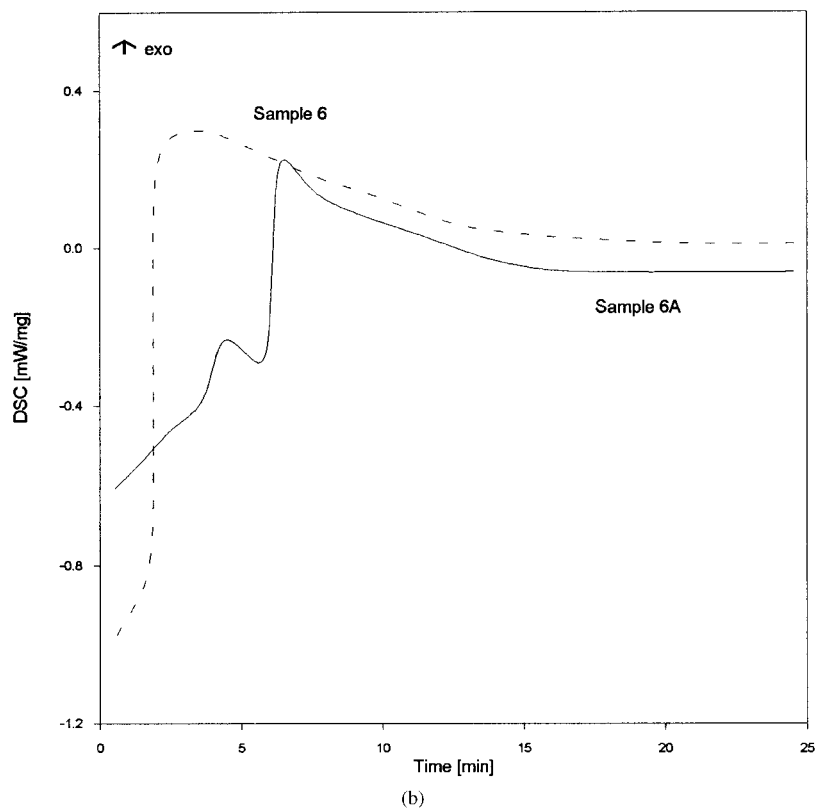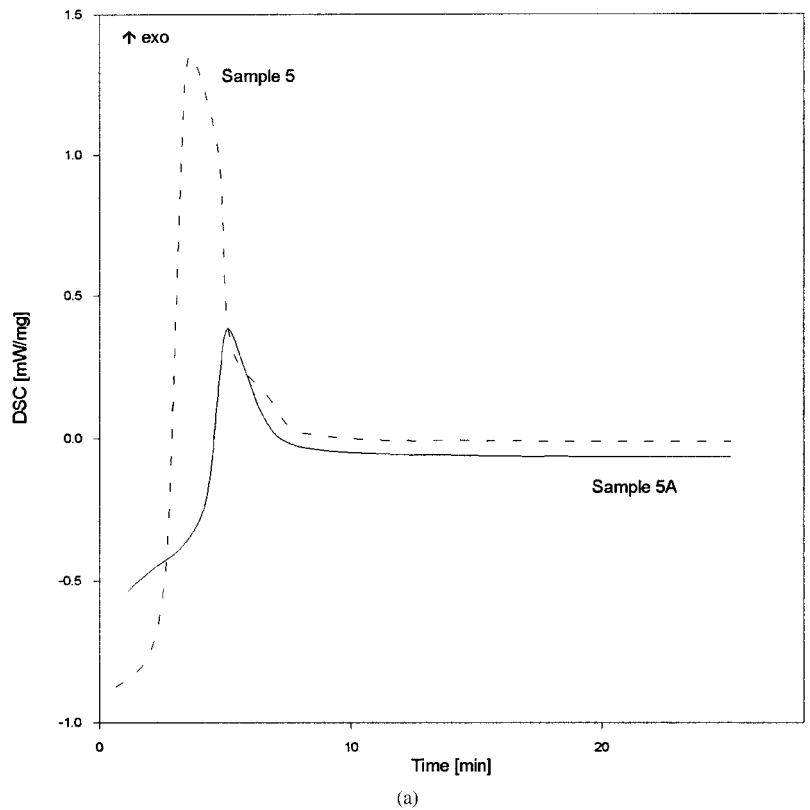

Scheme 4

Figure 5 (a) Isothermic DSC scans of samples 5 and 5A. (b) Isothermic DSC scans of samples 6 and 6A.

due to steric hindrance afforded by a branched alkil or phenyl group. The cure process proceeds probably via an ionic mechanism with a ring-opening reaction (Scheme 4). (1,3-Dioxolane-2-thione)s have ΔH_c and T_{max} even lower than their analogues (1,3-oxothiolane-2-thione)s.

