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# Synthesis, characterization and polymerization of isobutylbis(glycidylpropylether) phosphine oxide

M$^a$ José Alcón, Gemma Ribera, Marina Galià, Virginia Cádiz*

*Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Plaça Imperial Tarraco, 1, 43005 Tarragona, Spain*

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## Abstract

In an attempt to obtain flame-retardant epoxy resins, a new diglycidylphosphine oxide, isobutylbis(glycidylpropylether)phosphine oxide (IHPO-Gly) was synthesized by reaction of isobutylbis(hydroxypropyl)phosphine oxide with epichlorohydrin and NaOH under phase transfer catalyst conditions. The thermal behaviour of IHPO-Gly was investigated by DSC and TGA and, together with thermal homopolymerization, isomerization and decomposition were detected. The reactivity of this novel diglycidyl compound was studied using boron trifluoride monoethylamine ($BF_3$·MEA) or 4-dimethylaminopyridine (DMAP) as catalysts and 2,4-diaminotoluene (DAT), hexahydrophtalic acid anhydride (HPA) or dicyandiamide (DICY) as hardeners. The thermal and flame retardant properties of the final thermosets were studied and V-0 materials were obtained in all cases except when $BF_3$·MEA was used as catalyst.

*Keywords:* Phosphine oxide; Flame retardant; Crosslinking; Epoxy phosphorilated

## 1. Introduction

Epoxy resins have the following excellent characteristics: moisture, solvent, and chemical resistance; toughness; superior electrical and mechanical properties; and good adhesion to many substrates. Their versatility has led to their being widely applied industrially [1]. However, their main disadvantage is that they are more flammable than similar thermosets since they have a reduced tendency to carbonize. After the ignition source has been removed they continue to burn on their own. In recent years, modification of epoxy resins has received increasing attention in an attempt to improve their flame resistance. So-called intumescent systems are currently being developed to be environmentally friendly fire retardants, providing low smoke and toxicity exposure, as possible alternatives to traditional halogen-based systems [2,3].

Phosphorus compounds are well established as components of flame retardant additives [4]. Phosphorous-containing flame retardants influence the reaction taking place in the condensed phase. Their effectivity depends on the chemical structure of the polymer and they are particularly effective in materials with a high oxygen content such as epoxies [5]. Phosphorus additives operate predominantly through a mechanism in which combustion of the outer layers of the polymeric material containing the flame retardant leads to an intumescent carbonaceous char. This acts as a physical and thermal barrier to further combustion, by impeding heat transfer to the underlying layers of polymer and, therefore, impeding the release of further flammable volatiles.

The use of additives as flame retardants, however, has disadvantages. If they are to be effective, for example, concentrations must be relatively high and they may be lost from the polymer during service. To address some of the problems associated with the additive route to flame retardant, we have turned our attention to flame retardant strategies that involve chemically attaching flame retardant moieties directly to the polymer backbone in a reactive strategy. In this case, it is important for the phosphorus to have bonds with carbon atoms. Indeed, the P–C bond in a phosphonate is more stable to hydrolysis than the P–O–C bond in a phosphate and more stable than the P–H bond in a dialkyl phosphite. Moreover, the P–C bond is broken just before the C–C bond because of its lower atomic bond energy [6].

Various diglycidylether compounds have been

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* Corresponding author. Tel.: +34-977559557; fax: +34-977559563.
*E-mail address:* cadiz@quimica.urv.es (V. Cádiz).

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synthesized from phosphoric, phosphonic or phosphinic acids and, therefore, they contain low stability P–O–C bonds [7]. In recent years, some diglycidyl ethers have been synthesized from a bulky and rigid phosphorus-containing reactive 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide [8–11]. All these aryl phosphinate compounds contain P–O–C bonds, but show a thermal stability unusually high. This stability has been attributed to the O=P–O group being protected by phenylene groups.

In a previous paper we studied the synthesis and polymerization of a novel glycidyl phosphinate, containing the moiety 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, where the glycidylic group was directly attached to the phosphorus atom [12]. In our search for new phosphorus-containing glycidyls with high thermal and chemical stability without P–O bonds, we considered phosphine oxides. The nature of this group has improved the flammability properties in thermosets while the polarity of the bond increases the hydrogen bonding ability of the resulting epoxy, possibly improving network adhesion to various substrates [13,14]. So, in this study, we report the synthesis of isobutylbis(glycidylpropylether) phosphine oxide (IHPO-Gly) and its reactivity.

## 2. Experimental part

### 2.1. Materials

Commercial isobutylbis(hydroxypropyl) phosphine oxide (IHPO) was a gift from Cytec Canada Inc. (trade name Cyagard RF1243). Epichlorhydrin (EPC) (Fluka) and tetrabutylammonium hydrogen sulfate (Aldrich) were used as received. All solvents were purified by standard procedures. The curing agents 2,4-diaminotoluene (DAT), phthalic and hexahydrophthalic acid anhydride (PA and HPA), 4-dimethylaminopyridine (DMAP), boron trifluoride monoethylamine ($BF_3$·MEA) and dicyandiamide (DICY) were purchased from Aldrich and used without any further purification.

