

Synthesis and Curing of New Epoxycycloaliphatic Polyesterimides with Dianhydrides and Diisocyanates as Hardeners

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"In memoriam" to Prof. Félix Serratos

SYNOPSIS

New epoxy resins obtained from a series of bis(4,5-epoxytetrahydrophthalimides) and three different dicarboxylic diacids were prepared and characterized by spectroscopic techniques and thermal analyses. Homopolymerization of epoxy groups was observed as a parallel process to the polycondensation reaction. Using Epiclon B with a tertiary amine and hexamethylene diisocyanate as hardeners, we studied the reaction of epoxy groups and hydroxylic groups attached to the cycloaliphatic moiety in the main chain. No exotherms were clearly detected by DSC, and during the curing process, only increases in the T_g values were observed. These cycloaliphatic epoxy polyesterimides have similar thermal characteristics to related aromatic epoxy polyesterimides, but have better processability. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Since Castan's seminal work¹ over half-a-century ago, epoxy resins have graduated from being a laboratory curiosity to having a multitude of applications in the adhesive, electronic, and aerospace industries. Nowadays, there are numerous formulations which have a wide variety of compositions and properties and which all have different uses.

Cycloaliphatic epoxy resins have lower resin viscosities and good high-temperature electrical characteristics and are known to be superior in arc and track resistance.² This is an advantage over commercialized bisphenol A-type epoxy resins (DGEBA). Several modifications of DGEBA have been reported,^{3,4} with difunctional compounds containing imide rings to improve the thermal stability of the epoxy resins. In this way, we reported the synthesis of new symmetric epoxy cycloaliphatic

compounds from bis(tetrahydrophthalimides) which have aliphatic or aromatic moieties.⁵

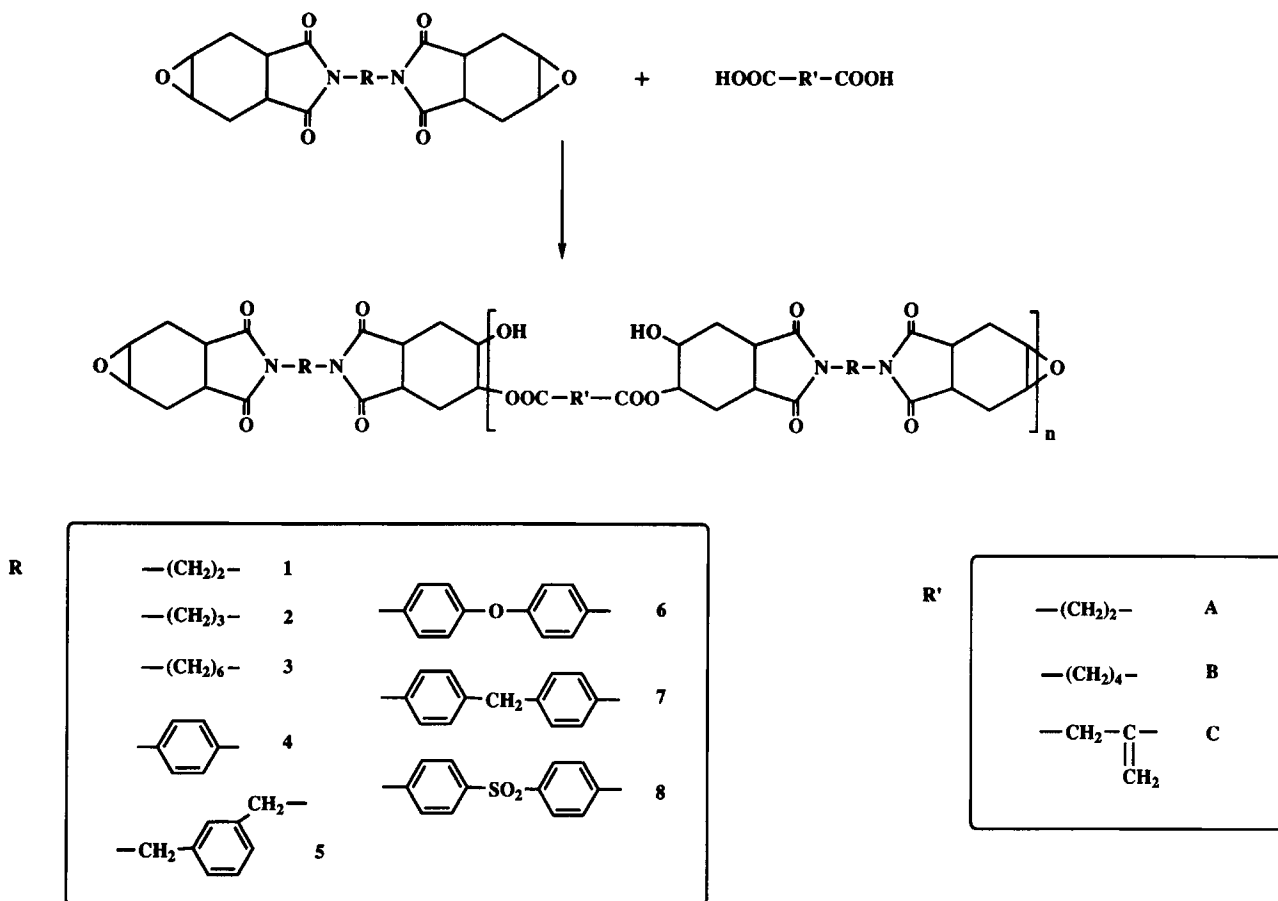
Moreover, cycloaliphatic epoxy resins are less reactive toward nucleophilic agents than are glycidic compounds. So, they do not react with amines but they do react with acids and anhydrides.⁶ In this article, we report the synthesis of several epoxycycloaliphatic polyimides from the epoxycycloaliphatic compounds and carboxylic diacids as can be seen in Scheme 1. The prepolymers obtained contain epoxy cycloaliphatic end groups and pendant hydroxylic groups, so they can be crosslinked in a further step using anhydrides or isocyanates as hardeners.

