

Modification of DGEBA with Diimide–Diacids Derived from Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic Dianhydride and Crosslinking Study

M. GALIÀ, D. MONTE, A. SERRA, A. MANTECÓN, and V. CÁDIZ*

Universitat Rovira i Virgili, Departament de Química (Q. Orgànica), Facultat de Química, Plaça Imperial Tàrraco 1, 43005 Tarragona, Spain

SYNOPSIS

Epoxy resins derived from diimide–diacids obtained from bicyclo[2.2.2]oct-7-en-2,3,5,6-tetracarboxylic dianhydride and diglycidyl ether of bisphenol A were synthesized and characterized by spectroscopic techniques and thermal analyses. A further crosslinking using hydroxylic groups using dianhydride or diisocyanate as a hardener was also carried out. These processes led to crosslinked materials, but a DSC study does not show a straightforward relationship between the amount of hardener used and reaction enthalpies, which suggests a complicated reaction mechanism. On the other hand, only a slight increase in T_g values was observed during the curing process. No substantial differences between the thermal characteristics of linear and crosslinked polymers were observed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides are one of the most important types of thermally stable polymers because of their high-performance properties, but they have the disadvantage of being very insoluble and unprocessable. Like epoxy prepolymers, these polyimides can be manipulated and then cured to obtain thermosets. Also, the presence of noncoplanar diimides is found to be effective in the improvement of solubility¹ with retention of excellent thermal stability due to the multibond and rigidity of the polycyclic structure.²

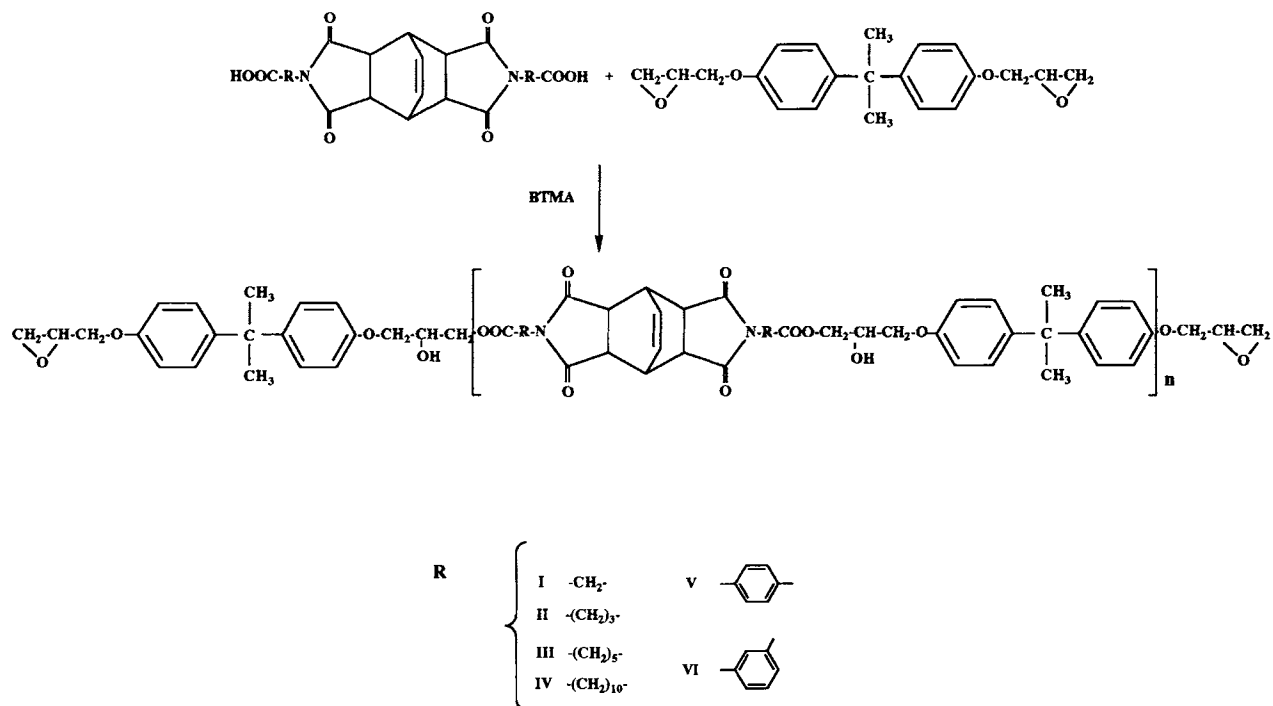
Several modifications of DGEBA with difunctional compounds containing imide rings were carried out to improve the thermal stability of epoxy resins.^{3–5} In previous studies,^{4,5} we reported the modification of the conventional DGEBA epoxy resin with diimide–diacids and diimide–diphenols and proved that no substantial differences between these resins and the completely imidized backbone exist. In this article, we report the study of a series