### 2.2. Synthesis of isobutyl bis(glycidylpropylether) phosphine oxide (IHPO-Gly) [15]

A mixture of 10 g (0.25 mol) of sodium hydroxide, 18.5 g (0.20 mol) of epichlorohydrin and 0.39 g (1.16 mmol) of tetrabutylammonium hydrogen sulfate was vigorously stirred with diethyl ether (100 ml), at room temperature. Then, 4.44 g (0.02 mol) of isobutylbis(hydroxypropyl)phosphine oxide was slowly added to the mixture, while cooling in ice so that the temperature did not exceed 25 °C. The progress of the reaction was monitored by TLC (acetone/methanol 4:1, $R_f = 0.45$). After stirring for 5 h at room temperature the reaction was complete. The reaction mixture was filtered and evaporated to dryness, and the brown oil obtained was purified by flash chromatography with a silica gel column and acetone and acetone/methanol (4:1) as the eluents. When the solvent was removed 5.16 g of pure isobutylbis(glycidylpropylether) phosphine oxide (yield 77%) was obtained as a brown oil.

$C_{16}H_{31}O_5P$ (334): calcd C 57.47%; H 9.34%; P 9.26%; Found: C 54.79%; H 9.18%; P 9.13%.

$^1H$ NMR ($CDCl_3$): $\delta = 3.74$ (dd, 2H, 2.8, 11.6 Hz); 3.58–3.48 (m, 4H); 3.33 (dd, 2H, 6.0, 11.6 Hz); 3.14–3.10 (m, 2H); 2.78 (t, 2H, 5,2 Hz); 2.58 (dd, 2H, 2.8, 5,2 Hz); 2.15–2.03 (m, 1H); 1.87–1.73 (m, 8H); 1.59 (dd, 2H, 6,8 Hz, $J_{H-P} = 10.8$ Hz); 1.06 (d, 6H, 6,4 Hz).

$^{13}C$ NMR ($CDCl_3$): $\delta = 71.64$ (t); 71.58 (t, $J_{C-P} = 13.0$ Hz); 50.93 (d); 44.29 (t); 37.07 (t, $J_{C-P} = 64.9$ Hz); 25.72 (t, $J_{C-P} = 65.6$ Hz); 24.95 (q, $J_{C-P} = 8.4$ Hz); 23.58 (d, $J_{C-P} = 3.8$ Hz); 22.42 (t, $J_{C-P} = 3.1$ Hz). $^{31}P$ NMR ($CDCl_3$): $\delta = 48.59$.

### 2.3. Instrumentation

$^1H$ 300 MHz, $^{13}C$ 75.4 MHz and $^{31}P$ 161.9 MHz NMR spectra were obtained using a Varian Gemini 300 spectrometer with Fourier transform, $CDCl_3$ as solvent and TMS or phosphoric acid as internal standards. Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer using $N_2$ as a purge gas (20 ml/min) at scan rates between 5 and 20 °C/min. Samples of ca. 5 mg were tested in closed aluminium pans by duplicated analysis. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with $N_2$ as a purge gas at scan rates of 10 °C/min. For thermal analysis powdered samples were used for uncured mixtures and block samples were tested for cured materials.

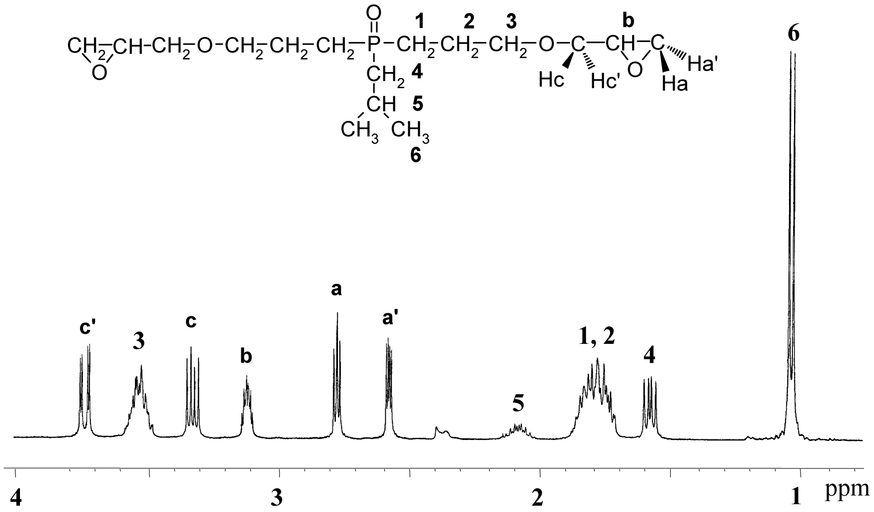
The quantitative analyses of C and H were carried out on a Perkin–Elmer 2400 CHN microanalyzer. P quantitative analysis was carried out on a Perkin–Elmer plasma 40 ICP spectrometer and the sample had previously been treated with nitric acid in a closed pan.

### 2.4. General procedure for modified UL-94 burn test

Five 4 mm diameter × 20 mm long sample bars were used for this test. The height of the Bunsen burner flame was 25 mm and the height from the top of the Bunsen burner to the bottom of the test bar was 10 mm. All test bars underwent two trials and each trial consisted of ignition for 10 s. The flame was then removed and we recorded the time for self-extinguishing and dripping characteristics.

