

# Synthesis and Properties of Multiacrylic Resins from Epoxy Resins

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## SYNOPSIS

The action of methacrylic acid onto tetraglycidyl methylene dianiline, tetraglycidyl sulfone dianiline, triglycidyl triphenylmethane (TACTIX), and epoxy novolac resins was performed using different catalysts. In each case, a comparative study of these catalysts was investigated depending upon the polarity of the solvent and of the temperature. Chromium complexes are better in low polar solvents. The reactions were monitored by  $^1\text{H-NMR}$ , by epoxide titration, and by size exclusion chromatography (SEC), and the reactivity of these resins could be compared. Finally, the study of these materials obtained after radical and photochemical cross-linking, especially by dynamic mechanical analysis (DMA), shows that these materials exhibit high  $T_g$ 's (200°C for methacrylated TACTIX) compared to those of the corresponding multi-epoxides cured by diamines. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Presently, epoxy resins are widely used as composite matrices in the aeronautic industry, thanks to the numerous properties that they exhibit: easy processing, low polymerization shrinkage, good adhesion on the used fibers, and good resistance to moisture, fire, and chemical agents.<sup>1</sup> Among these epoxy resins, tetraglycidyl methylene dianiline (TGMDA) and triglycidyl triphenylmethane (TACTIX) are the most used in this field and they belong to the systems called "180°C." Actually, they have a high binding density in their backbone (aromatic cycles), which leads to a good thermostability.<sup>2</sup>

However, cross-linking by the thermal route with hardeners (such as aromatic amines) is the main drawback of this kind of resin. As a matter of fact, this cure requires a long time and, generally, the amines used are toxic.

Thus, to solve this problem, we have planned to change epoxy resins into their methacrylic homologs, to obtain other methods of cross-linking (UV, electron beam, and other chemical initiators) that are easier to use.<sup>3</sup> Actually, in this process, flexible segments and less stable groups (e.g., methacrylic

groups) are brought, and, consequently, a decrease of the glass transition temperature ( $T_g$ ) might be expected.

The aim of this paper concerned the synthesis of methacrylic compounds from epoxy resins; then, their thermal characteristics were determined. Finally, comparison with their epoxy homologs are discussed.

## EXPERIMENTAL

We used

- as resins: TGMDA MY 720 supplied by Ciba Geigy Corp.; TACTIX 742, from Dow Chemical Co.; and epoxy-novolacs, from Dow (DEN 431  $n = 0.2$ ; DEN 438  $n = 1.6$ ; DEN 439  $n = 1.8$ ).
- as catalysts: dimethyl dodecyl amine (DMDA) and tetrabutylammonium bromide (TBAB), from Aldrich.
- as initiators: Trigonox C: tertibutyl peroxy benzoate from Akzo and DAROCUR 1173: 2-hydroxy 2-methyl 1-phenylpropane 1-one from Ciba Geigy Corp.
- as diluents: *N*-vinylpyrrolidone (NVP) and hydroxyethyl methacrylate (HEMA) from Aldrich.

The  $^1\text{H-NMR}$  spectra were recorded with a Brüker AC 250 apparatus using deuterated chloroform as

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solvent. The SEC was performed on a Spectra Physics SP 4290 chromatograph equipped with Phenomenex columns (limit permeabilities are 50, 100, 500, and  $10^3$  Å). The detector was an SP 8430 differential refractometer. THF was used as eluent with a flow rate of 1.5 mL/min. The epoxy functions were titrated according to the Jay method.<sup>4</sup>

### Synthesis of Methacrylated TGMDA

All reactions were performed at 100°C in an inactic round-bottom flask, with hydroquinone ( $200 \times 10^{-6}$ ) and air bubbling to inhibit any thermal polymerization.

#### Catalysis with DMDA

The reaction was performed in a two-necked round-bottom flask. Twenty grams of TGMDA was dissolved in 100 mL monochlorobenzene; this mixture was heated up to 100°C, and then a mixture of 16.3 g methacrylic acid and 1.011 g DMDA was added dropwise. The mixture was stirred at 100°C for 20 h. The organic phase was washed several times with 30 mL of water to get rid of hydroquinone and amine and was precipitated in petroleum ether. We obtained a brown viscous resin.

#### Catalysis with TBAB

In a two-necked round-bottom flask, 20 g TGMDA, 16.3 g methacrylic acid, and 2.44 g TBAB were stirred in 150 mL DMF, which was then heated at 100°C for 70 h. The organic phase was precipitated into little water fractions, and then the resin was dissolved in chloroform. The new organic phase was washed several times with water, dried over sodium sulfate, and filtered and the solvent was evaporated under vacuum.