of DGEBA resins which are modified with several cycloaliphatic diimide–diacids derived from bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. The synthesis of these resins was accomplished using DGEBA and the diimide–diacids according to Scheme I.

This modification produces telechelic epoxy–polyimides with pendant hydroxylic groups, which are capable of crosslinking in a further step using anhydrides or isocyanates as hardeners. The anhydride-curing system requires high temperatures, but has the advantage of good electrical properties and better thermal stabilities than those of similar amine-curing systems. The uncatalyzed reaction of anhydrides with epoxides is slow, and it seems to be initiated by hydroxylic groups. Thus, the presence of hydroxylic pendant groups in these epoxy–imide polymers can enhance the curing process and increase the crosslinking density.

Isocyanates react with alcohols to form carbamates and with epoxides to form 2-oxazolidones. Both reactions have the advantage of involving a simple addition reaction with no byproduct formation. Therefore, the use of isocyanates can also lead to crosslinked networks from these linear prepolymers.

* To whom correspondence should be addressed.



Scheme 1

EXPERIMENTAL

Chemicals

Diglycidyl ether of bisphenol A (DGEBA) was obtained by reaction of epichlorohydrin with bisphenol A and NaOH. Bicyclo[2.2.2]oct-7-ene-tetracarboxylic dianhydride (Aldrich), 4-aminobenzoic acid (Fluka), 3-aminobenzoic acid (Merck), 11-aminoundecanoic acid (Aldrich), 6-aminohexanoic acid (Fluka), 4-aminobutanoic acid (Fluka), glycine (Fluka), benzyltrimethylammonium chloride (BTMA, Fluka), tetraethylammonium bromide (Fluka), perchloric acid (Probus), Epiclon B-4400 (Merck), 4-dimethylaminopyridine (DMAP, Fluka), and hexamethylene diisocyanate (Fluka) were used without further purification. All solvents were purified by standard procedures. Diimide-diacids were obtained as described previously.⁶

Polymer Synthesis

The reactions were conducted in DMF at 110°C, using a reaction flask fitted with a stirrer and thermometer under an argon atmosphere. A typical run was as follows: 0.05 mol of diimide-diacid and 0.055 of DGEBA were mixed in DMF (50 mL). The mixture was heated under an argon atmosphere at

110°C and then benzyltrimethylammonium chloride (BTMA) (0.005 mol) was added in one batch. The disappearance of the initial diimide-diacid was controlled by acid index measurements. When the acid index values remained constant, the mixture was cooled and poured into ice water. The filtered product was washed several times with water and dried at 60°C in a vacuum for 48 h. Polymer yields were practically quantitative.

Characterization and Measurements

IR spectra were recorded on a Nicolet 5ZDX FT-IR spectrometer; ¹³C-NMR and ¹H-NMR spectra were obtained using a Gemini 300 spectrometer with CDCl₃ and DMSO-*d*₆ as solvents and TMS as the internal standard. Elemental analyses were carried out on a Carlo Erba 1106 device.

The epoxy content was expressed in gram/equivalent and determined by the Jay, Dijkstra, and Dahmen method, variation Ciba.⁷ The acid index value was determined as reported.⁸ Viscosity was measured in 5 g/L DMF solution at 30 ± 0.1°C with an Ubbelohde viscosimeter on a Schott AVS 310 automatic device.