### 2.5. Polymerization

Samples were prepared by dissolving isobutyl bis(glycidylpropylether) phosphine oxide (IHPO-Gly) in $CH_2Cl_2$ and mixing the resulting solution with the required amount of selected initiator or crosslinking agent previously dissolved in $CH_2Cl_2$. This solution was evaporated at room temperature under vacuum. About 5 mg of a known weight of the



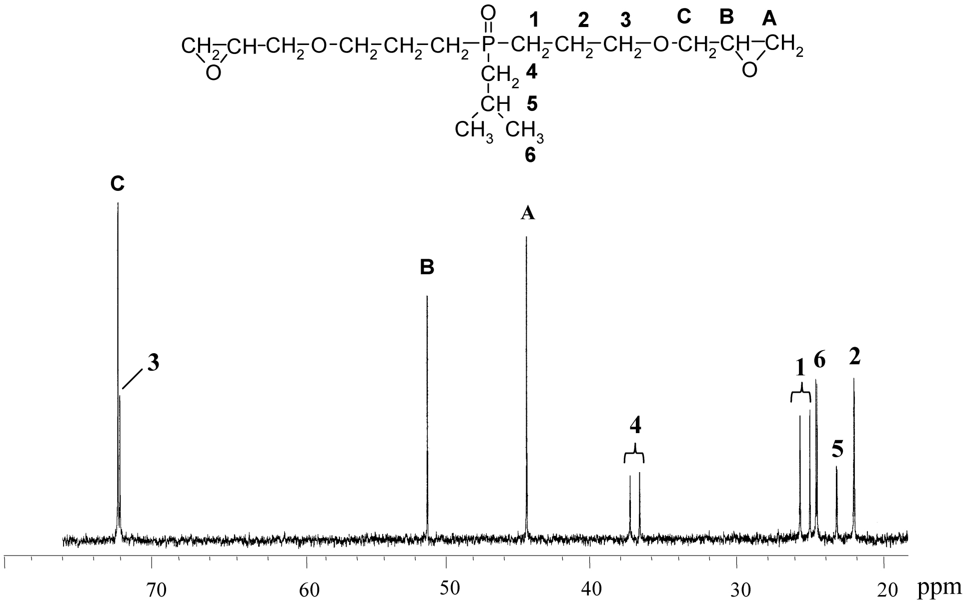


Fig. 1. $^1$H and $^{13}$C NMR spectra of IHPO-Gly.

mixture was put into the aluminum pan and polymerization was monitored in a DSC experiment.

Cured samples for thermogravimetric measurements and bars for the UL-94 test were prepared in the same way using silanized sealed glass tubes and carrying out the curing at 160 °C for 5 h. Post curing was carried out at 180 °C for 5 h.

## 3. Results and discussion

Phosphine oxide diols are used in epoxy resins as flame retardants [16] but, to our knowledge, glycidylic derivatives from these compounds have not been reported. In this study we use isobutylbis(hydroxypropyl)phosphine oxide as a starting material to synthesize the diglycidyl derivative.

Several procedures have been described in the literature to transform 1-alkanols to the corresponding alkyl-1-glycidylethers but in the present case some restrictive considerations had to be taken into account because of the presence of the phosphoryl bond. Thus, these compounds can be prepared in a two step synthesis by reacting the alcohol and EPC under a Lewis acid catalyst and subsequently dehydrochlorinating the intermediate halohydrin to yield the desired glycidylic compound [17]. In this case the coordination of the Lewis acid to the oxygen in the phosphine oxide prevented catalytic activity, so a mixture of undesired compounds was obtained. Another successful method for obtaining glycidyl derivatives uses a large excess of EPC and benzyltrimethylammonium bromide (BTMA) as catalyst [18]. This method gave good results in the synthesis of glycidylesters, glycidylimides, and glycidyl ethers from phenols, but not from alkanols because of their

