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# CURING OF *N*,*N*′-DIGLYCIDYLIMIDES WITH POLYFUNCTIONAL COMPOUNDS

A. Mantecón, V. Cádiz, A. Serra and P. A. Martínez
Departament de Química Orgànica, Facultat de Químiques, Plaça Imperial Tarraco 1,
Tarragona 43005, Spain

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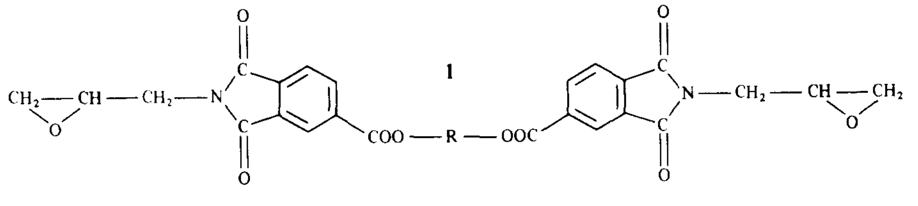
**Abstract**—This paper describes the curing reactions of new *N*,*N*′-diglycidylimides containing trimellitimide units. Reactions were carried out using several polyfunctional curing agents, viz. aromatic primary diamines and phthalic anhydride. Spectroscopic techniques were used to study the curing process. The course of reaction was followed by i.r. spectroscopy. Some intermediate species were detected by recording $^{13}$C-NMR spectra until the products became insoluble in the usual deuterated solvents.

## INTRODUCTION

The chemical structure, functionality, composition and extent of reaction can influence the properties of the polymeric materials. High thermal stability of imide groups is well documented; it is therefore expected that polymers including these units should have good thermal behaviour.

On the other hand the use of epoxy resins has been widely developed in order to obtain three dimensional polymers. The purpose in this work has been the preparation of crosslinked epoxy resins containing imide rings to improve the mechanical and thermal properties and control of crosslinking reactions. The following structures were employed [1].



Ia R : — $(CH_2)_2$ —
Ib R : — $(CH_2)_6$ —
Ic R : — $(CH_2)_{10}$ —

Scheme 1

To obtain three-dimensional polymers, some polyfunctional compounds capable of reacting with groups in the polymer were used. Several types of curing agents such as aromatic and aliphatic primary diamines, acid anhydrides and borine derivatives have been described in the literature with the aim of achieving materials having good properties.

Borine derivatives belong to the catalyst hardener type, and have not been considered in the present study. The remaining curing agents mentioned above are polyfunctional reagents, which remain in the backbone of the polymer after reaction. We have used polyfunctional hardeners, viz. 4,4′-diaminediphenylmethane (DDM), *m*-phenylenediamine (*m*-PDA) and phthalic acid anhydride (PAA).

The functionality of a glycidyl group depends on the curing agent employed, i.e. when it reacts with an amine its functionality is one, but when an acid anhydride is used it is two. For this reason the amines must have functionality greater than two, while a monofunctional acid anhydride can be utilized in this process.

## EXPERIMENTAL

### *Reagents*

*N*,*N*′-diglycidylimides 1a–c were obtained and characterized as described before [1]. 4,4′-Diaminediphenylmethane (DDM), *m*-phenylenediamine (*m*-PDA) and phthalic acid anhydride (PAA; Merck) were used without further purification. Chloroform and acetone (Probus) were purified by distillation under normal pressure.

### *Synthesis of crosslinked polymers*

*With aromatic primary diamines. N*,*N*′-diglycidylimides and aromatic diamines (molar ratio 1:0.5) were mixed and dissolved in the smallest possible amount of chloroform. The solvent was removed under vacuum at room temperature. Then the mixture was submitted to the cure cycle of 100°C for 21 hr and 130°C for 4 hr.

*With phthalic acid anhydride. N*,*N*′-diglycidylimides and phthalic anhydride (molar ratio 1:2) were mixed and dissolved in the smallest possible amount of acetone. Solvent was removed under vacuum at room temperature. The curing cycle was 150°C for 14 hr and 180°C for 8 hr.