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

Table I Synthesis of Polymers

	Compound					
	I	II	III	IV	V	VI
Reaction time (min)	550	265	357	745	305	415
EE (g/eq)	7240	6338	6113	2590	4726	5505
η (L/g)	0.009	0.018	0.014	0.025	0.019	0.020
IR (ν , cm^{-1})	3600-3200, 1754, 1711, 1107, 710	3600-3200, 1769, 1736, 1103, 727	3600-3200, 1769, 1734, 1106, 720	3600-3200, 1760, 1733, 1108, 719	3600-3200, 1770, 1716, 1104, 720	3600-3200, 1780, 1716, 1106, 710
$^{13}\text{C-NMR}$ (DMSO- d_6 , TMS) δ (ppm)	176.7(s), 166.8(s), 156.4(s), 143.1(s), 130.7(d), 127.7(d), 114.2(d), 74.6(t), 69.7(t), 66.8(d), 66.6(t), 63.0(d), 59.6(t), 42.6(d), 41.4(s), 33.4(d), 31.0(q)	177.4(s), 172.0(s), 156.2(s), 142.7(s), 130.7(d), 127.4(d), 113.8(d), 72.7(d), 69.0(t), 66.8(d), 65.2(t), 59.4(t), 42.2(d), 41.2(s), 37.1(t), 33.4(d), 30.7(q), 30.5(t), 22.4(t)	177.4(s), 172.8(s), 156.2(s), 142.7(s), 130.6(d), 127.4(d), 113.8(d), 72.6(d), 68.9(t), 66.2(d), 65.1(t), 59.5(t), 42.2(d), 41.1(s), 33.4(d), 33.2(t), 30.7(q), 26.7(t), 25.5(t), 23.8(t)	177.3(s), 172.8(s), 156.2(s), 142.7(s), 130.5(d), 127.4(d), 113.8(d), 72.6(d), 68.9(t), 66.7(d), 65.0(t), 59.5(t), 42.2(d), 41.1(s), 37.8(t), 33.6(t), 30.7(q), 28.7(t), 28.4(t), 27.0(t), 26.0(t), 24.4(t)	176.4(s), 165.0(s), 156.2(s), 142.8(s), 136.2(s), 131.2(d), 129.9(d), 129.5(s), 127.5(d), 126.9(d), 73.1(d), 68.9(t), 66.9(d), 66.3(t), 59.7(t), 42.6(d), 41.2(s), 34.0(d), 30.7(q)	176.6(s), 164.9(s), 156.2(s), 142.8(s), 132.4(s), 131.6(d), 131.1(d), 130.6(s), 129.5(d), 129.3(d), 127.4(d), 113.9(d), 73.5(d), 69.0(t), 66.8(d), 66.5(t), 62.5(t), 59.9(t), 42.6(d), 41.1(s), 34.0(d), 30.7(q)