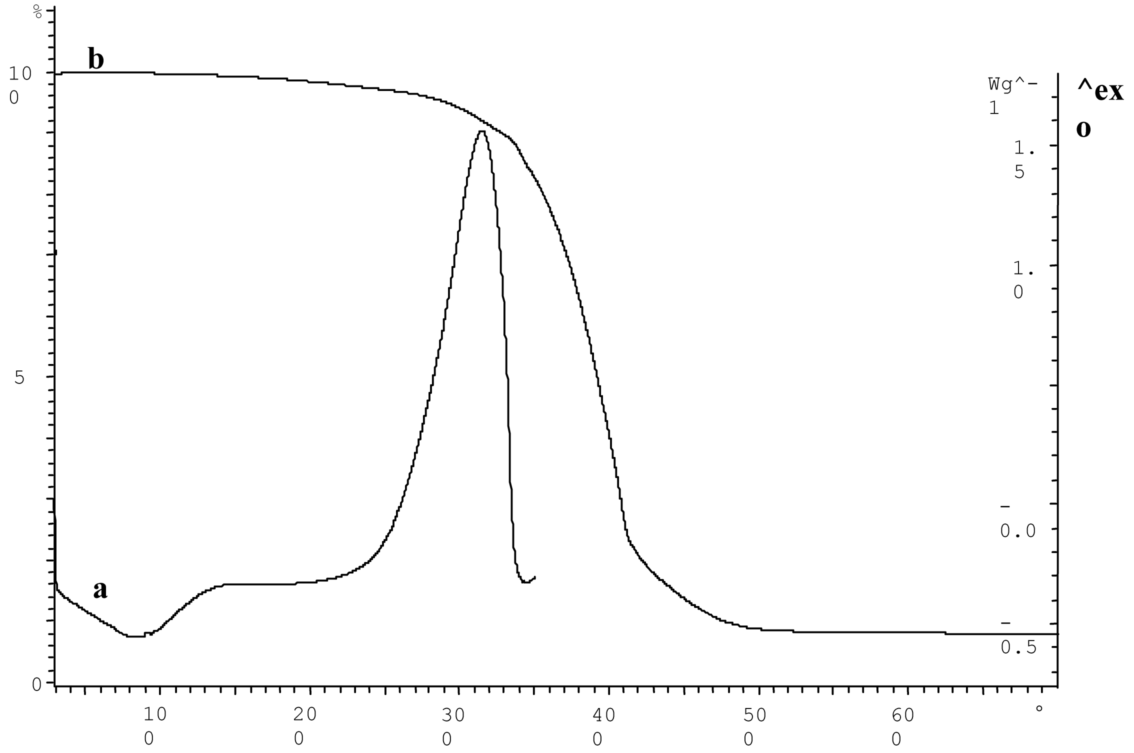
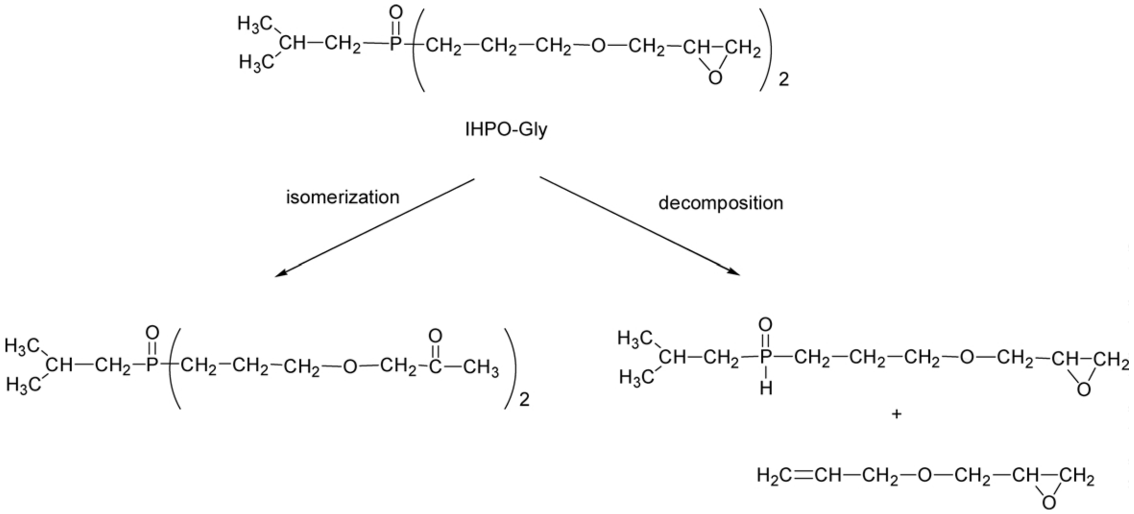


Fig. 2. DSC (a) and TGA (b) plots of IHPO-Gly (10 °C/min).

lower acidity. Here, the method used was to react the starting phosphine oxide containing primary alcohols, EPC and NaOH under phase transfer catalyst conditions [15,19]. The reaction was carried out at room temperature for 5 h. $^{31}$P NMR measurements showed that the signal of the starting compound appeared at 52.9 ppm and that there was a new signal at 51.3 ppm, corresponding to the mono glycidylic compound at 20 min of reaction time. At 30 min, a new signal, attributable to the diglycidylic compound, appeared at 48.6 ppm. At the end of the reaction this last signal was the only one observed. Fig. 1 shows the $^1$H and $^{13}$C NMR spectra, respectively, with all the assignments. The oxirane ring signals in the $^1$H NMR spectrum show the expected pattern for the diastereotopic protons. $^{13}$C NMR spectrum shows the signal splitting of the carbons close to the phosphoryl group and $J^1$, $J^2$ and $J^3_{\mathrm{C-P}}$ could be calculated and are in agreement with the reported data [20].

The thermal behaviour of IHPO-Gly was investigated by DSC and TGA (Fig. 2). The dynamic DSC plot of IHPO-Gly shows a broad exotherm centered at 315 °C and the TGA plot shows that no significant degradation takes place below this temperature. After this thermal treatment the final material was soluble in common organic solvents. IR absorptions at 3384, 1720 and 1636 cm$^{-1}$ suggest the



Scheme 1.