#### Catalysis with Chromium III Diisopropylsalicylate (Cr-Dips)

The synthesis of the catalyst was as follows: Chromium III triacetate 1.55 g, and 2.5 g diisopropylsalicylic acid were dissolved in 100 mL ethanol. This mixture was refluxed for 3 h in a reactor equipped with a stirrer and a nitrogen flow. Finally, the ethanol and secondary products were evaporated under vacuum.

In a flask equipped with a mechanical stirrer, 100.25 g TGMDA were dissolved in 110.10 g toluene. This mixture was heated up to 100°C; then 81.52 g methacrylic acid and 0.1822 g Cr-Dips were dropwise added. The solvent was evaporated under vacuum.

The catalysis with DMDA does not seem to be convenient for such a reaction, and, consequently,

we have performed the methacrylation of the other epoxy resins with both other catalysts. The experiment procedure of the catalyses with TBAB and Cr-Dips are the same in each case. Table I lists the weights of resins, methacrylic acid, and catalysts, and also the solvents and the reaction times for each epoxy resin.

### Thermal Curing of Multiacrylic Resins

We describe below an example of the formulation of methacrylated TACTIX/NVP/Trigonox C. The amount of reactive diluent depends upon the viscosity of the initial resin. Methacrylated TACTIX is very viscous, and, thus, 30% NVP is added.

Methacrylated TACTIX: 7 g (70%)  
NVP: 3 g (30%)  
Trigonox C: 0.25 g (2.5% weight of mixture).

The homogeneous mixture is poured into an aluminum cup and these cups are put in a Memmert ULE 500 drying oven. The curing cycle is as follows: 14 h at 65°C, 4 h at 80°C, and 12 h at 130°C.

### UV Cross-linking of Multiacrylic Resins

For example, the formulation of methacrylated TACTIX/NVP/DAROCUR 1173 is

Methacrylated TACTIX: 7 g (70%)  
NVP: 3 g (30%)  
DAROCUR 1173: 0.3 g (3%).

For increasing the adhesion on an aluminum sheet, we add 0.5% (w) of surfactant for each formulation.

### Different Tests Performed on These Films

#### Adhesion

First, a square pattern (the square area is 1 mm<sup>2</sup>) is made with a cutter on the coating. Then, we note whether the film is flaked off. The mark is 0 if no square has been flaked off, and 5 if all the squares are taken off.

Second, we perform a "Scotch test": Scotch tape is stuck on the former square pattern, and it is pulled up. If the film sticks, the mark is 5/5, whereas for a taken-off film, the mark is 0.

#### Solvent Resistance

We used methyl ethyl ketone (MEK) for this test. Several round trips of cotton saturated with this

Table I Experimental Conditions of Methacrylation for Different Multi-epoxy Resins

Epoxy Resin	Catalysis by TBAB					Catalysis by Cr-Dips						
	w (g) Epoxy Resin	w (g) Acid	w (g) Catalyst	Solvent	Reaction Time (h)	Aspect of the Resin	w (g) Final Resin	w (g) Acid	w (g) Catalyst	Solvent	Reaction Time (h)	Aspect of the Final Resin
TGMDA (I)	20	16.3	2.46	DMF 150 cc	70	Black, viscous	100.2	81.52	0.182	Toluene 110 g	20	Brown, viscous
Tetraglycidyl sulfone diamine (II)	50	36.44	5.46	DMF 50 g	7	Brown, viscous						
TACTIX (III)	20	11.2	1.68	DMF 150 cc	48	Black, viscous	100.0	56.1	0.157	Toluene 100 g	10	Green, very viscous
DEN 431 (IV, n = 0.2)	20	11	1.65	DMF 30 cc	20	Viscous	100.2	55.03	0.155	Toluene 100 g	6	Green, viscous
DEN 438 (IV, n = 1.6)							100.0	54.27	0.155	Toluene 100 g	8	Green, viscous
DEN 439 (IV, n = 1.8)							100.0	54.14	0.154	Xylene 100 g	10	Green, very viscous

solvent are executed. We count the number of runs until the aluminum sheet appears. Up to 100 runs, the coating resists the solvent.