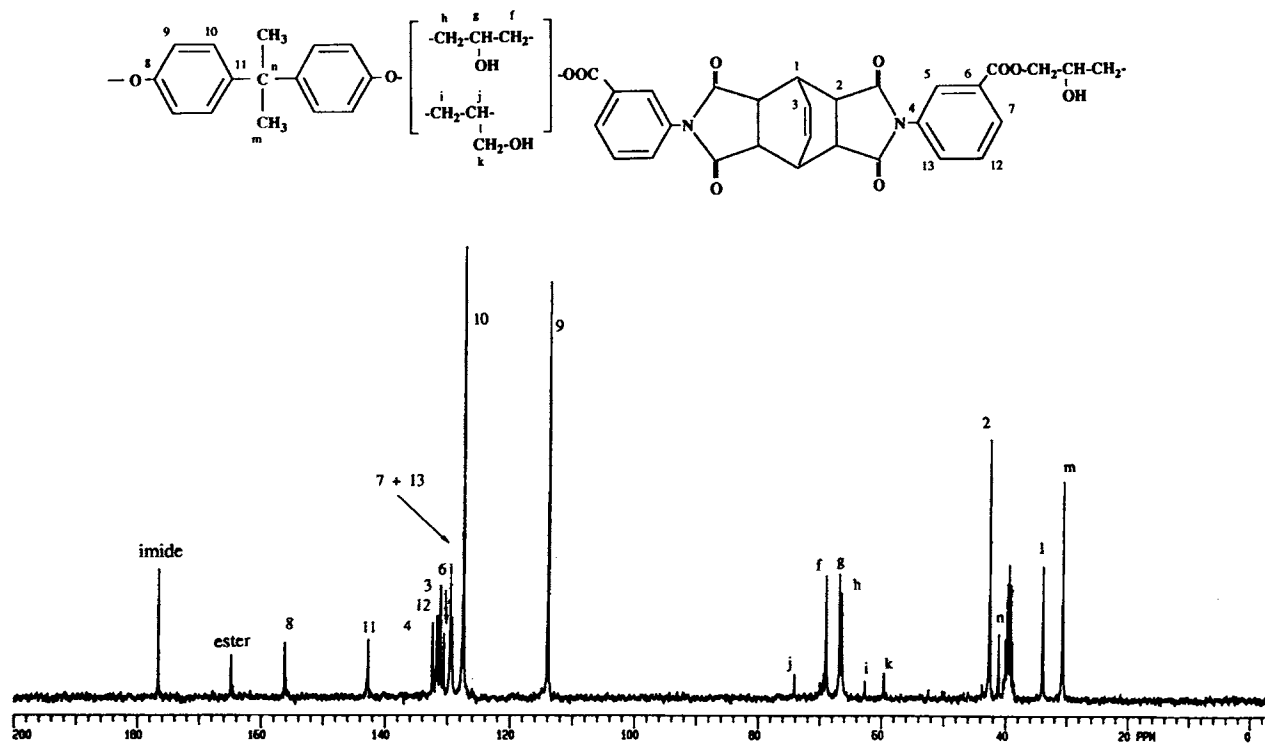


Figure 1 ^{13}C -NMR spectrum of prepolymer IV (DMSO- d_6 , TMS, δ [ppm]).

epoxy resin was kept in a vacuum at 60°C for about 24 h to remove moisture. The mixtures were prepared by mechanically stirring the resin and anhydride or dissolving the resin and isocyanate mixture in anhydrous CH_2Cl_2 and then drying under a vacuum at room temperature. The resin-hardener mixture of known weight (about 5 mg) was put into an aluminum pan. The maximum T_g achieved was evaluated using dynamic DSC experiments. Isothermal crosslinking experiments were carried out at several temperatures for 30 min. After these treatments were complete, the samples were cooled to room temperature, and the T_g of the cured polymer and the residual enthalpy of curing (if present)

were tested in a second dynamic experiment. Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-7 system in N_2 at a heating rate of $20^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The polymerization reactions were carried out in DMF at 110°C with BTMA as the catalyst. The molar ratio diimide-diacid/DGEBA was always 1 : 1.1 to ensure that the end groups were oxirane rings

Table II Thermal Data of the Prepolymers

	Compound					
	I	II	III	IV	V	VI
T_g ($^\circ\text{C}$)	126	96	74	49	168	156
T_i ($^\circ\text{C}$)	418	436	430	452	430	422
$T_{10\%}$ ($^\circ\text{C}$)	397	412	410	439	408	402
T_{max} ($^\circ\text{C}$)	453	472	463	496	460	454
dW/dt (%/min)	26	29	28	32	28	30
$T_{700^\circ\text{C}}$ (%)	12	8	17	4	13	11

Data obtained at $20^\circ\text{C}/\text{min}$.