Isothermal Curing DSC

In the DSC isothermal curing experiment, the raw resin mixture is heated to the isothermal curing temperature, T_{iso}, at a highest heating rate possible, and then held at T_{iso} until the rate of heat releases from cure subsides close to the background heat flow. Figure 5(a) and (b) present DSC curves that show the heat release for samples 5 and 5A and 6 and 6A.

There is only one main peak observed; this would rather exclude any initial adduct formation or —OH propagation reaction because of the moieties presence in the system. The integration of the isothermal curve is rather imprecise due to baseline noise at low temperatures and because of an asymptotic character of the heat curve, leading to lower ΔH_c values.

Thermogravimetric Analysis

TGA was performed to ascertain the thermal stability of some products of the curing reaction. For the epoxides studied (Fig. 6), it can be found that they are stable up to 100–150°C, as evidenced by the initial decomposition temperature (IDT) (Table IV), and the degradation profile is of a single-step type.

The analyzed samples with the (1,3-oxothiolane-2-thione) group are thermally more stable than the epoxides, with IDT values higher up to 25°C, as shown in Figure 7.

When stability is compared within the samples of this group, it can be seen that the samples 5 and 5A proved to be more thermally resistant than samples 7 and 7A containing phenyl ring connected with epoxy group by ether linkage. The IDT value for these samples is considerably higher than for chain-linear compounds (6 and 6A). This fact can be interpreted in terms of the aromatic ring presence that usually causes an increase of the thermal stability. Epoxypropylmethacrylate and its sulphur-derivative are the most stable compounds thermally; it may be interpreted in terms of branched molecules interacting
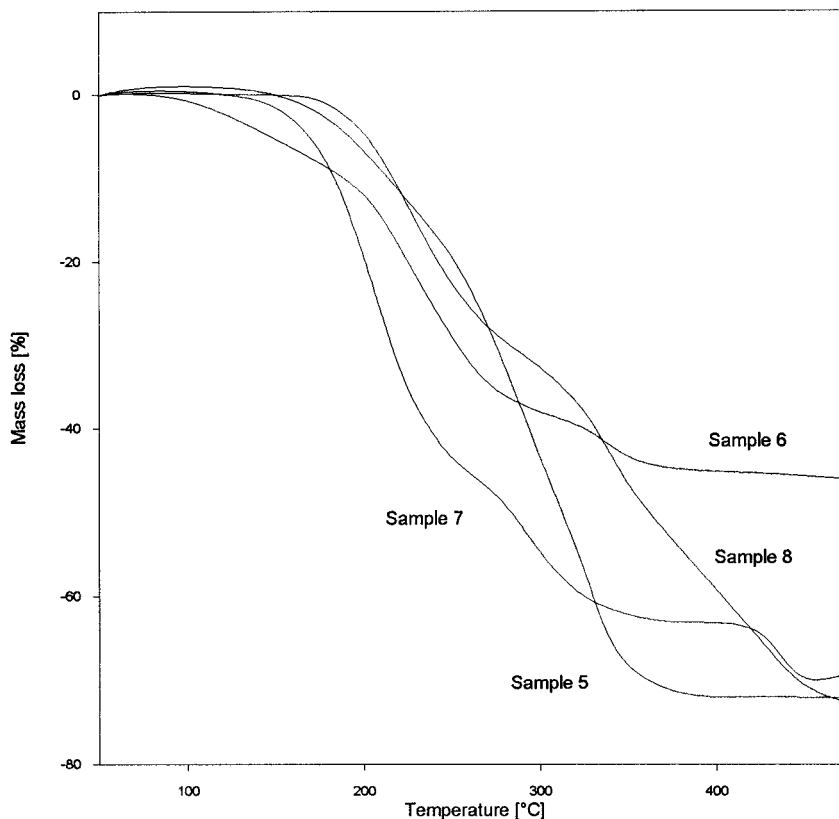

Figure 6   TGA profiles of chosen epoxy compounds.