EXPERIMENTAL

Reagents

cis-1,2,3,6-Tetrahydrophthalic anhydride (THPA) (Aldrich), Epiclon B-4400 (Merck), and hexamethylenediisocyanate (HMDI) (Fluka) were used without further purification. Ethylenediamine, propylenediamine, *p*-phenylenediamine, and bis(4-ami-

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Scheme 1

nophenyl)sulfone (Merck), hexamethylenediamine, *m*-xylilenediamine, and bis-(4-aminophenyl)ether (Fluka), bis(4-aminophenyl)methane (Aldrich), and succinic, adipic and itaconic acids (Probus) were used without purification. 4-Dimethylaminopyridine (DMAP) (Fluka) was used as supplied. Pure *m*-chloroperbenzoic acid, 50–60%, (MCPBA) (Aldrich) and benzyltrimethylammonium chloride (BTMA) (Fluka) were used as received. All solvents were purified by standard procedures. Bis(tetrahydrophthalimides) and epoxyaliphatic compounds were obtained as previously described.⁵

Polymer Synthesis

A typical run is as follows: One gram of the diepoxide compound, the corresponding amount of diacid (molar ratio diepoxide/diacid 1.1 : 1), 0.01 g of BTMA, and 2 mL of DMF were put into a screwed tube under an argon atmosphere and heated at 110°C for 3 days. The mixture was poured into ice water and the filtered products were dried *in vacuo* at 40°C for 24 h.

Characterization and Measurements

The melting points are uncorrected and were determined on a Tottoli capillary melting point apparatus. ¹H- and ¹³C-NMR spectra were obtained using a Gemini 300 spectrometer with CDCl₃ and DMSO-*d*₆ as solvents and TMS as the internal standard.

Calorimetric studies were carried out on a Mettler DSC-30 thermal analyzer in covered Al pans under N₂ at various heating rates (5–20°C/min). The epoxy resin was kept in a vacuum at 60°C for about 24 h to remove moisture. Then, the resin or the resin/hardener mixture of about 5 mg of known weight was put into an aluminum pan. Crosslinking experiments were carried out at several temperatures for 10 min. After the isothermal treatment was complete, the sample was cooled to room temperature and the cured polymer *T*_g and residual curing enthalpy of (if present) were tested dynamically. Thermogravimetric analyses were carried out on a Perkin-Elmer TGA-7 system in N₂.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

Polymers were prepared from the cycloaliphatic diepoxy diimides and one of the three different carboxylic diacids: succinic, adipic, and itaconic, as can be seen in Scheme 1. The reactions were conducted in a screwed tube following a modified Klee⁷ method which is designed to polymerize low melting point monomers. The original Klee method is very advantageous from an experimental point of view, but it failed in our case due to the high melting points of the diepoxides. Thus, a small amount of DMF was added to homogenize the reaction mixture. The polymers were prepared using a diepoxide/diacid molar ratio of 1.1/1 to ensure epoxy end groups that could be crosslinked in a further step to three-dimensional networks. The conversions obtained from the polycondensations of the aliphatic diepoxides were not quantitative as they should be. This could be explained if we consider the formation of oligomers with carboxylate end groups, soluble in polar solvents such as water, DMF, etc. In the case of aromatic diepoxides, quantitative yields were obtained, as may be expected because of their low solubility.