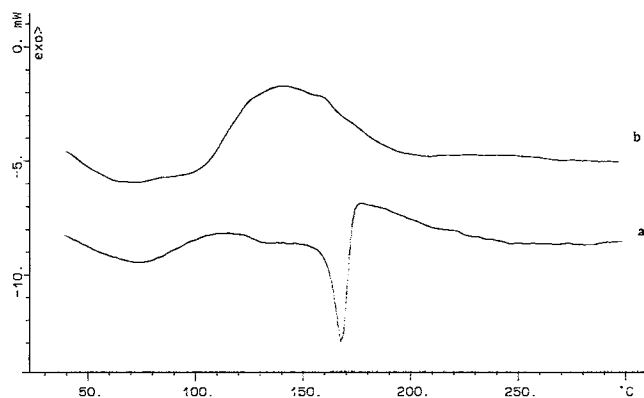


Figure 2 DSC plots of (a) prepolymer I and Epiclon (20 phr) mixture and (b) prepolymer I and hexamethylene diisocyanate (20 phr) mixture. Data obtained at 20°C/min.

which were capable of crosslinking. The disappearance of diimide-diacid, and, therefore, the evolution of the reaction, was monitored by acid index value determination. Thus, when these values remained constant, the reaction stopped. Reaction times are summarized in Table I. The polymers obtained were characterized by IR and ^{13}C -NMR spectroscopy. The assignments were made on the basis of empirical calculations and DEPT and HETCOR experiments. The IR absorptions as well as the ^{13}C -NMR chemical shifts are also collected in Table I.

IR spectra of these resins show strong absorptions of around 3500 cm^{-1} due to OH st. The diminution of the epoxy band at 910 cm^{-1} and the disappearance of carboxylic acid bands can be observed. By ^{13}C -NMR spectroscopy, it was possible to verify two types of attack on the oxirane rings. As can be seen in Figure 1, six lines appear in the zone between 59 and 75 ppm. The most intensive ones, f, g, and h, correspond to the attack on the least-substituted carbon (normal opening) and the other three less intensive ones (i, j, and k) correspond to the attack on the most substituted carbon (abnormal opening).

All polymers were soluble in chloroform and acetone and in polar solvents such as NMP, DMF, and DMSO. Epoxide equivalent (EE) as well as viscosity values, collected in Table I, suggest that low molecular weights are achieved. The thermal behavior of the polymers was measured by DSC and TGA. The good thermal properties of the resins are evident by looking at the parameters collected in Table II. T_g values can be related to the chemical structure of the diimide-diacid unit; thus, the more rigid the moiety introduced, the higher the T_g value. In all cases, these values are lower than those of conventional polyimides. Thermal stability of the polymers,

Table III Thermal Data of Prepolymer I Crosslinked Using Epiclon B as Hardener

	Epiclon Concentration (phr)			
	10	20	30	50
T_g ($^{\circ}\text{C}$)	144	165	166	166
ΔC_p ($\text{J/g } ^{\circ}\text{C}$)	0.26	0.23	0.27	0.19
T_i ($^{\circ}\text{C}$)	319	322	253	286
$T_{10\%}$ ($^{\circ}\text{C}$)	372	392	338	362
T_{max} ($^{\circ}\text{C}$)	456	468	456	480
dW/dt ($\%/ \text{min}$)	24	25	25	19
$Y_{700^{\circ}\text{C}}$ (%)	16	13	10	17

Data obtained at 20°C/min.

evaluated from TGA data, is higher than for other previously reported polyester-imides.^{5,8} However, char yields are lower, as expected for cycloaliphatic imides.

Crosslinking Study

The relation between the chemical structure and the physical properties of the cured material is a complicated subject. The structure of the crosslinks, the structure and length of the chains between the crosslinks, substituents, and network density are the structural factors that influence the properties of the cured material. Also, the structure and the properties of the networks are influenced by the curing conditions. So, the glass transition temperature of the network depends on the curing temperature and the ratio between the functional groups in the resin-hardener mixture influences the network formation process. Moreover, the presence of an accelerator in the curing process can affect the characteristics of the crosslinked structure.

Table IV Isothermal Curing of Prepolymer I Using Epiclon B as Hardener

Curing Temperature ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$) ^a	ΔC_p ($\text{J/g } ^{\circ}\text{C}$) ^a	Crosslinking Degree (%) ^b
170	133	0.26	16
180	138	0.25	29
190	146	0.27	49
200	155	0.24	73
210	159	0.25	82
220	165	0.30	98

Anhydride concentration: 30 phr; curing time: 30 min.