*Instrumentation*

$^{13}$C-NMR spectra were recorded on a Varian XL 200 spectrometer, operating at 50.3 MHz. Samples of the resins were dissolved in DMSO-$d_6$, with TMS as internal standard.

i.r. Spectra of the samples were recorded on a Beckman i.r. 4260 spectrometer, using films of resin prepared on KBr pellets. The same sample was taken through a given cure cycle. i.r. Spectra of the sample were taken at selected times through the cure cycle.

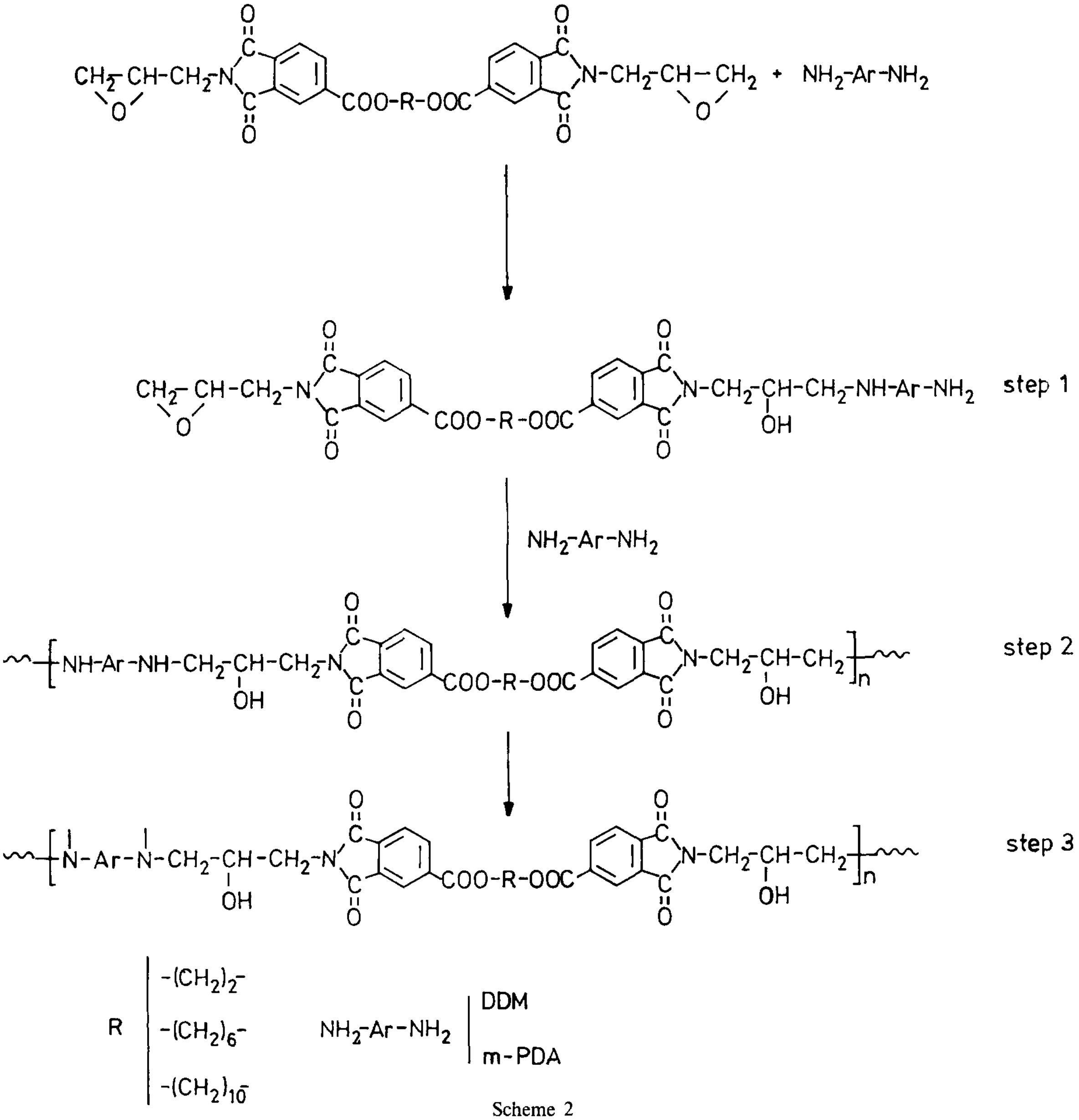
Thermogravimetric studies were carried out with a Perkin–Elmer TGS-2 thermobalance in $N_2$ at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