### Hardness

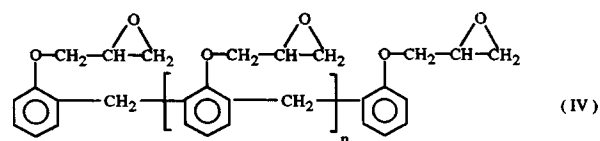
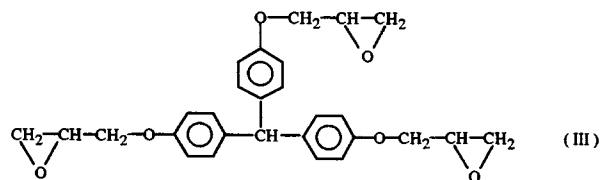
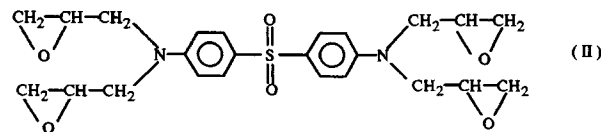
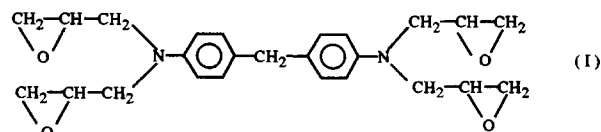
Two tests of hardness are performed on our films:

**The Hardness Test with a Pendulum.** This test consists of measuring the oscillation absorption of a pendulum put on a coating. We release the pendulum, without initial speed, at 12° about the vertical, and we measure the time required to reach 4° of amplitude. An average measurement is determined by three tests at different points of the film. The longer the absorption time, the harder the coating.

**Impact Resistance.** A weight from different heights falls down onto a template (coating + aluminum sheet). Also, we measure the level at which the film begins to take off.

## RESULTS AND DISCUSSION

Epoxy resins that have good thermal properties can be obtained either commercially: TGMDA (I), TACTIX (III), epoxy novolac (IV) tetra, tri, and multifunctional, respectively, or synthesized (II)<sup>5</sup>:



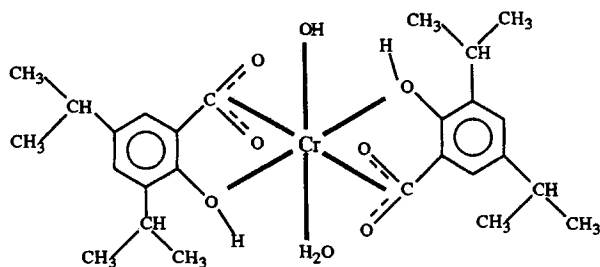
We have studied the reaction of methacrylation on these four resins. This reaction has been known for years and also acrylic epoxy resins and urethane acrylics can be found. Our group has been working in this field of research in order to prepare telomers that exhibit lateral acrylic groups<sup>6</sup> and polybutadienes having lateral acrylic groups,<sup>7</sup> and, more recently, we have obtained unsaturated silicones.<sup>8</sup>

The main reaction concerns the action of an epoxy group onto a carboxylic acid (methacrylic acid in our case) and it has been studied in the literature. However, several side reactions may occur<sup>9</sup>:

- the sense of the acid addition onto the two carbons of the epoxy group leads to  $\alpha$  or  $\beta$  isomers;
- the etherification reactions between the produced alcohols and the epoxy groups;
- the esterification reactions between the formed alcohols and acids in excess in the medium;
- and, finally, other minor reactions such as dismutation of alcohols and esters into diesters diols mixtures or hydrolysis of epoxides.

In this article, we do not describe these reactions and their mechanisms; furthermore, the use of various catalysts has already been reviewed.<sup>10</sup> Actually, the solubility and the nature of the components allow one to use several reactants, such as:

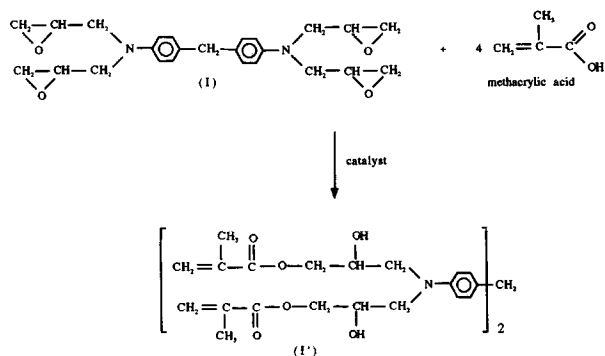
- tertiary amines in solvents of various polarities<sup>11</sup>;
- salts of quaternary ammonium<sup>12</sup>;
- bases other than amines<sup>13</sup>;
- metals derivatives<sup>14</sup>; and, among them, the most used is the chromium III diisopropylsalicylate (Cr-Dips):



According to this information, we studied the methacrylation of the above epoxy resins with various catalysts.