^a Obtained at 20°C/min.

^b From Couchman's approach.

Table V Thermal Data of Prepolymer I Crosslinked Using Hexamethylene Diisocyanate as a Hardener

	Hardener Concentration (phr)				
	10	20	30	40	50
T_g (°C)	127	139	148	149	152
ΔC_p (J/g °C)	0.26	0.18	0.18	0.16	0.11
T_i (°C)	337	312	302	307	300
$T_{10\%}$ (°C)	384	373	355	347	309
T_{\max} (°C)	461	491	464	463	470
dW/dt (%/min)	20	17	22	19	16
$Y_{700^\circ\text{C}}$ (%)	16	17	9	9	7

Data obtained at 20°C/min.

The optimum quantities of resin and curing agent may be calculated from the EE values of the resin and the equivalent weight of the hardener. This assumes that networks result exclusively from the complete reaction of epoxy and the curing agent. This is an approximation since steric and diffusion restrictions and epoxide homopolymerization also occur. Consequently, the quantities of the reactants are usually determined empirically by varying their proportions, curing as completely as possible and measuring the ΔH of the crosslinking or determining the T_g or the heat-deflection temperature of the cured material. In our case, there are also hydroxy groups in the prepolymer which are capable of reacting with anhydrides, and this fact prevents the optimum quantities of resin and curing agent from being calculated. Thus, to determine these optimum quantities, several proportions of Epiclon B dianhydride (10, 20, 30, and 50 phr) were tested. In all cases, materials which are completely insoluble in common polar solvents were obtained.

In a typical DSC run [Fig. 2(a)], a melting endotherm centered at 167°C followed by an exotherm associated with the crosslinking were observed. This fact prevents an accurate measurement of the ΔH of the reaction. So, to determine the optimum reactant ratio to carry out the curing, the T_g of the completely crosslinked material, determined in a second dynamic DSC run, was used. Although the ΔH of the reaction was not accurate, the values obtained were relatively low ($\Delta H \approx 20$ J/g), which suggests that the degree of crosslinking must be low. Moreover, as can be seen in Table III, the T_g of the completely cured material remains practically unchanged when the anhydride amount increases (around 165°C, for resin I). Thermogravimetric studies did not show remarkable differences between the hardener percentages tested. Thermal parameters are also summarized in Table III.

The curing reaction with anhydride proceeds rapidly with either an acidic catalyst, which favors etherification, or a basic one, which favors esterification.⁹ In a previous study,¹⁰ we observed that the higher the tertiary amine concentration, the lower the peak temperature of the diglycidylester-anhydride curing reaction. In this way, dimethylamino-pyridine (DMAP) was tested as an accelerator to improve the curing process, but no differences were observed. Therefore, no amine was added to the resin-Epiclon B mixture.

The data obtained from dynamic DSC allowed us to choose several temperatures to carry out isothermal treatments for 30 min. In Table IV, the T_g values of the isothermally cured materials measured in a second dynamic run are collected, as well as the degree of crosslinking obtained from Couchman's 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 $T_{g\infty}$. It is worth pointing out that these degrees of crosslinking are obtained assuming that the maximum degree of crosslinking achieved in a dynamic experiment is complete crosslinking. Moreover, the value obtained for λ is practically 1, which is in accordance with the above-mentioned low degree of crosslinking.

The reaction of alcohols with isocyanates to form carbamates is well known and similar reactions with polymers containing hydroxylic groups would be expected. Thus, crosslinking may also be effected by reacting the pendant hydroxyl groups along the prepolymer backbone with diisocyanate to give ure-

thane crosslinks. Polymers such as poly(vinyl alcohol) were crosslinked using hexamethylene diisocyanate.¹² Furthermore, methods of preparing polyurethanes also include the reaction of diisocyanates with diepoxides to yield poly(2-oxazolidone)s.¹³ Thus, this reaction can be used to crosslink our prepolymers, since they contain the two reactive groups.