Two series of experiments were made with diamines as curing agents. (a) Comparison of the behaviour of the two aromatic diamines (DDM and *m*-PDA) towards the same *N,N'*-diglycidylimide, in order to identify the fastest hardener (4,4'-diaminediphenylsulphone was not tested because of the slower reaction observed previously. [2]). (b) *N,N'*-diglycidylimides were submitted to the same curing cycle with DDM that showed the fastest evolution.

The initial curing temperature in all cases was 100°C because at lower temperatures the reactions did not occur. It was necessary to increase the temperature to 130°C to complete the crosslinking.

The chemistry of cure of epoxy resins by amine hardeners was studied using model compounds [3–5]. When primary aromatic amines react with an epoxy resin, it is possible to detect a linear polymer intermediate because of the smaller reactivity of the formed secondary amines, compared with primary amines, with epoxy groups. According to this feature, we have detected some intermediate stages in our curing processes as shown in Scheme 2.



Scheme 2

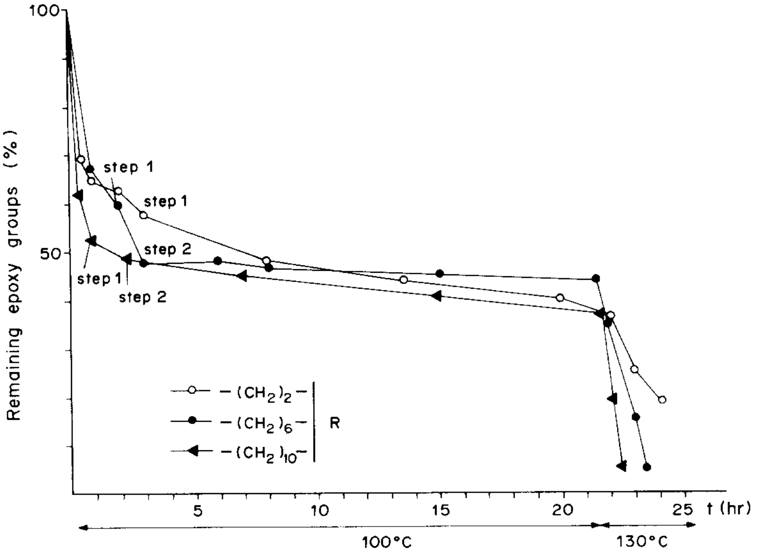


Fig. 1. Remaining epoxy groups (%) as a function of cure time.

The $N,N'$-diglycidylimide 1(b) was also cured with phthalic anhydride. The use of acid anhydrides as curing agents has been previously reported [6, 7] with or without catalysts.

Uncatalyzed reactions require higher temperatures. So, in our case a temperature of 150°C was necessary to initiate the process. It was also reported that etherification takes place between the epoxy and the hydroxyl group, so it is not possible to define successive steps as in the curing with amines.

### *i.r. Spectroscopy*

It has been shown that i.r. spectroscopy may be used to determine the epoxy content of an epoxy resin [8]. The absorbance at about 910 $cm^{-1}$ due to the epoxy group is proportional to the epoxy content determined chemically. As the epoxy content decreases with the extent of curing, it is possible to follow the reaction by this technique up to the end of the crosslinking. Chemically, this is not possible because of the high insolubility of the products in the advanced stages of the curing.

We have used as the reference band needed in the base line method [9], the band at 1780 $cm^{-1}$ ($\nu_{C=O}$ imide). Using this technique, we have observed that faster reactions took place with DDM as curing agent. For this reason, DDM was utilized for comparing the reactivities of the various $N,N'$-diglycidylimides. Figure 1 shows the remaining epoxy content (%) against time. It can be seen that curing rate increases slightly with aliphatic chain length in the epoxy resin, mainly at the beginning probably because melting point decreases in the same order. It can also be observed that after about 8 hr the reactions stopped and increase of the temperature was necessary to complete them.

