Study of the Crosslinking Reaction between Bisphenol A Diglycidyl ether (BADGE) and a Zinc Porphyrin by Fourier Transform Infrared Spectroscopy.

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ABSTRACT

The curing reaction of a system consisting of a diglycidyl ether of bisphenol-A (n=0) and ZnTPyP (Zinc 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphyrin) was studied by Fourier Transform Infrared Spectroscopy (FTIR). A semi-empirical quantum chemistry program (MOPAC) was used to corroborate the experimental data. The tertiary amine ZnTPyP not only initiates the reaction but also reacts with the resin forming pyridone. This study demonstrates that macrocycles can be used as cross-linking agents forepoxy resins and that when metallomacrocycles are used, metal ions can be introduced into the network structure.

KEYWORDS: FTIR; porphyrins; epoxy resins, tertiary amines

INTRODUCTION

Epoxy resins have a position of great importance in polymer industries because of their many different applicationsindustry (electrical, naval, aerospace, construction...) as well as in sports, medicine, and so on. The great success of epoxy resins are related to their light weight compared to other materials, high mechanical characteristics, great resistance to corrosion, and the possibility of different designs for particular applications[1]. On the other hand, porphyrins and related compounds, such as chlorophyll andhemin, are essential to many biological energy transduction processesincluding light harvesting and photocatalytic processes [2-5].For this study, the zinc meso-tetra (4-pyridyl) porphyrin (ZnTPyP, a tertiaryamine) has been chosen as the curing agent for the epoxy resin bisphenol-A diglycidyl ether (n=0) (BADGE).

The epoxy homopolymerization caused by tertiary amineshas been studiedby several authors[6-17]. This is a very complex process due to the concurrence of multiple reactionsinvolving at least the following steps: (1) initiation by adduct formation with transfer to hydroxyl compound; (2) propagation by any alkoxide anion present in thesystem; (3) chain transfer between any alkoxide anion and hydroxylic species and

(4) initiation regeneration by elimination or substitution.Recovering of the tertiary amine has been frequentlyreported in the literature[8-9,14,16,18]. However,the occurrence of termination reactionswithout regeneration of the tertiary amine, leading toincomplete curing of epoxy resins[14,16], has also been proposed.In fact, although epoxy homopolymerization with tertiary amines has been extensively studied [13-15,19-21], *apparently contradictory results concerning*the network formation have been reported.

This study is part of a project in which the effects of introducing macrocycles derivatives on the epoxy resinnetwork are investigated [22]. These crosslinking agents improve the stability of the resin at high temperatures, besides they have the ability to strongly bind metallic ions, forming complexes. *This could lead to develop epoxy polymers with new unexpected properties.*

EXPERIMENTAL

Materials and Sample preparation

Diglicidyl ether of bisphenol A (BADGE, n=0) (Resin 332, Sigma Chemical Co., St Louis, USA) and ZnTPyP (Sigma-Aldrich Chemie GmbH, Germany) were used without further purification.The structures of these compounds are shown in Fig. 1.
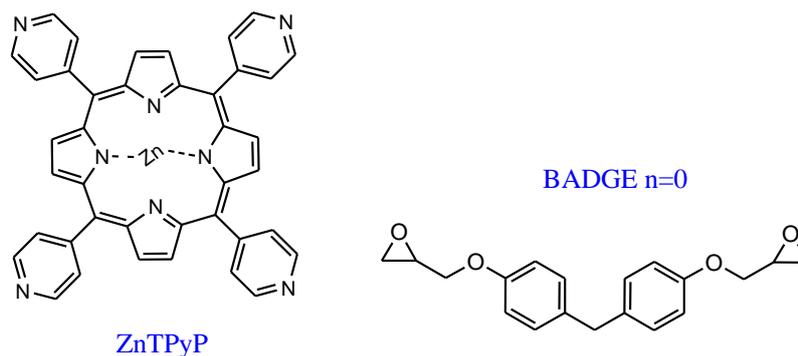
BADGE n=0

ZnTPyP

Figure 1.*Structures of BADGE, n=0 and ZnTPyP.*

First, epoxy resin and curing agent were carefully and homogeneouslymixed at the 9:1 (mol/mol) ratio at room temperature. Second, a sample ofthis mixture (typically 8–10 mg) was encapsulated in aluminumpans for the differential scanning calorimeter (DSC) analysis.The optimum (BADGE, n =0)/ZnTPyP ratio was determined bycuring experiments at different values of the epoxy/curingagent ratio by the dynamic method.The curing reaction was programmed between 50ºC and 350ºC at a heating rate of 10ºC/min.