To study the reaction, several epoxy resin/hexamethylenediisocyanate mixtures were prepared with different hardener ratios. These mixtures were heated and the resulting materials were insoluble in common polar solvents, indicating their crosslinked nature. Several experiments were carried out to monitor their behavior using the DSC technique, paying special attention to the changes observed in T_g values, enthalpies, and activation energies. A typical DSC plot is shown in Figure 2(b). As can be seen, a broad exotherm centered at 140°C appears. It should be pointed out that only one exotherm is observed, although two different reactions can take place in this curing process, in addition to the afore-said homopolymerization.

The ΔH values are higher than the ones previously obtained using anhydride as a hardener (50–100 J/g). No relationship could be established among these values, the maximum temperature of the exotherm, and the amount of hardener used. This is in accordance with the coexistence of the three above-mentioned processes, the total enthalpy being the addition of the corresponding enthalpies of these three mechanisms. Depending on the amount of hardener used, the competition among them leads to a different maximum peak temperature and enthalpy. This prevents information being obtained on the extent of the reaction and the degree of crosslinking reached. Activation energy values (about 90 kJ/mol), obtained from the shift in the maximum of the exotherm with the heating rate,¹⁴ gave no additional information. Similarly to the curing with anhydride, a slight increase in T_g values of the completely crosslinked material is observed when the diisocyanate concentration increases. Table V summarizes these values and other thermal data. Thermogravimetric parameters did not show noteworthy differences when compared with the prepolymers and anhydride-cured materials.

These studies prove that telechelic epoxy polyimides with pendent hydroxylic groups can be

crosslinked using anhydrides and isocyanates as hardeners. The complexity of the curing process in both cases prevents the obtention of accurate kinetic parameters. The thermal stability of the materials shows no significant improvement with the crosslinking process.

The authors express their thanks to DGICYT (Dirección General de Investigación Científica y Tecnológica) for providing financial support to this work and to Sr. Ramón Guerrero for his helping in the NMR spectra recording.

REFERENCES

1. P. A. Falcigno, S. Jasne, and M. King, *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 1433 (1992).
2. S. Itamura, M. Yamada, S. Tamura, T. Matsumoto, and T. Kurosaki, *Macromolecules*, **26**, 3490 (1993).
3. Jpn. Pat. 8,207,028 (1982) (to Mitsubishi Electric Corp.); *Chem. Abstr.*, **97**, 40008t (1982). Jpn. Pat. 57145218 (1982) (to Mitsubishi Electric Corp.); *Chem. Abstr.*, **98**, 73541k (1983).
4. V. Cádiz, A. Mantecón, A. Serra, and C. Thepaut, *Angew. Makromol. Chem.*, **195**, 129 (1992).
5. A. Serra, V. Cádiz, and A. Mantecón, *Angew. Makromol. Chem.*, **155**, 93 (1987).
6. M. Galià, A. Serra, A. Mantecón, and V. Cádiz, *J. Appl. Polym. Sci.*, **56**, 193 (1995).
7. B. Dobinson, W. Hofman, and B. P. Stark, *The Determination of Epoxide Groups*, 1st ed., Pergamon, London, 1970, p. 40.
8. A. Serra, V. Cádiz, P. A. Martínez, and A. Mantecón, *Angew. Makromol. Chem.*, **138**, 185 (1986).
9. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1982.
10. M. Galià, A. Serra, A. Mantecón, and V. Cádiz, *J. Appl. Polym. Sci.*, **57**, 413 (1995).
11. C. Mathieu, M. Fève, G. Seytre, and G. Boiteux, *Angew. Makromol. Chem.*, **206**, 39 (1993).
12. S. V. Caro, Jr., C. S. Paik Song, and E. W. Merrill, *J. Appl. Polym. Sci.*, **20**, 3241 (1976).
13. M. P. Stevens, *Polymer Chemistry. An Introduction*, 2nd ed., Oxford University Press, New York, 1990.
14. R. B. Prime, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, London, 1981.

Received December 28, 1994

Accepted December 6, 1995