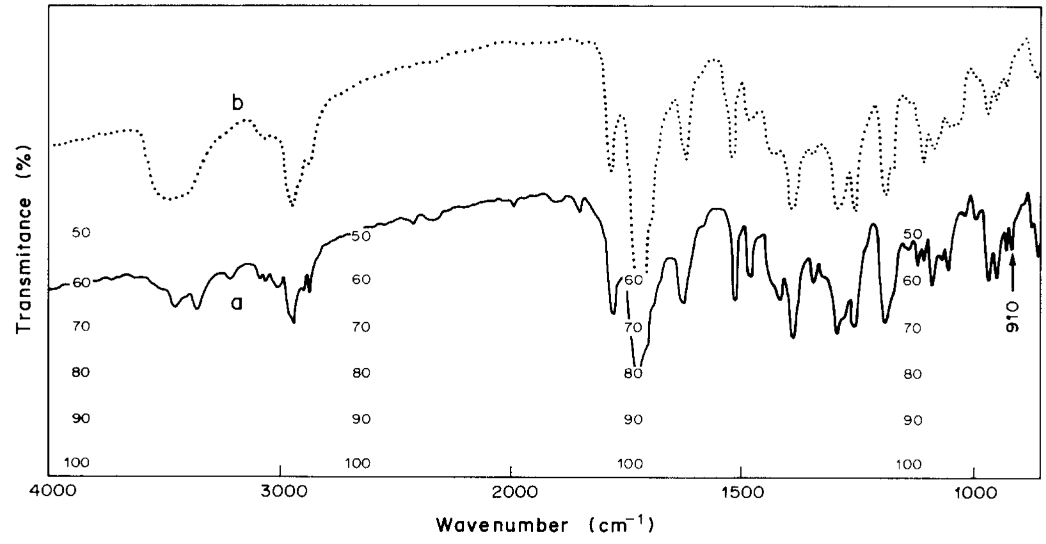


Fig. 2. i.r. Spectra of the reaction mixture (1b + DDM): (a) at the start; (b) at the end of the reaction.