## Methacrylation of TGMDA (I)

The general reaction scheme is as follows:

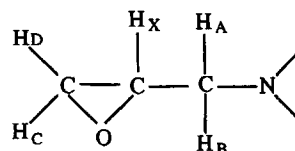


Three catalysts have been tested:

- Dimethyl dodecyl amine (DMDA)
- Chromium III diisopropylsalicylate (Cr-Dips)
- Tetrabutyl ammonium bromide (TBAB).

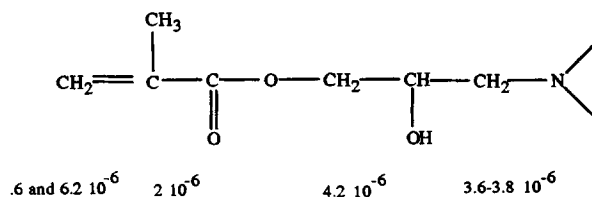
Experiments have been performed in an inactinic round-bottom flask, with hydroquinone ( $200 \times 10^{-6}$ ) and air bubbling to inhibit any reaction from thermal polymerization of multiacrylic compounds.

Reactions have been monitored by <sup>1</sup>H-NMR. As mentioned below, we note the particularity of epoxy groups in Figure 1:



- CD part    2 multiplets     $H_C, H_D = 2.57$  and  $2.77 \cdot 10^{-6}$
- X part    multiplet     $H_X = 3.15 \cdot 10^{-6}$
- AB part    2 multiplets     $H_A, H_B = 3.43$  and  $3.72 \cdot 10^{-6}$

When the esterification was complete, we noted the absence of the peaks of the CD protons at  $3 \times 10^{-6}$  and we observed, on the <sup>1</sup>H-NMR spectrum, the presence of the signals of the ethylenic protons adjacent to the ester group:



The <sup>1</sup>H-NMR spectrum of this product is more difficult to describe than that of the epoxy because