FTIR

The curing process was monitored with an*Varian 670-IR* spectrophotometer with aresolution of 4cm^{-1}.Furthermore, an attenuated total reflection accessory with adiamond crystal (*PIKE GladiATR*; range: 4000–100 cm^{-1}) was used to determineFTIR spectra.

RESULTS AND DISCUSSION

The vibration band at 915 cm^{-1} has been chosen as areference band for the different vibration bands of the epoxygroups (760, 915, and 970 cm-1).Figure 2 shows the infrared spectra of the epoxy resin BADGE n=0 (blue line), the epoxy systemheatedfrom 50ºC to 230ºC (red line) and the epoxy system heated from 50ºC to 350ºC (purple line). It can be seen that the intensity of the vibration band of the terminal epoxy groups decreases during the curing reaction; at the same time ν(OH$^-$) at 3450 cm^{-1} increases in intensity.The ring-opening of the epoxy group generates a strong band at about 1130 cm^{-1}assigned to the asymmetric C-O-C stretching vibration[14]. The band at 710 cm^{-1} assigned to the stretching *vibrations of C-H bonds* in a *pyridine* ring practically disappears, suggesting that the pyridine ringswere destroyed upon reacting with BADGE n=0. At thesame time, new bandsappear at 1470 and 1650 cm^{-1}, which could be assigned to the carbonyl of pyridone and the unconjugated carbon double bonds. Therefore the tertiary amine ZnTPyP not only initiates the homopolimerization reaction but also reacts with the resin forming pyridone.
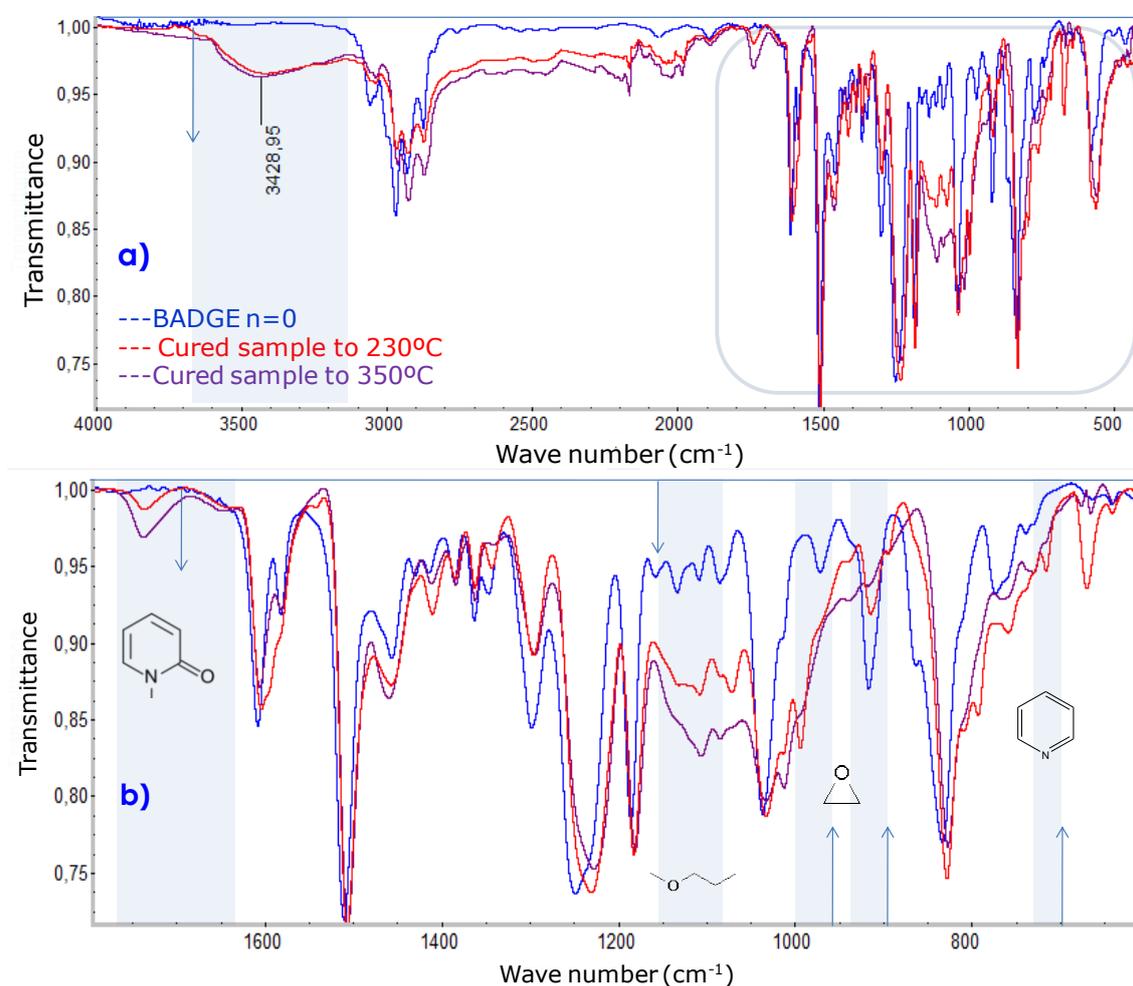
Figure 2.a)Comparison of FTIR spectra of BADGE n = 0 (blue line), the epoxy systemheatedfrom 50ºC to 230ºC (red line) and the epoxy system heated from 50ºC to 350ºC (purple line); b) FTIRspectra enlargement between1800 and 600 cm^{-1}.