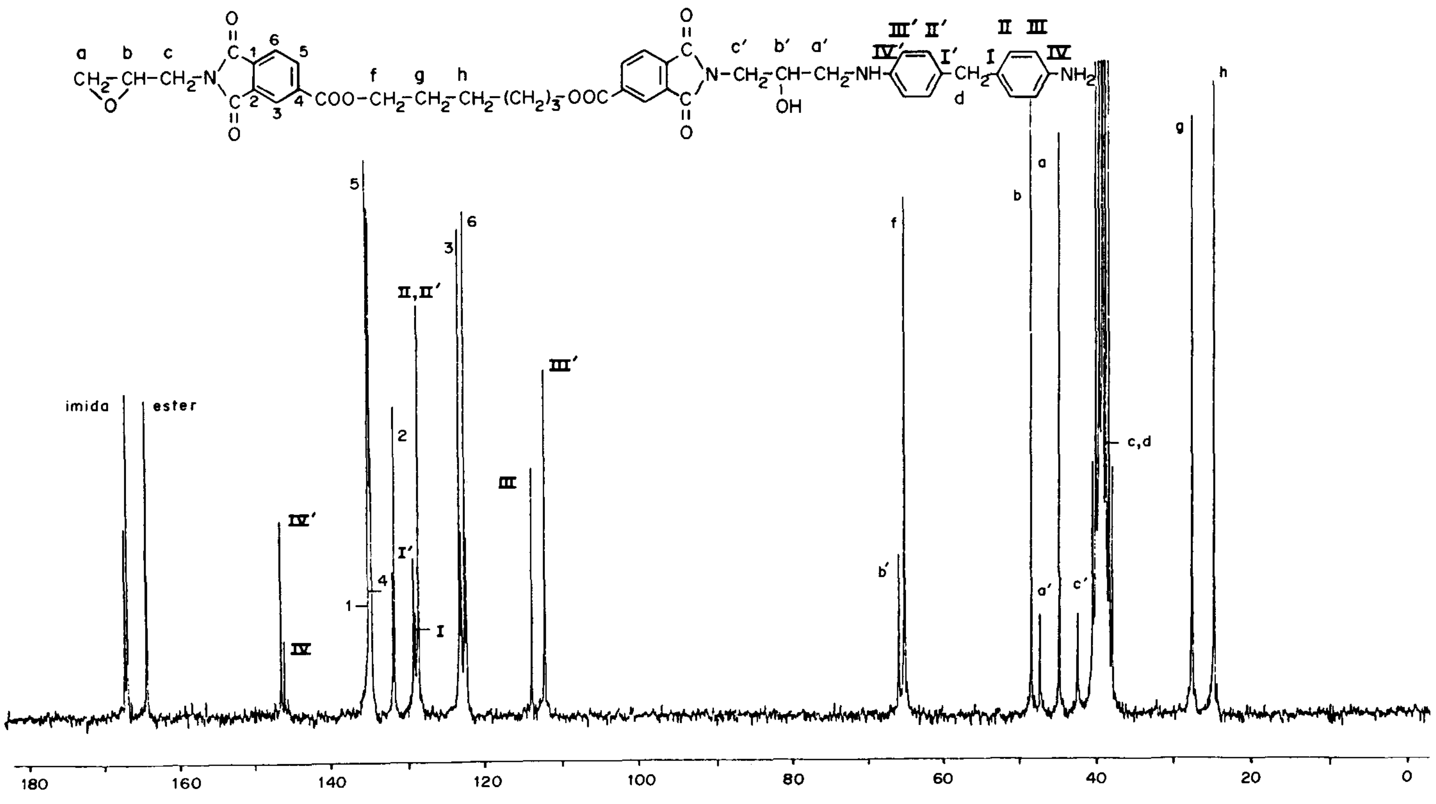


Fig. 3. $^{13}$C-NMR spectrum of the reaction mixture (1b + DDM) at 20 min heating, corresponding to the first step.