Table IV   TGA Data of Some Epoxides and (1,3-Oxothiolane-2-thione)s

No.	R	IDT (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	Char Residue (%)
5	Ph	145.0	208.0	248.0	307.5	34.6
5A	Ph + CS$_2$	160.0	200.0	212.5	262.5	26.2
6	isopropyl—O—CH$_2$	100.0	175.0	217.5	382.5	46.2
6A	isopropyl—O—CH$_2$ + CS$_2$	125.0	165.0	185.0	242.5	10.0
7	Ph—O—CH$_2$	131.0	182.5	200.0	278.8	36.4
7A	Ph—O—CH$_2$ + CS$_2$	151.0	190.0	207.5	257.5	9.2
8	CH$_3$C(CH$_2$)C(O)OCH$_2$	150.0	212.5	232.5	335.0	16.2
8A	CH$_3$C(CH$_2$)C(O)OCH$_2$ + CS$_2$	165.0	192.5	220.0	295.0	28.5

with each other while the system is subjected to an external heating. Moreover, one can observe that the mass loss above the temperature of 300°C differs essentially for samples 6 and 6A and for samples 7 and 7A, respectively. It can suggest that the rate of volatile products formation above a certain threshold temperature is much higher for thio-derivatives.

CONCLUSIONS

The curing process of classical epoxides and their novel analogues with the (1,3-oxothiolane-2-thione) group was examined by DSC. It was found that the enthalpy of curing (ΔH_c) was much lower

for thio-derivatives, indicating that lower stress occurs in a five-membered ring rather than within the epoxy group with the ring number of 3. The thio-systems need a higher cure temperature, as reflected in a shift of the exothermic peak to higher and broader temperature range. Use of other catalysts should be considered to accelerate the rate of reaction, thus contributing to a decrease of the the curing temperature. Analysis of the nonisothermal DSC data revealed that there is one main peak of curing; such an observation would indicate that any other side reactions (for example, any adduct formations) are rather neglectible. Several of the cured samples were subjected to TGA; it revealed that some of the (1,3-oxothiolane-2-thione) derivatives are thermally
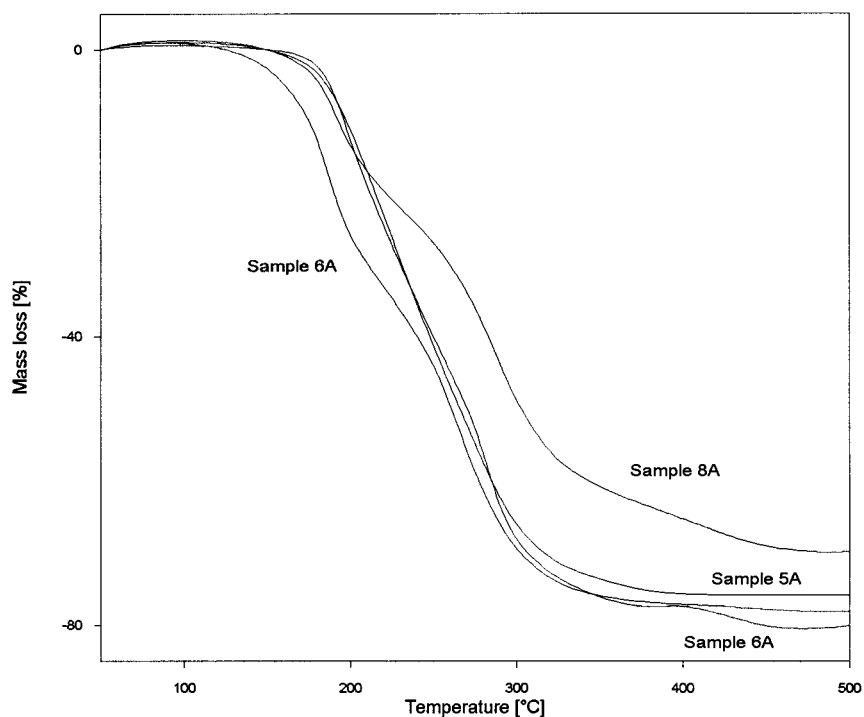

Figure 7   TGA profiles of chosen (1,3-oxothiolane-2-thione)s.

Table V   GPC Data of Some Cured Products

No.	R	M_n	M_w	M_w/M_n
5	Ph	228	1284	5.63
5A	Ph + CS$_2$	409	2976	7.28
6	isopropyl—O—CH$_2$	304	390	1.28
6A	isopropyl—O—CH$_2$ + CS$_2$	341	1067	3.13
7	Ph—O—CH$_2$	249	488	1.96
7A	Ph—O—CH$_2$ + CS$_2$	455	16,120	35.46
8	CH$_3$C(CH$_2$)C(O)OCH$_2$	383	1569	4.10
8A	CH$_3$C(CH$_2$)C(O)OCH$_2$ + CS$_2$	204	1404	6.89

more stable than their epoxy precursors. The difference in the IDT values remains up to 25°C. On the basis of the results collected, one can consider these novel resins as an interesting subject of research, both basic and for any technological application. For this, the fundamental questions concerning kinetics of cure are to be answered. Such studies are underway.

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