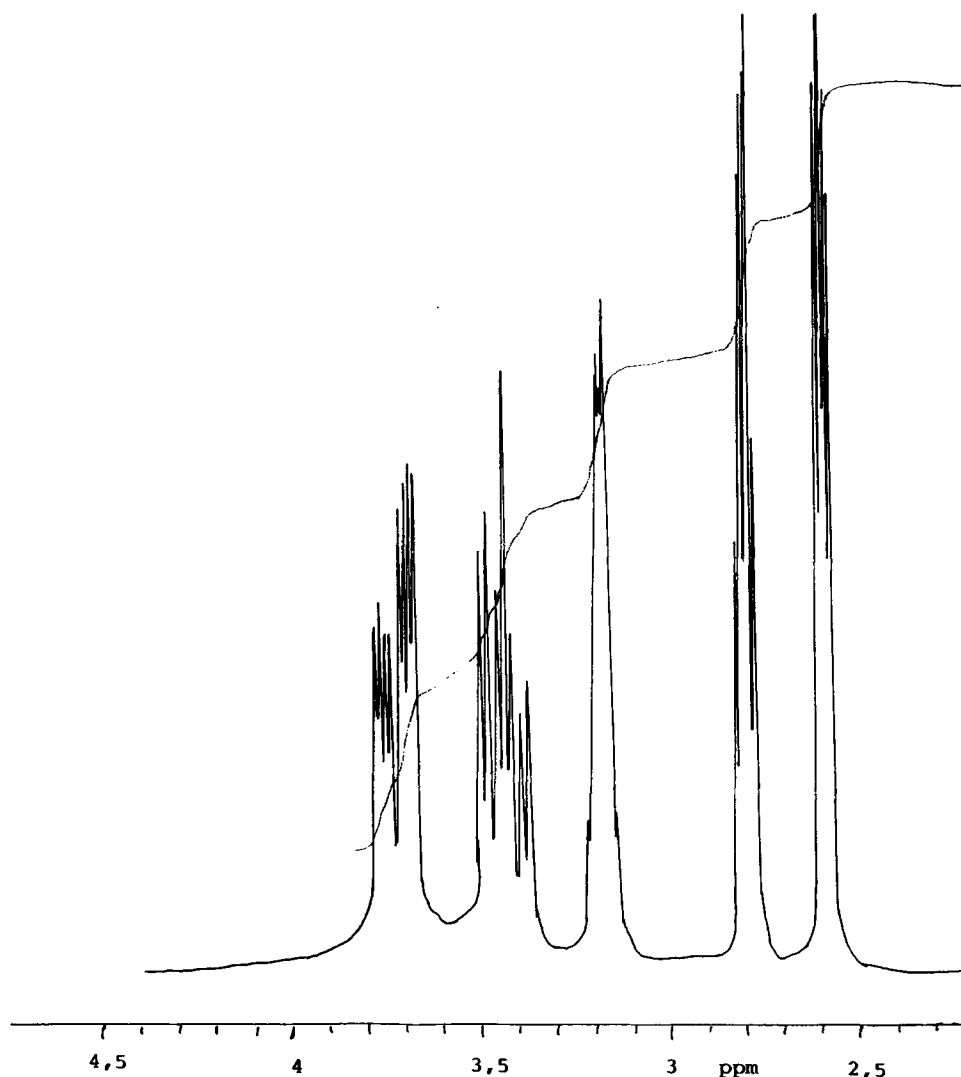


Figure 1  $^1\text{H-NMR}$  spectrum, 250 MHz, of the epoxy part of TGMDA.

there is a mixture of isomers that may be produced from the side reactions. However, the presence of the ethylenic protons and that of the methyl group at 5.6/6.2 and  $2 \times 10^{-6}$ , respectively, allows one to quantify the unsaturation of the resin and to compare the different catalysts.

#### **Catalysis with DMDA**

In THF at 60°C and for different samplings (13, 20, 42, and 80 h), we always note the presence of epoxy groups. In the monochlorobenzene at 100°C during 20 h, these groups are still present but at a lower amount. Consequently, the DMDA is not a good catalyst for such a reaction.

#### **Catalysis with Cr-Dips**

In THF at 60°C during 40 h, we noted the presence of epoxy groups, but the polarity of this solvent does not favor the activation of this catalyst.<sup>14</sup> We studied this reaction at 100°C in toluene during 20 h. We note that it gives better results, with, however, a low residual epoxy amount. Yet, we note that TGMDA is not totally soluble in this solvent and even at high temperatures.

#### **Catalysis with TBAB**

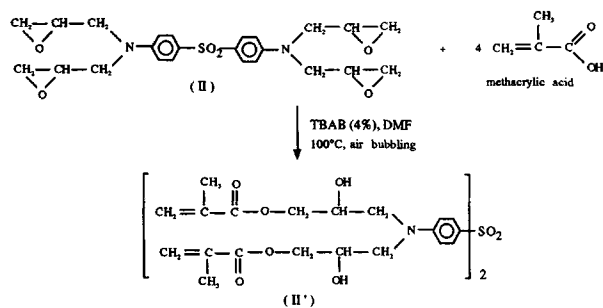
In the same conditions as those described by Coqueret et al.,<sup>12</sup> the reaction was carried out, at 100°C

in DMF during 70 h, using 4% molar of the catalyst about the acid. We note the absence of the epoxy groups. However, the elimination of the solvent and the catalyst is difficult to achieve: We cannot get rid of all the DMF and this mixture has to be precipitated in water in order to eliminate this solvent. Thus, the tetraacrylic compounds can be obtained with Cr-Dips in toluene or with TBAB in DMF. The final product is a viscous colored liquid. The double-bond titration gives a functionality of 3.8, which is similar to that of the TGMDA.

### Methacrylation of Product (II)

The tetraglycidyl sulfone dianiline (II), which was previously prepared,<sup>5</sup> is not soluble in low polar solvents such as toluene, xylene, and monochlorobenzene. Thus, according to the above-obtained results on TGMDA, we have used TBAB in DMF. Also, we note that DMF is a good solvent for the product (II).

The reaction is as follows:



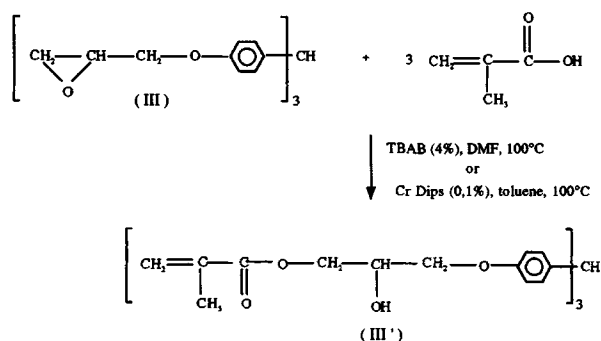
We note the great reactivity of this multiepoxy. This reaction has been very exothermic and 30% of epoxy groups have reacted at the end of the addition of methacrylic acid. The reaction was complete in 4 h.