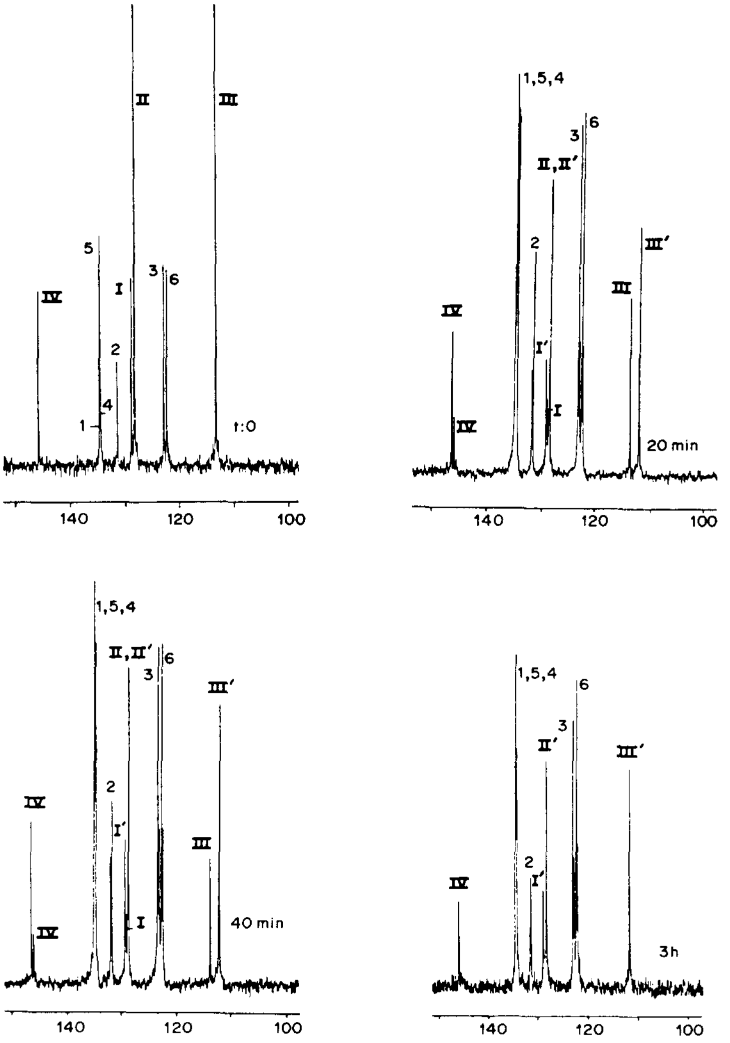


Fig. 4. Aromatic region of $^{13}$C-NMR spectra of the reaction mixture (1b + DDM) at 100°C and various reaction times.

The initial and final spectra of the mixture of *N*,*N*′-diglycidyl-1,6-bis(imidetrimellitate)hexane (1b) and DDM are collected in Fig. 2. In the former, two bands corresponding to the asymmetric and symmetric vibrations of aromatic primary amines are observed at 3475 and 3380 cm$^{-1}$ respectively. In the same way, the band due to the epoxy ring is seen at 910 cm$^{-1}$. In the spectrum of the cured product, a broad band at around 3500 cm$^{-1}$ characteristic of –OH groups is present, and corresponding epoxy and primary amine groups have disappeared.

### *$^{13}$C-NMR spectroscopy*

By $^{13}$C-NMR spectroscopy, it was possible to detect some intermediate species in the curing process and, when aromatic primary diamines were used as hardener, steps 1 and 2 have been characterized.

Figure 3 shows the $^{13}$C-NMR spectrum for the curing reaction between 1b and DDM. It shows eight signals assignable to aromatic carbons of the DDM. This splitting is attributable to the loss of molecular symmetry in the aromatic diamine at the first step of the reaction (see Scheme 2).

The progress of reaction can be observed with the evolution of the aromatic diamine carbons as shown in Fig. 4.

The spectrum recorded after 3 hr heating was simplified again, because of the recovery of the molecular symmetry in the second step (see Scheme 2). Subsequent steps could not be detected due to the insolubility of the products in the usual deuterated solvents.

The aliphatic region in Fig. 3 shows glycidyl and methylene signals and three new peaks assignable to the newly formed unit (a′, b′, c′). Notice the splitting of the carbonylic and some aromatic carbons of the imidic structure.

The same study was done for the other *N*,*N*′-diglycidylimides (1a and 1c) confirming the relative reaction rate. Thus 1c with a longer aliphatic chain reaches the second step in only 2 hr; while 1a with the shortest chain remains at the first stage at this time.