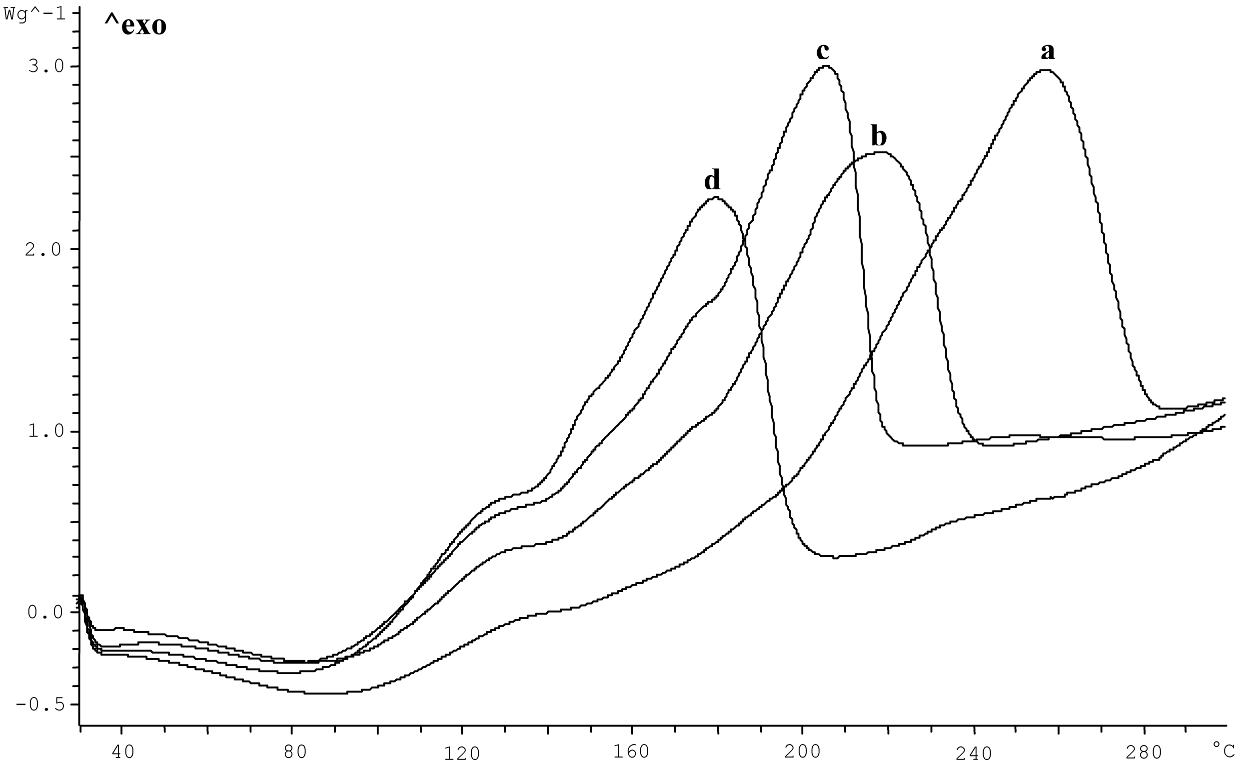


Fig. 3. DSC plots of IHPO-Gly with $BF_3$·MEA (a) 1% mol; (b) 5% mol; (c) 10% mol; (d) 30% mol.

presence of hydroxyl, carbonyl groups and C=C bonds, respectively. $^1$H NMR spectroscopy shows the disappearance of the signals attributed to the glycidylic protons and the appearance of signals due to vinylic protons. $^{13}$C NMR spectroscopy confirms these findings and also shows signals at about 70 ppm corresponding to the polyether main chain and a small signal at about 190 ppm attributable to the carbonyl group. All these results lead us to conclude that, together with thermal homopolymerization, an isomerization process takes place. This is shown in Scheme 1. It has been reported that the phosphoryl group of tertiary phosphine oxides can act as a nucleophile and can be involved in the isomerization of epoxides to carbonyl compounds [21]. Moreover, it has been reported that aliphatic tertiary phosphine oxides that contain β-hydrogens thermally decompose, presumably by a cyclic concerted mechanism, to give the corresponding alkene and the secondary phosphine oxide (Scheme 1) [21]. Thus, thermal crosslinking of IHPO-Gly does not take place due to these secondary reactions at high temperature. The DSC exotherm can be attributed to isomerization and degradation, while weight loss in TGA curve must be due to degradation process.

### *3.1. Polymerization reaction*

The oxirane ring has a wide range of reactivity and an easy opening process. Epoxides can be cationically polymerized by various types of protonic and Lewis acid systems. They can also be anionically and coordinatively polymerized. Moreover, epoxy resins can be prepared by a step polymerization reaction between an epoxide and curing agents such as amines or carboxylic acid anhydrides.

The reactivity of synthesized novel diglycidyl compound has been studied using cationic catalysts such as $BF_3$·MEA [22], anionic catalysts such as 4-dimethylaminopyridine (DMAP) [23], and stoichiometric ratios of curing agents such as 2,4-diaminotoluene (DAT), phthalic and hexahydrophthalic acid anhydride [24] or dicyandiamide [25].

The polymerization of IHPO-Gly initiated by $BF_3$·MEA and monitored by DSC, shows a small exotherm at 120 °C followed by a much larger exotherm whose maximum temperature decreases when the catalyst ratio increases (Fig. 3). The first small exotherm was caused by the formation of the epoxide and $HBF_4$ complex (previously formed by thermal conversion of $BF_3$·MEA) [22]. When 1% $BF_3$·MEA was used a second exotherm centred at about 250 °C appeared due to homopolymerization. When the amount of $BF_3$·MEA was increased (from 1 to 30%) this exotherm shifted to lower temperatures and, at the highest ratio the homopolymerization reaction took place at 180 °C. This behaviour is in accordance with the fact that, at low concentrations, the Lewis acid catalyst coordinates to the oxygen in the phosphine oxide. This prevents its catalytic activity and retards the reaction at lower catalyst ratio. However, at higher catalyst concentrations the reaction temperature decreases.