This reaction was monitored by colorimetric titration of the epoxy groups. We can also control it by <sup>1</sup>H-NMR: We have noted the absence of methylene of the epoxy groups and the presence of methacrylic functions.

### Methacrylation of TACTIX (III)

As this resin is soluble in DMF and in toluene, we performed the reaction with both kinds of catalysts.

The scheme is as follows:



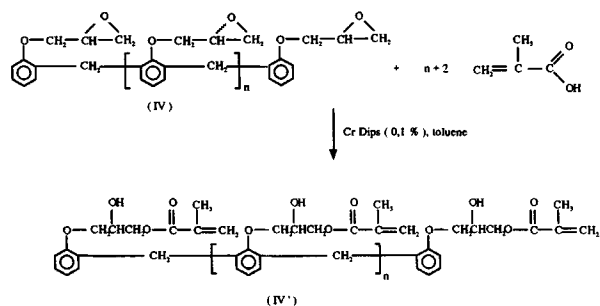
The evolution of the reaction was investigated by the epoxy-group titration and we plotted the conversion of the epoxy group vs. time in Figure 2. We note that there is 80% of conversion after 10 h. Furthermore, the reaction has been monitored by SEC, because the methacrylic compound (III') has a lower retention time than that of the product (III).

We note a brown coloration of the resin obtained with the TBAB catalyst, whereas that obtained with the Cr-Dips catalyst is green (because of the chromium salts). Therefore, we chose the Cr-Dips catalyst because it is easier to purify.

### Methacrylation of Epoxy Novolac Resins (IV)

This reaction has already been described<sup>15</sup> and the final product is used as a stiffener in coatings of common acrylated epoxy resins (e.g., acrylated DGEBA). We have employed three kinds of epoxy novolac resins (IV), which exhibit different chain lengths ( $n = 0.2, 1.6, \text{ and } 1.8$ ).

The reactional scheme is as follows:



We have also tested both catalysts on the product (IV,  $n = 0.2$ ) used as a model for our study, and we prefer the Cr-Dips catalyst because we have obtained 95% of conversion after 5 h, whereas it requires 70 h to obtain the same result with TBAB.

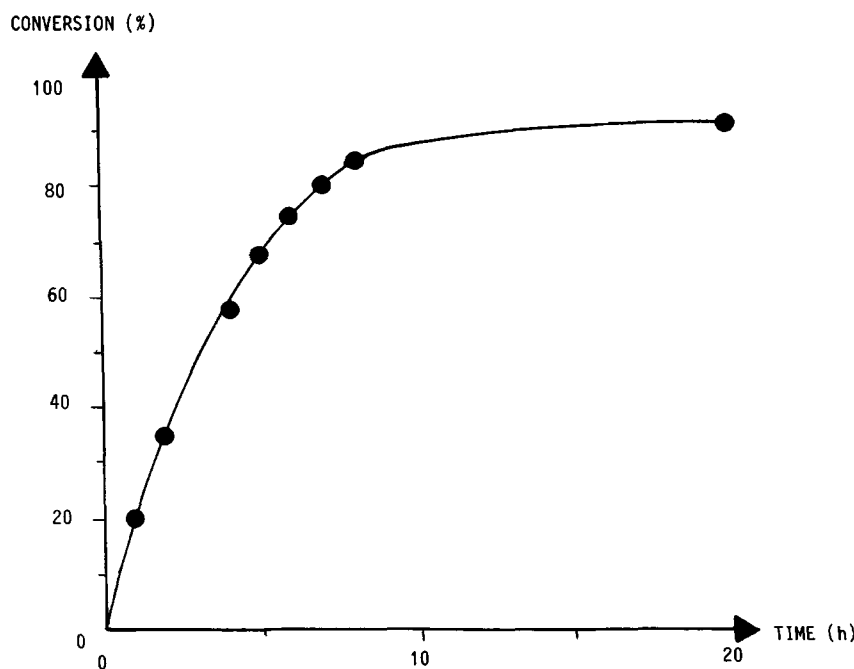


Figure 2 Time dependence of the TACTIX methacrylation, catalyzed by Cr-Dips.