The polymers were characterized by ¹³C-NMR spectroscopy. It should be pointed out that the epoxidation of the diimide-diacid led to two different isomers: *cis* and *trans*, according to the relative position of imide and oxirane rings. Therefore, diepoxide **6** showed split signals in the ¹³C-NMR spectrum of the tetrahydrophthalimide moiety. Figure 1 shows the ¹³C-NMR spectrum of the polymer derived from diepoxide **6** and adipic acid with all the

carbon signals labeled. A signal which can be attributed to the ester formed by the attack of the carboxylic acid on the oxirane ring can be seen at 171 ppm. Moreover, this attack leads to a new splitting of the signals, because of the unsymmetry of the cycloaliphatic moiety obtained (1,1', 2,2', and 3,3'). The spectrum did not show the signals expected for the epoxydic chain end, with the exception of the itaconic derivatives. This suggests that although the diepoxy/diacid ratio used was 1.1/1, the polymers have high molecular weights. This may be due to the homopolymerization reaction that takes place at the same time as the desired polymerization, as can be seen from the signal (h) at 70 ppm.⁸ The homopolymerization signal was assigned on the basis of the derivatization experiments with trifluoroacetic anhydride. The derivatization produces a deshielding of 7.5 and 5.3 ppm of the signals C1 and C1', respectively, whereas signal *h* only undergoes a deshielding of 1.7 ppm due to the change in solvent polarity.

This homopolymerization should be avoided if linear polymers are to be obtained, since it produces a crosslinking of the growing network. For this reason, reaction temperatures of 90, 110, and 130°C were tested with the aim of reducing this side reaction. For all the polymers obtained at 90°C, end-group signals were observed, suggesting that they were of low molecular weight. Signals due to homopolymerization can also be observed. At 130°C, there was no notable improvement, so all the polymerizations were conducted at 110°C.

The spectra of the polymers obtained from itaconic acid showed no ester signals. Likewise, the intensity of signals C1 and C1' was smaller than the

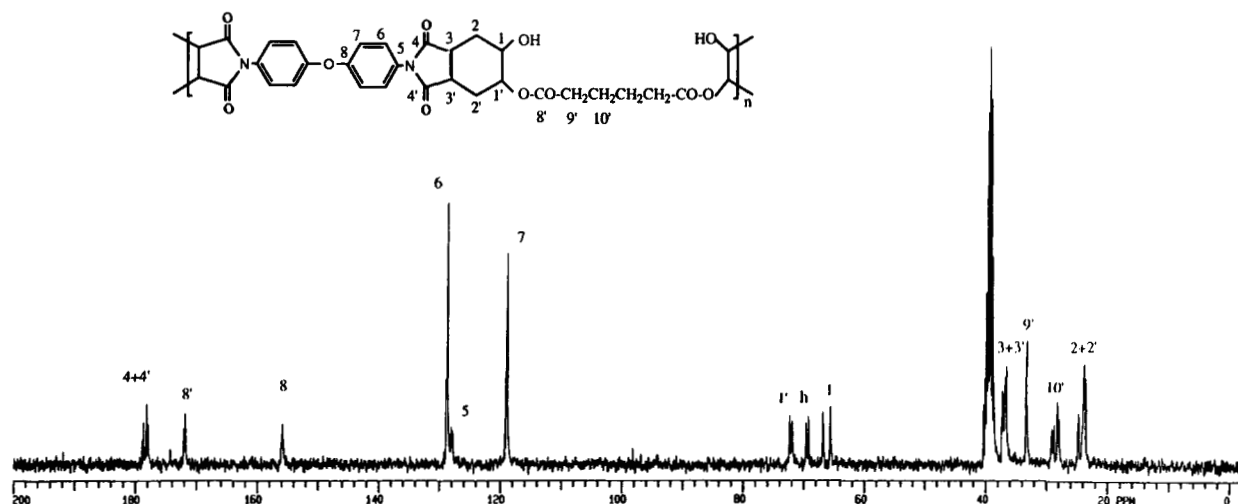


Figure 1 ¹³C-NMR spectrum of prepolymer **6B** in DMSO-*d*₆. δ in ppm.

homopolymerization signal, showing that the latter becomes the main reaction, in accordance with the previously observed low reactivity of this acid.⁸ Further experiments carried out in the same conditions but without diepoxide resulted in a total decomposition of the diacid and a release of CO₂.