The polymerization of IHPO-Gly initiated by 4-dimethylaminopyridine (DMAP) was investigated by DSC. Depending on whether the concentrations of the

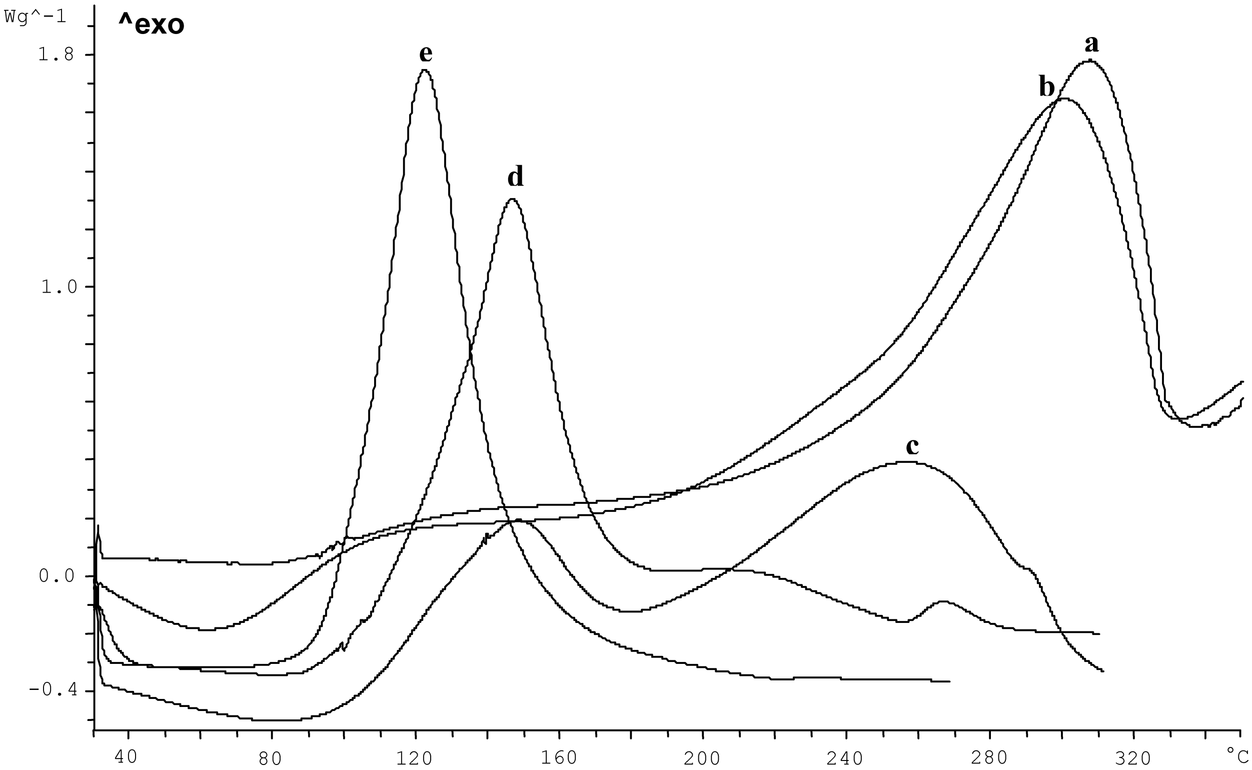


Fig. 4. DSC plots of IHPO-Gly with DMAP (a) 1% mol; (b) 2% mol; (c) 10% mol; (d) 20% mol; (e) 30% mol.