The  $^1\text{H-NMR}$  spectrum and the SEC chromatogram show that the reaction is complete. As previously, we obtained a green viscous resin.

A similar catalysis has been performed on the other epoxy novolac resins. We note that the higher the molecular weight the lower the reactivity. However, we have the same conversion (85%) in 8 h and in 10 h for products (IV,  $n = 1.6$ ) and (IV,  $n = 1.8$ ), respectively. For product (IV,  $n = 1.8$ ), xylene was preferred to toluene in order to improve the solubility and also it exhibits a higher viscosity; however, several problems occur to get rid of the solvent.

In conclusion, both kinds of catalysts can be used: TBAB in DMF and Cr-Dips in low-polar solvents. However, we prefer the chromium catalyst for soluble resins in these solvents, whereas for insoluble ones, we choose the TBAB catalyst in DMF.

In the second part of the experiment, the polymerizations and the thermal properties of these multiacrylic resins were investigated.

#### **Polymerizations and Thermal Properties of Multiacrylic Resins**

The cross-linking of the resins [(I)–(IV)] was studied using three methods:

- thermal,
- UV,
- and electron beam (EB).

#### **Thermal Cross-linking**

We used Trigonox C as a thermal initiator, and we chose the following cycle of curing: 14 h at 65°C, then 4 h at 80°C, and, finally, 12 h at 130°C. In each case, we added a reactive diluent (NVP) in order to control the viscosities of the resins. The amount of reactive diluent depends upon the viscosity of the initial resin. The amounts are

- 30% for methacrylated TACTIX (III'),
- 30% for (IV',  $n = 1.8$ ),
- 30% for (IV',  $n = 1.6$ ),
- 20% for (IV',  $n = 0.2$ ),
- 20% for methacrylated TGMMA (I'), and
- 10% for (II').

We also used another reactive diluent (HEMA), in the case of product (III'), in order to compare it with NVP. Cross-linking occurred in all cases, and