It is proposed that epoxy groups of BADGE n=0 could be involved in two reactionsduring the curing process. At the same time that epoxy groups react with the pyridine rings (Figure 3), the homopolymerization mechanism of the epoxy groups could

appearwhich implies the formation of aliphatic ethers (Figure 4). Both reactions could be catalyzed by zinc, which would act as a Lewis acid.
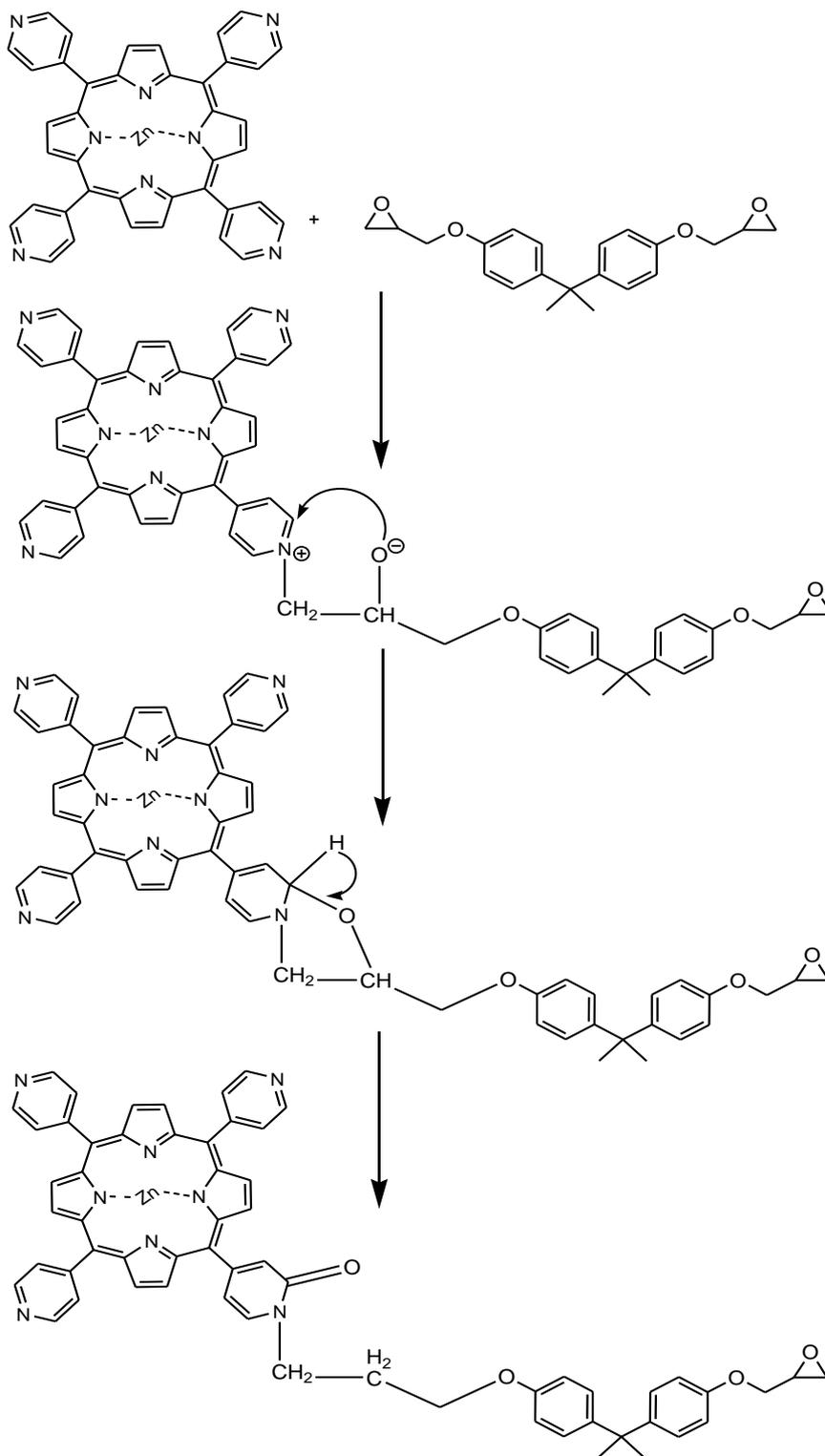
Figure 3.*Proposed mechanism for the heteropolymerization. Formation of the pyridone.*