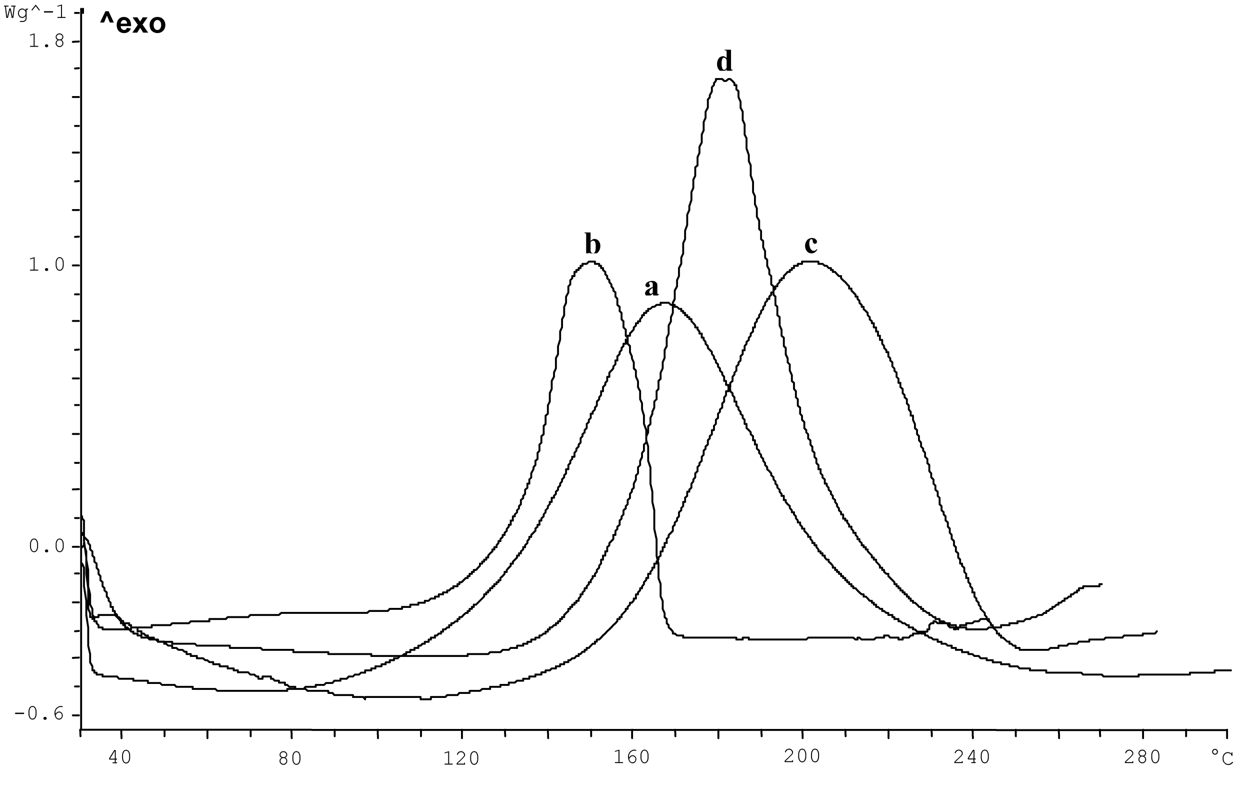


Fig. 5. DSC plots of IHPO-Gly with (a) DAT; (b) HPA; (c) DICY; (d) DICY-2-methylimidazole.

tertiary amine catalyst are high or low the mechanism that has been proposed for this kind of reaction shows different reaction types [26]. The first step is the opening of the oxirane ring by the amine followed by a homopolymerization reaction. On the other hand, at high concentration of tertiary amine, the epoxide group could be catalyzed by this amine for isomerization to occur and also to form allyl alcohol, which acts as a proton donor. Then, the allyl alcohol, tertiary amine, and epoxide group react together to form an active complex and polymerization begins. In contrast, at low concentrations of tertiary amine this last step can be negligible. We tested how adding catalytic amounts of tertiary amine influences the crosslinking behaviour of this new glycidyl compound. Fig. 4 shows the DSC curves of the mixtures containing 1, 2, 10, 20 and 30 mol%. As can be seen, at low concentrations, an exotherm appears above 300 °C (curves a and b), similar to the temperature mentioned above for the thermal behaviour of IHPO-Gly. When the amine catalyst concentration was increased to 10 mol% (curve c) a new exotherm appeared at lower temperatures which was attributed to amine catalyzed curing. For higher amine concentrations (curves d and e) only this latter process was observed.

When we used a primary amine such as 2,4-diaminotoluene (DAT) in stoichiometric amounts, the only reaction that occurred at about 160 °C (Fig. 5(a)) was the expected curing reaction, as can be seen from NMR analysis of the swelling polymer before the last steps of the reaction.

When phthalic and hexahydrophthalic acid anhydride were used as polyfunctional hardeners, the results were different. With the former, the mixture was found to be non-homogeneous and, therefore, only tests with hexahydrophthalic acid anhydride were carried out. As can be seen in Fig. 5(b), a broad exotherm corresponding to the expected crosslinking appears at 150 °C.

Table 1
Thermal properties of the crosslinked materials

| Curing agent | % P | $T_g$ (°C) | Nitrogen | | | Air | | |
|---|---|---|---|---|---|---|---|---|
| | | | $T_{10\%}$ (°C) | $T_{max}$ (°C) | $R_{700\ °C}$ | $T_{10\%}$ (°C) | $T_{max}$ (°C) | $R_{700\ °C}$ |
| $BF_3$·MEA | 8.1 | 13 | 331 | 380 | 14 | 320 | 372 | 10 |
| DMAP | 8.4 | 10 | 349 | 396 | 13 | 316 | 377 | 19 |
| DAT | 7.8 | 72 | 357 | 400 | 15 | 337 | 385 | 18 |
| HPA | 6.4 | 11 | 344 | 398 | 9 | 283 | 387 | 10 |
| DICY (3:1) | 8.6 | 37 | 339 | 390 | 10 | 308 | 364 | 20 |

Dicyandiamide (DICY) is one of the most widely used latent hardeners for epoxy resins. The mechanism for curing epoxy resins with DICY is complex and involves an initial reaction between all four active hydrogens with epoxy resins in the presence of an accelerator such as 2-methylimidazole. In addition to the usual amine/epoxide reaction, however, cyano and hydroxyl groups were consumed according to a final cure reaction between these groups. It was showed that 3 mol of epoxy per 1 mol of DICY was the ratio at which the reaction pathway was most similar to the one for the crosslinking that used primary amines as hardeners [25]. In this case a crosslinking exotherm centred at 200 °C was observed (Fig. 5(c)). Moreover, when 2-methyl-imidazole was added as an accelerator, there was a slight decrease in the maximum temperature of the crosslinking exotherm (Fig. 5(d)).