Table I shows the viscosity measurements and some thermal characteristics of the polymers obtained. The polycondensation/homopolymerization ratio (P/H) was obtained by comparing the integration of ¹³C-NMR h and 1 or 1' signals. It should be pointed out that the degree of homopolymerization was higher when using succinic acid than adipic acid, possibly due to its higher acidity, as previously reported results have shown.⁸ As can be seen, higher *T_g* values were observed for polymers obtained from succinic acid than from adipic acid. Polymers obtained from itaconic acid had the highest *T_g* values, because of the greater extent of the homopolymerization reaction. Similarly, the polymers containing aromatic moieties in the bis(tetrahydrophthalimide) structure had higher *T_g* values than the ones containing aliphatic moieties, as was to be expected. These cycloaliphatic epoxy polyesterimides have

good thermal stability as is evident from the parameters listed in Table I. The maximum degradation temperatures are, in general, higher than 400°C, comparable to previously reported aromatic resins.⁹ However, the weight residue at 600°C is lower due to the less unsaturated structure. These results confirm that the good thermal stability remains unaltered by substituting aromatic rings by cycloaliphatic moieties.

Crosslinking Study

The epoxy polyesterimides which have pendant hydroxylic groups can be subsequently crosslinked by using anhydrides or isocyanates as hardeners. The process of forming networks by polymer crosslinking is complex although it is of special interest in both basic and applied research.

As well known, the structure and properties of the networks are influenced by the hardener and the curing conditions. Moreover, the presence of an accelerator in the curing process may affect the characteristics and properties of the crosslinked structure.

Table I Some Characteristics of Linear Polymers

Polymer ^a	η_{inh} (mL/g)	P/H ^b	<i>T_g</i> ^c (°C)	<i>T_{onset}</i> ^d (°C)	<i>T</i> _{10%} (°C)	<i>T</i> _{max} (°C)	<i>R</i> _{600°C} (%)
1A	107	1.0	104	352	384	431	3
1B	259	1.8	71	314	374	429	5
1C	384	—	121	332	361	432	5
2A	—	—	92	362	387	490	2
2B	—	—	61	355	381	479	3
2C	—	—	78	267	348	442	4
3A	228	0.4	58	354	386	436	3
3B	336	3.0	52	365	372	428	3
3C	148	—	74	355	381	445	4
4A	81	—	—	304	329	329	21
4B	158	—	—	301	327	329	21
5A	43	0.5	95	338	368	436	4
5B	146	1.2	77	348	388	439	4
5C	148	—	106	330	360	441	7
6A	233	0.5	148	357	391	422	12
6B	333	1.3	137	384	402	427	14
7A	30	0.4	118	337	363	413	13
7B	41	1.0	111	348	380	414	16
7C	—	—	133	351	374	500	14
8A	125	0.5	130	327	343	489	23
8B	212	0.7	117	301	340	477	19
8C	—	—	140	327	361	498	22

^a See Scheme 1.

^b Polycondensation/homopolymerization ratio from ¹³C-NMR measurements.

^c Obtained at 20°C/min.

^d Obtained at 10°C/min.

Table II T_g Values for Prepolymers 5B and 7B Crosslinked with Different Amounts of Epiclon (phr), Using DMAP as Accelerator (10 phr)

Prepolymer	Epiclon Concentration (phr)	T_g (°C)
5B	—	77
	10	93
	20	110
	40	133
	60	142
7B	—	111
	10	121
	20	159
	40	152
	60	174

In a previous study,¹⁰ we attempted to crosslink a series of epoxy resins derived from diimide-diacids which had been obtained from bicyclo[2.2.2]oct-7-en-2,3,5,6-tetracarboxylic dianhydride and diglycidyl ether of bisphenol A using dianhydride or diisocyanate as hardeners. The optimum quantities of resin and curing agent were determined empirically by varying their proportions, curing as completely as possible and measuring the T_g of the cured material, since hydroxy groups in the prepolymer are capable of reacting with the hardener, thus preventing the optimum quantities of resin and curing agent from being calculated. The curing with anhydride did not require a tertiary amine. On the other hand, the crosslinking of cycloaliphatic bis(epoxytetrahydrophthalimides) with anhydrides failed without the presence of a tertiary amine as an accelerator.⁵

In the present study, we attempted the curing with anhydrides without amines and no crosslinking took place, so we tested several proportions of Ep-

iclon B dianhydride (10–100 phr) with dimethylaminopyridine (DMAP, 10 phr) as the accelerator. After heating in a dynamic DSC run from room temperature to 250°C, materials which were completely insoluble in common polar solvents were obtained, although no exotherm was clearly detected. It should be pointed out that T_g values increased from 10 to 60 phr of anhydride, suggesting an increase in the degree of crosslinking. These values are shown in Table II for two different prepolymers.