The reaction was initiated by the nucleophilic attackof the tertiary nitrogen atom of ZnTPyP on the epoxide groups of BADGE, forming a salt. In the second step, the

oxygen ion immediately attacks the α-position ofpyridine ring and the aromatic structure of pyridinering is destroyed, forming pyridone[23].
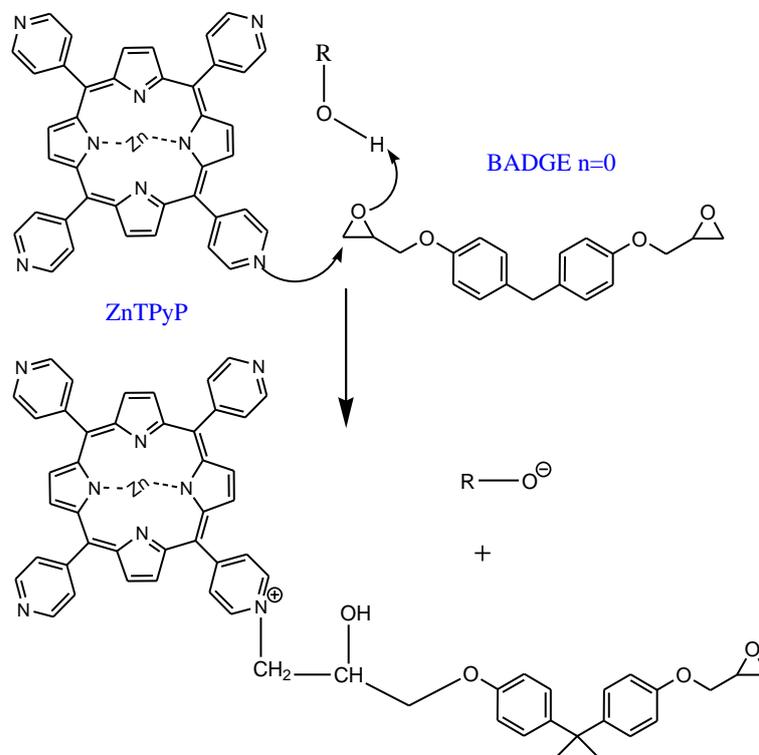
Figure 4.*Proposed mechanism for the homopolymerization*

It is proposed that the homopolymerization of epoxide groups could be initiated by the nitrogen atoms of pyridine rings [24].Note that *the homopolimerizationunder identical conditions but in the absence ofZnTPyP,is a fairly slow process.*

A semi-empirical quantum chemistry program was used for verifying the occurrence of the pyridone formation. Various molecular *properties* of different *chemical* structures *werecalculated* for predicting thebehavior of the system. The *choice* of *method* (semi-empirical or ab-initio) is a key factor to calculate the structures and properties of molecules and solids. Both *ab initio* and semi-empirical approaches involve approximations. The ab-initio methods are more accurate but need more computer time; whereas simplifications introduced by semi-empirical approaches assume that the chemical behavior exclusively depends on the valence shell, not including internal electrons.