Table 1 shows the glass transition temperatures of the cured polymers. When crosslinking was carried out with $BF_3$·MEA or DMAP, a polyether network was obtained which had $T_g$ values of around 10 °C. When crosslinking took place through a step polymerization, $T_g$ values were higher except when an aliphatic curing agent such as hexahydrophthalic acid anhydride was used.

The thermal properties of the cured epoxy resins with the different curing agents were evaluated by TGA under nitrogen and air. Table 1 shows the temperature of the 10% weight loss, the temperature of the maximum rate of weight loss and the char yield at 700 °C. The polymers lose weight because the resin matrix decomposes, and unlike most phosphorus-containing compounds they do not show quite complicate weight loss behaviour from its derivative curves. This phenomenon plays an important role in improving the flame retardance of the phosphorus-containing resins and results in a high char yield at higher temperatures [27]. Increasing char formation can limit the production of

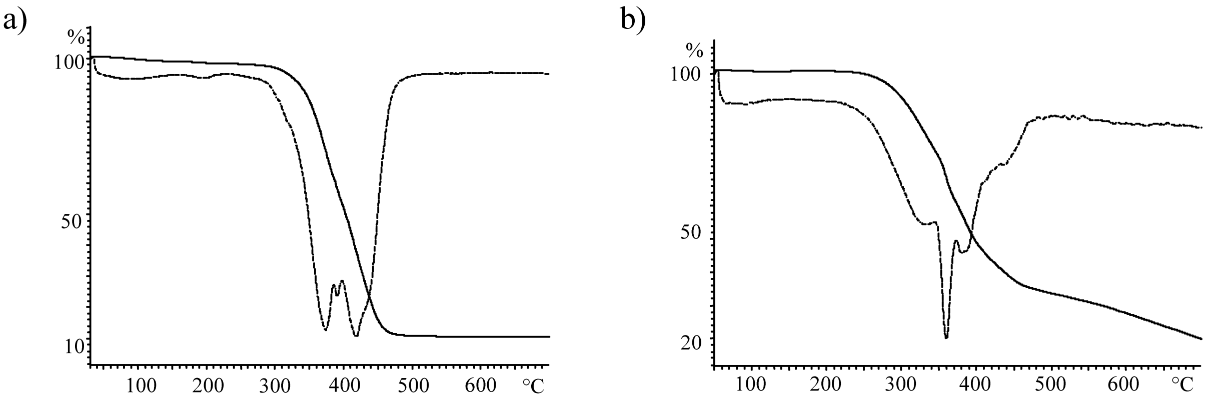


Fig. 6. TGA plots and derivative curves of IHPO-Gly cured with DICY (a) in $N_2$; (b) in air.

Table 2
UL-94 flame test results of the crosslinked materials

| | 1st Ignition[a] (s) | Obsd dripping[b] | 2nd Ignition (s) | Obsd dripping | UL-94 test |
|---|---|---|---|---|---|
| $BF_3$·MEA | 3,4,4 | No | 39,31,35 | No | V-1 |
| DMAP | 0,0,0 | No | 0,2,1 | No | V-0 |
| DAT | 0,0,0 | No | 1,0,2 | No | V-0 |
| DICY | 0,0,0 | No | 0,5,3 | No | V-0 |

[a] Time to self-extinguish after ignition. The three numbers are for three separate tests on separately cylindrical samples.
[b] Indicates that the sample did or did not drip onto the cotton patch below the test samples.

combustible gases, decrease the exothermicity of the pyrolisis reaction and decrease the thermal conductivity of the burning materials, and consequently, limit the flammability of the materials. However, in any case the obtained polymers exhibit char yields higher than 20%, what can be explained by considering the aliphatic structure of these networks. A complicated decomposition process was observed in nitrogen and in air for the novel epoxy resins, which contain P and a higher amount of N (DICY as crosslinker) and a second maximum in the derivative TGA appears (Fig. 6). The resins were less thermally stable in air than in nitrogen as can be seen from the temperature at which the resins showed its 10% weight loss as well as from the temperature corresponding to the maximum weight loss rate.

We tested the flame retardant properties of the synthesized material using UL-94 flame test, in which the sample was suspended above cotton [28]. The sample was subjected to two 10 s ignitions with a calibrated methane-fueled flame in a controlled-size unit that was free of passing air currents. After the first ignition, the flame was removed and the time for the polymer to self-extinguish was recorded. The second ignition was then performed on the same sample and the self-extinguishing time/dripping characteristics were recorded. If the sample self-extinguished in less than 10 s with no dripping, we considered it to be a V-0 material, which is an industry standard for flame retardancy. The results of burn tests are shown in Table 2. We can see that, according to the UL-94 test, almost all the polymer samples produced a V-0 material, as can be expected for the high phosphorus content, but a V-1 grade for UL-94 is achieved for $BF_3$·MEA.

This behaviour needs to be investigated further and experiments must be carried out with different phosphorus contents and/or nitrogen to tailor flame retardant epoxy resins with thermal and mechanical requirements for specific applications.

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