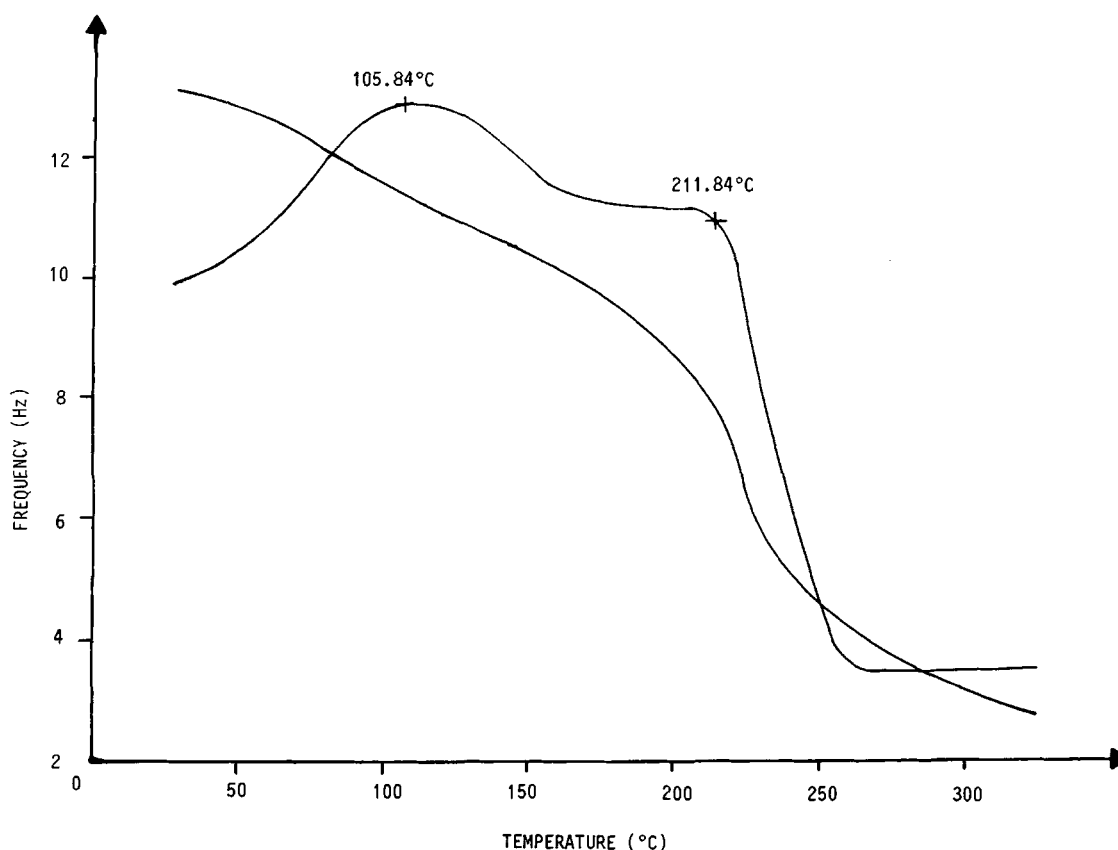


Figure 3 DMA curve of the formulation methacrylated TACTIX/NVP/Trigonox C.

resins with various colorations (yellow to brown) were obtained.

The determination of the  $T_g$  of the acrylics was not obvious by differential scanning calorimetry (DSC), and, thus, dynamic mechanical analysis (DMA) was preferred. We present here only the results obtained on the methacrylated TACTIX (III'). In Figure 3, we note a transition at 212°C corresponding to the  $T_g$ , and when we have cured

epoxy resins by the thermal way with diamines, we achieved both the following results:

$T_g = 205^\circ\text{C}$  with diaminodiphenyl sulfone,

$T_g = 263^\circ\text{C}$  with diethyl toluene diamine.

These methacrylic resins exhibit thermal properties as interesting as those of epoxy resins. There-

Table II Irradiation Times and Tests on Various Formulations

Formulation	Irradiation Time (s)	Square Pattern Test	Impact Resistance		Hardness (s)
			400 g	1000 g	
III'/30% NVP	4	1		20 cm	310
	8	3		20 cm	285
IV', n = 1.6/30% NVP	12	0		20 cm	240
	10	2	50 cm		285
I'/20% NVP	12	3	30 cm		270
	10	2	40 cm		255
II'/10% NVP	4	1	40 cm		265
	8	2	30 cm		270



**Table III** Glass Transition Temperatures of Various Methacrylic Formulations

Resin	Dose (Mrads)	$T_g$ (TMA) (°C)	$T_g$ (DMA) (°C)	$T_g$ (DSC) (°C)
III'/NVP (20%)	15	207	181	—
IV', $n = 0.2$ /NVP (10%)	15	169	180	—
IV', $n = 1.6$ /NVP (10%)	10	170	168	164
IV', $n = 1.8$ /NVP (20%)	10	169	—	160

fore, the introduction of a methacrylic group does not decrease these properties as expected.

#### Photochemical Cross-linking by UV

DAROCUR 1173 (2-hydroxy-2-methyl-1-phenylpropane 1-one) and NVP were used as initiator and reactive diluent, respectively. The resins were spread on aluminum sheets by hand-coating. The films were cross-linked in a microtunnel UV during the time required to obtain a dry coating (when touched by fingers).

Table II lists several tests performed on these coatings. We note that the Scotch test was very bad for every resin. The methyl ethyl ketone (MEK) test did not change the surface of the film even after 100 round trips. Therefore, these resins have no adhesion on aluminum but the coatings are resistant to MEK. Finally, the hardnesses of these materials are high but their impact strengths are low; these coatings have a great stiffness.

#### Cross-linking by Electron Beam

We used high doses (10–15 Mrad) and we measured the  $T_g$ 's by thermal mechanical analysis (TMA), DMA, and DSC. The results are summarized in Table III.

We conclude that methacrylated TACTIX and methacrylated novolac exhibit  $T_g$ 's of about 200°C and 170°C, respectively. These results are similar to those obtained from the thermal studies. The thermal gravimetric analysis (TGA), performed under nitrogen, shows that the thermal degradation temperatures are higher than 350°C and gives evidence that these materials have good thermal properties.

#### CONCLUSION

In this study, we carried out the syntheses of multiacrylic compounds from multi-epoxy resins. For this, we used several catalysts according to the solubility of the initial epoxy resin.

The chromium catalyst was preferred in low-polar aromatic solvents, because the reactions are shorter and produced less-colored resins. In the other cases, when epoxy resins are not soluble in low-polar solvents, we used the TBAB catalyst in DMF.

These methacrylic compounds can be cross-linked by radical or photochemical routes. The final materials exhibit high  $T_g$ 's, similar to those obtained in a chemical way onto initial epoxy resins (cured using diamines). Therefore, these materials can be used for interesting applications at high temperatures (higher than 150°C).

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