The software MOPAC2012[25] was chosen in order to make all the calculations needed for this study. Different Hamiltonians available inMOPAC2012 (AM1, PM3, MNDO, PM5, PM6 and PM7) were used for studying the1-methyl-2-pyridone, used as a model compound for assessingthe validity and reliability of the calculated vibration frequencies. Experimental data of 1-methyl-2-pyridone are shown in Figure 5.

HIT-NO=2787	SCORE= ( )	SDBS-NO=4795	IR-NIDA-02746 ; LIQUID FILM
1-METHYL-2-PYRIDONE			
C$_6$H$_7$NO			

3240	81	2647	84	1496	42	1166	16	766	11
3132	68	1833	79	1470	36	1136	31	729	26
3074	49	1801	79	1437	46	1053	29	595	28
3031	47	1748	66	1413	26	1003	68	562	37
2987	58	1658	4	1385	41	941	74	530	31
2954	56	1584	6	1320	18	876	21	461	20
2921	60	1639	10	1241	44	843	32	452	66
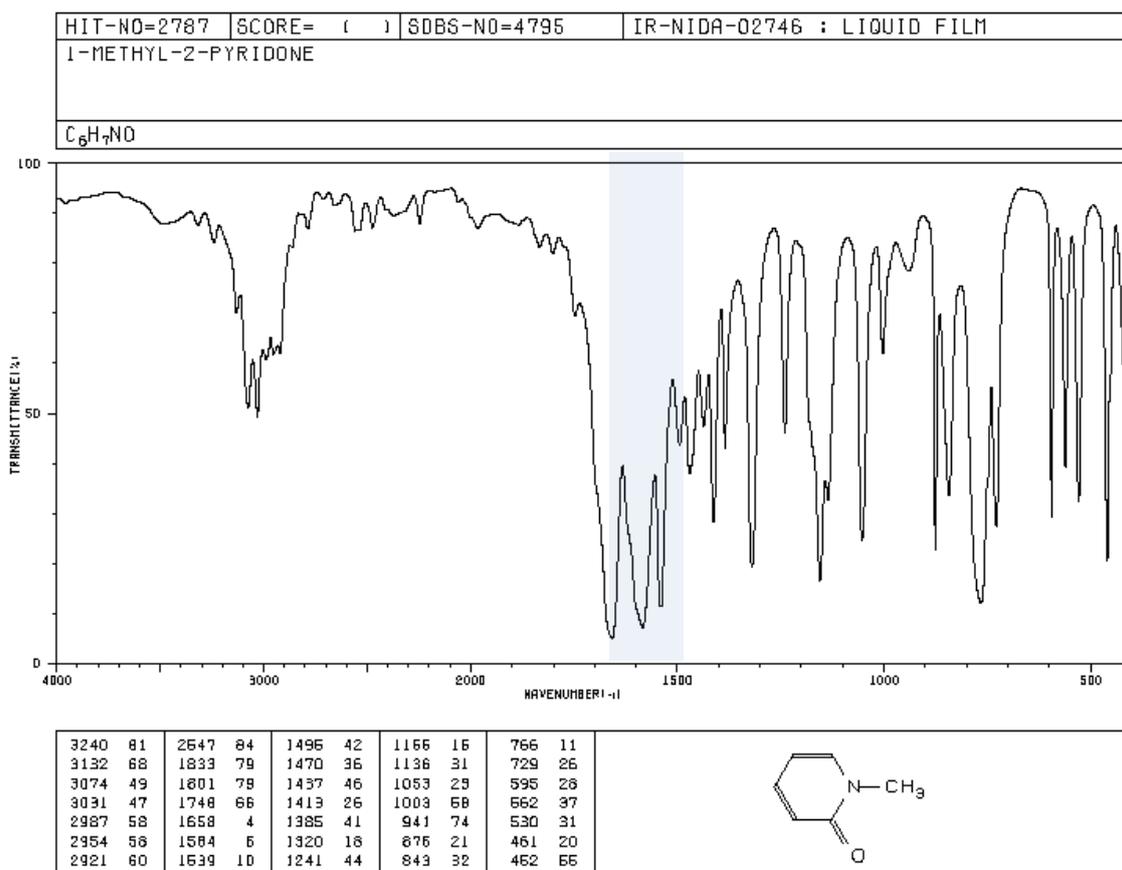
Figure5. ExperimentalFTIR spectrum of 1-methyl-2-pyridone(SDBSNo. 4795).