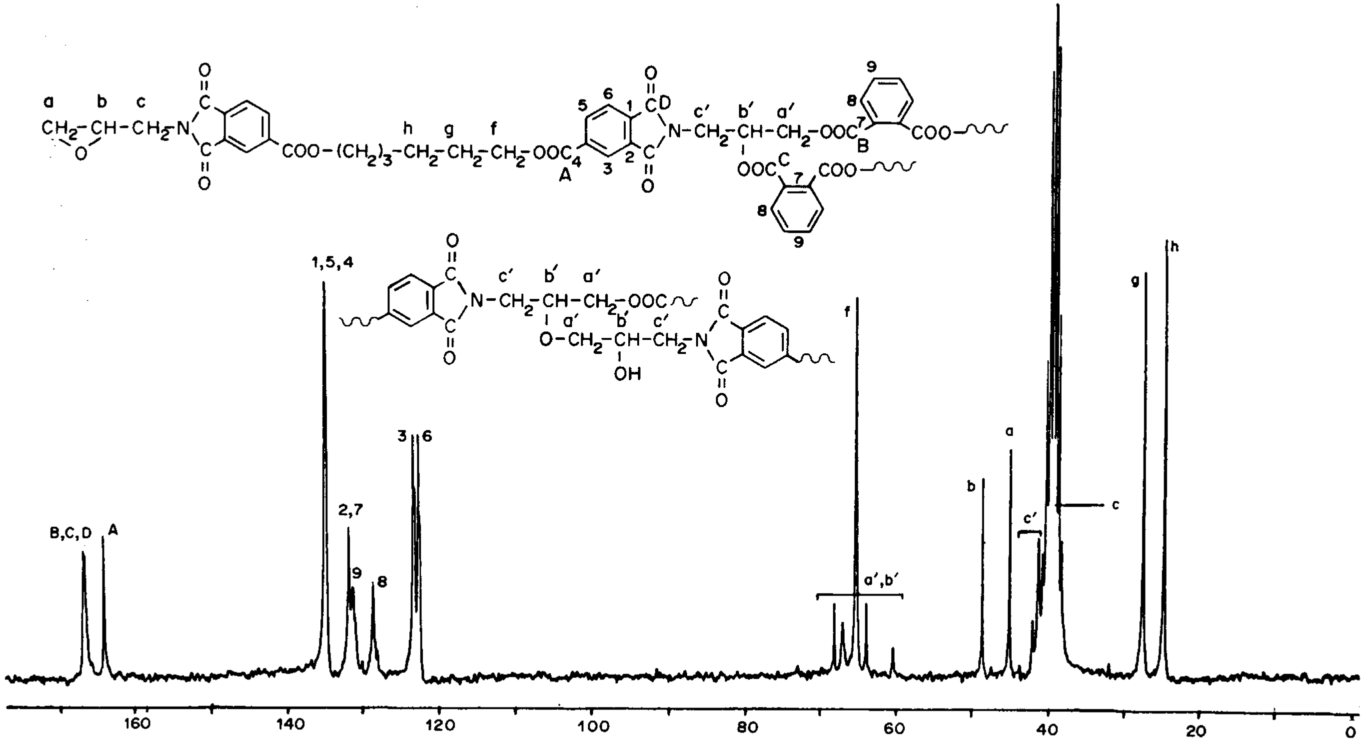
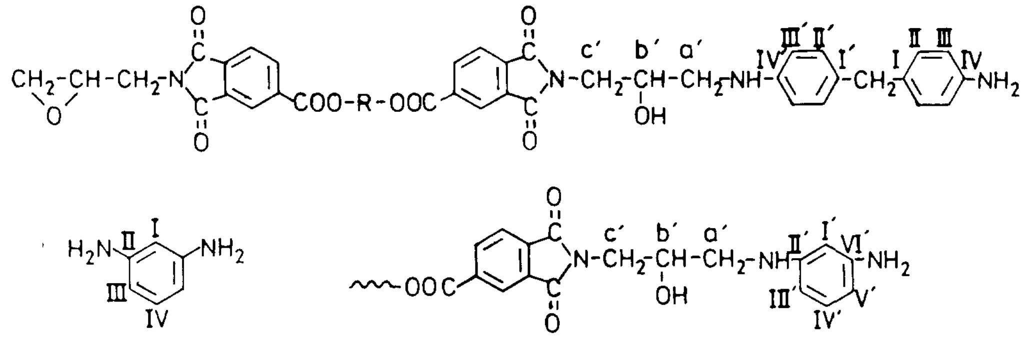


Fig. 5. $^{13}$C-NMR spectrum of the reaction mixture (1b + PPA) after 2 hr heating.

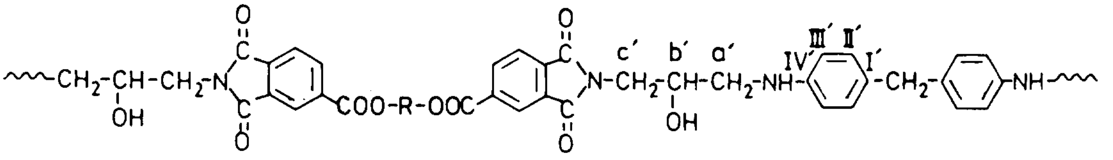
Table 1. Chemical shifts of the more significant signals corresponding to the first step intermediate in DMSO-$d_6$ ($\delta$ in ppm)