Isothermal experiments were also carried out to determine the temperature necessary for a complete curing in a given period of time (10 min). Table III shows the T_g and ΔC_p as well as the degree of crosslinking calculated by the Couchman approach¹¹:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad \lambda = \frac{\Delta C_{p\infty}}{\Delta C_{p0}}$$

ΔC_{p0} is the isobaric heat capacity of the initial mixture, with a glass transition temperature of T_{g0} and $\Delta C_{p\infty}$ is the isobaric heat capacity of the maximum crosslinked network with a glass transition temperature of $T_{g\infty}$. Assuming that the maximum degree of crosslinking achieved in a dynamic experiment is the complete crosslinking, the degree of crosslinking that is summarized in Table III can be obtained for each selected temperature.

To study the curing of the present prepolymers with isocyanates, several epoxy resin/hexamethylenediisocyanate mixtures were prepared with different ratios of hardener. As well known, polymers containing hydroxylic groups can be cured to give urethane crosslinks and epoxides can also react with isocyanates to give 2-oxazolidone rings.

The curing process can be monitored using the DSC technique. In this case, a typical DSC plot shows a broad exotherm at about 140°C attributable to the two different reactions mentioned above. Low

Table III Isothermal Crosslinking of Compound 7B using Epiclon (60 phr) as Hardener and DMAP (10 phr) as Accelerator^a

Curing Temperature (°C)	T_g (°C)	ΔC_p (J/g K)	Degree of Crosslinking ^b (%)
120	117	0.20	23
140	127	0.16	48
160	124	0.16	42
180	141	0.13	71
200	168	0.14	95

^a Curing time 10 min.

^b Couchman's approach.

Table IV Crosslinking of Prepolymer 7B Using Hexamethylenediisocyanate as Hardener

HMDI Concentration (phr)	T_g (°C)	ΔC_p (J/g K)
—	111	0.29
5	111	0.22
10	120	0.29
20	128	0.18
40	123	0.15
60	131	0.17
80	136	0.14
100	154	0.07

ΔH values (about 60 J/g) were always obtained, although the unreliable base lines prevent accurate measurements. Thus, kinetic analyses were only possible from the shift of the exotherm maximum with the heating rate.¹² The activation energy values' (E_a) calculated range was between 60 and 80 kJ/mol and no relationship could be established between these values and the amount of hardener used. Conversely, the T_g values of the completely crosslinked materials increase with the diisocyanate concentration, as can be seen in Table IV. These T_g values are lower than the ones obtained in the curing with Epiclone B, as can be expected from the differences in the chemical structure of both hardeners. Thermogravimetric analyses did not show noteworthy differences between linear and crosslinked products and the results did not depend on the nature and amount of the hardener used.

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REFERENCES

1. P. Castan, Swiss Pat. 211,116 (1940).
2. P. F. Brunis, Ed., *Epoxy Resin Technology*, Interscience, New York, 1968.
3. V. Cádiz, A. Mantecón, A. Serra, and C. Thepaut, *Angew. Makromol. Chem.*, **195**, 129 (1992).
4. A. Serra, V. Cádiz, and A. Mantecón, *Angew. Makromol. Chem.*, **155**, 93 (1987).
5. D. Monte, M. Galià, V. Cádiz, A. Mantecón, and A. Serra, *Macromol. Chem. Phys.*, **196**, 1051 (1995).
6. A. Roig, M. Galià, V. Cádiz, A. Mantecón, and A. Serra, *Makromol. Chem.*, **194**, 411 (1993).
7. J. Klee, H. H. Hörhold, and H. J. Flammerschein, *Angew. Makromol. Chem.*, **178**, 63 (1990).
8. A. Roig, A. Serra, V. Cádiz, and A. Mantecón, *Angew. Makromol. Chem.*, **199**, 75 (1992).
9. A. Serra, V. Cádiz, P. A. Martínez, and A. Mantecón, *Angew. Makromol. Chem.*, **138**, 185 (1986).
10. M. Galià, D. Monte, A. Serra, A. Mantecón, and V. Cádiz, *J. Appl. Polym. Sci.*, to appear.
11. C. Mathieu, M. Fève, G. Seytre, and G. Boiteux, *Angew. Makromol. Chem.*, **206**, 39 (1993).
12. R. B. Prime, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, London, 1981.

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