Obtained values for the *C=O vibration*are given in Table 1. The *best agreement* between the *calculated* and *experimental* values is *obtained withthe RM1 semi-empirical Hamiltonian. However, this method is not parameterized for Zinc, so the* PM6 model was chosen for calculations with the simplified model molecule shown in Figure 6, which after minimization rendered the structure shown in Figure 7, over which the oscillation frequencies were calculated.

Table 1. Values for the *C=O vibration*obtained using the different Hamiltonians available in*MOPAC2012.*

Hamiltonians	Vibration C=O (cm^{-1})
AM1	1992,06
pm3	1903,76
pm5	1827,88
PM6	**1778,2**
PM7	1830,28
MNDO	2087,9
RM1	**1762,39**
MNDOD	2088,04
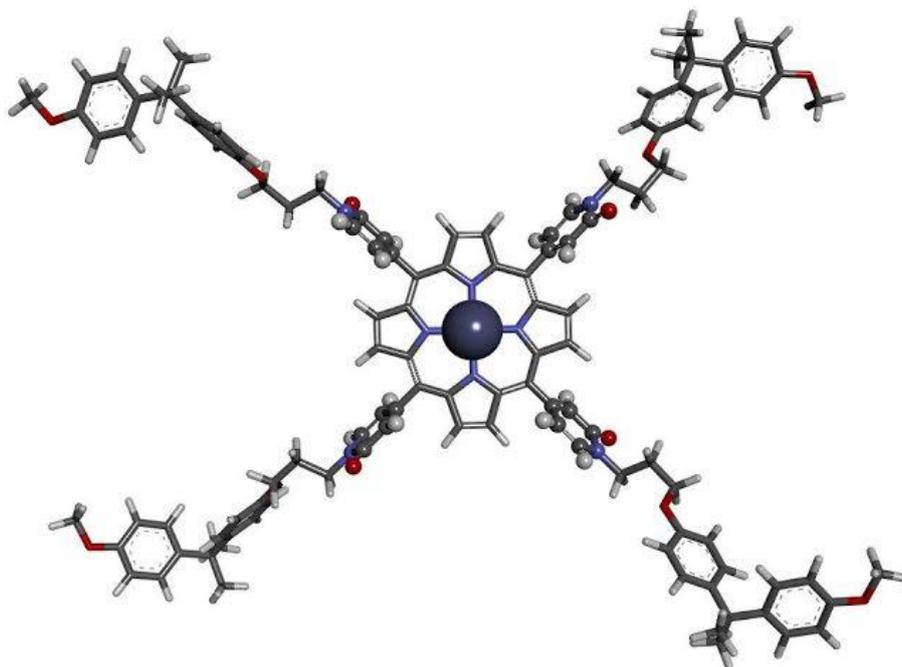
Figure 7. *Minimized structure used for calculating the IR frequencies*

The Table 2 shows the theoretical results for the *stretching vibration of the lactam carbonyl group. Values fall between 1782 and 1785* cm[-1]. *It perfectly matches with experimental values for the epoxy resin.*

Table 2. *Stretching vibration of the carbonyl group inlactams*

VIBRATION	ATOM PAIR
1781.90	C 45 -- O 52
1782.30	C 42 -- O 95
1783.02	C 30 -- O 50
1785.44	C 30 -- O 50

CONCLUSIONS

Simultaneous use of FTIR technique and theoretical calculations by means of standard semiempirical software can help elucidating the curing process as well as the products obtained when macrocycles are used for curing epoxy resins.

ACKNOWLEDGMENTS

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