| R | a′ | b′ | c′ | I | II | III | IV | I′ | II′ | III′ | IV′ | V′ | VI′ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $-(CH_2)_2-$ | 47.6<br>(t) | 66.3<br>(d) | 42.7<br>(t) | 129.4<br>(s) | 129.0<br>(d) | 113.9<br>(d) | 145.9<br>(s) | 129.6<br>(s) | 129.0<br>(d) | 112.3<br>(d) | 146.7<br>(s) | — | — |
| $-(CH_2)_6-$ | 47.5 | 66.2 | 42.6 | 129.3 | 128.8 | 113.9 | 146.2 | 129.5 | 128.8 | 112.6 | 146.6 | — | — |
| $-(CH_2)_{10}-$ | 47.5 | 66.2 | 42.6 | 129.3 | 128.8 | 113.9 | 146.2 | 129.5 | 128.8 | 112.2 | 146.6 | — | — |
| $-(CH_2)_6-$* | 47.6 | 68.2 | 42.3 | 104.0<br>(d) | 148.8<br>(s) | 105.7<br>(d) | 129.7<br>(s) | 99.7<br>(d) | 148.8<br>(s) | 103.0<br>(s) | 129.7<br>(s) | 105.1<br>(d) | 148.8<br>(s) |

*Obtained with *m*-PDA as curing agent in $CDCl_3$.

Table 2. Chemical shifts of the more significant signals corresponding to the second step intermediate in DMSO-$d_6$ ($\delta$ in ppm)



| R | a′ | b′ | c′ | I′ | II′ | III′ | IV′ |
|---|---|---|---|---|---|---|---|
| $-(CH_2)_6-$ | 47.5<br>(t) | 66.2<br>(d) | 42.6<br>(t) | 129.5<br>(s) | 128.8<br>(d) | 112.2<br>(d) | 146.6<br>(s) |
| $-(CH_2)_{10}-$ | 47.5 | 66.2 | 42.6 | 129.4 | 128.8 | 112.2 | 146.6 |

Table 3. Thermal parameters of crosslinked polymers

| Glycidylic compound | Curing agent | $T_{max}$ (°C) | Weight loss at temperature (°C) 10% | 20% | 30% | 50% | Weight residue (%) at 500°C |
|---|---|---|---|---|---|---|---|
| 1a | DDM | 350 | 272 | 330 | 350 | 400 | 42 |
| 1b | DDM | 367 | 335 | 353 | 370 | 400 | 36 |
| 1c | DDM | 362 | 348 | 357 | 365 | 390 | 29 |
| 1b | *m*-PDA | 358 | 330 | 348 | 360 | 382 | 32 |
| 1b | PAA | 390 | 330 | 350 | 360 | 385 | 15 |

Figure 1 shows the times that different steps have been detected by $^{13}$C-NMR spectroscopy.

Table 1 includes the $^{13}$C-NMR chemical shifts of the more significant signals, including the results obtained by using DDM and m-PDA. Table 2 summarizes data for the second step.

A similar study has been carried out using PAA as curing agent. In this case, it was not possible to detect different steps as in the preceding experiments.

Due to both esterification and etherification occurring to similar extents in uncatalyzed conditions, it was very difficult to assign all the observed signals.

Figure 5 shows the spectrum of the 1b and PAA reaction mixture, while it was soluble in DMSO-$d_6$. In this spectrum, the splitting of the carbons 3 and 6 in the aromatic region is shown, indicating that curing occurs. About 40 ppm, two new signals corresponding to carbons c′ appear. Between 60 and 70 ppm several peaks can be seen due to both esterification and etherification processes.

### *Thermal behaviour*

Thermogravimetric analysis has allowed us to compare the thermal stabilities of the crosslinked polymers obtained. The relative thermal stabilities of the three-dimensional polymers were assessed by comparing the parameters listed in Table 3, obtained from the TGA curves. It was found that polymer obtained with PAA shows the highest temperature for maximum rate of weight loss ($T_{max}$), while its char yield at 500°C is the smallest. Although the differences in weight loss between the polymers obtained from the three diglycidylimides with the same curing agent were not significant, the char yield increases when the aliphatic chain is shortened.

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