

# Synthesis of Polyglutarimides from P(methyl methacrylate) and Cyclohexylamine. I. Influence of Working Conditions on Imidization Reaction

RICHARD LEGAY, JOËL ROUSSEL, BERNARD BOUTEVIN

ENSCM, Laboratory of Macromolecular Chemistry, UPRES A, CNRS 5076, 8 Rue Ecole Normale, 34296 Montpellier, Cedex 5, France

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**ABSTRACT:** Over the last 50 years methacrylic polymers, especially poly(methyl methacrylate) (PMMA), have reached a noteworthy place in world polymer production. However, for special applications that require thermal properties, polycarbonates take the place of PMMA because of the latter's low glass transition temperature ( $T_g$ ) of 105°C. The aminolysis reaction of PMMA with cyclohexylamine in xylene was studied to obtain a polyglutarimide exhibiting higher  $T_g$  values. The mechanism involving aminolysis and further amidization of ester groups was correlated with the experimental characterization of all the species created during the reaction. Poly(*N*-cyclohexylacrylamide) and polyglutarimide (prepared from this precursor) were prepared in order to determine the special characteristics of these model compounds by FTIR. This method allowed the quantification of ester, amide, acid, and imide groups. This aminolysis reaction was optimized (190–250°C; ratio of constituents, 0.5: 3) by spectroscopically following the different groups and monitoring the increase of the  $T_g$ . Poly(*N*-cyclohexyl glutarimide) (65%) containing amide groups (25%) and acid groups (10%) presents a  $T_g$  value of 195°C. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1876–1888, 2000

**Key words:** polyglutarimide; cyclohexylamine; imidization reaction; methylamine

## INTRODUCTION

Because of their industrial development in the 1930s, which was launched by Röhm (Germany) and I.C.I. (England), methacrylic polymers, particularly poly(methyl methacrylate) (PMMA), have reached a privileged place in worldwide polymer production. They are best known commercially as Plexiglas (Röhm and Haas, United States), Altuglas (Elf-Atochem, France), Acrylite (Mitsubishi, Japan), and Perspex (I.C.I., England). The use of PMMA has increased over the last 50 years because of its properties of excellent transparency; very good thermoforming ability; good resistance to aging, cor-

rosion, and atmospheric agents; and interesting biocompatibility characteristics.

However, for some applications that need to use transparent, thermoplastic, rigid, and thermally stable materials, polycarbonates are preferable to PMMA because they offer excellent optical and mechanical properties and especially better thermal resistance. Nevertheless, these materials have a rather high manufacturing cost.

Therefore, there is a niche for the industrial development of (meth)acrylic polymers with improved thermal resistance that would be able to compete with polycarbonates from an economic point of view.

As early as the late 1930s Dupont de Nemours, followed by Röhm and Haas and I.C.I. in the 1960s and Mitsubishi and Asahi in the 1980s, attempted to take up the challenge to prepare

Correspondence to: B. Boutevin.

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transparent methacrylic polymers with a higher thermal resistance than PMMA.

Numerous processes involving PMMA and its derivatives have been developed to increase the glass transition temperature ( $T_g$ ) of polymethacrylic chains.

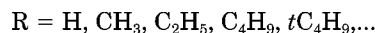
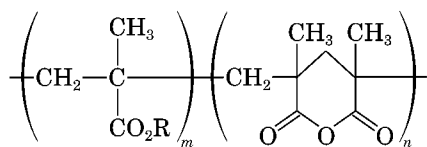
These different techniques rely on PMMA macromolecular structure modification.

Several researchers attempted to insert groups exhibiting the following characteristics into the polymethacrylic structure:

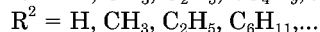
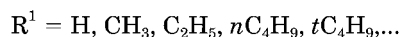
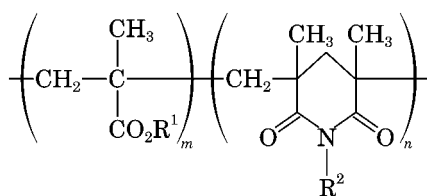
1. high polarity, which increases the cohesive energy between chains (i.e., resulting in strong inter- and intramolecular associations)<sup>1,2</sup>;
2. high dissociation energy ensuring the desired thermostability<sup>3</sup>; and
3. cyclic structure on the main chain that creates internal strains, leading to increased chain stiffness.

Among the groups most studied with the aim of stabilizing PMMA are cyclic anhydrides and especially cyclic imides, which exhibit the three previous characteristics.

There are three main techniques used to insert these groups into the polymethacrylic chain. The first is the chemical modification of methacrylic polymers, such "reactive" processes, that are much used at present (because they are simple and economical from the processing point of view). This technique leads to the elaboration of glutaric polyanhydride and polyglutarimide materials with the following respective structures:

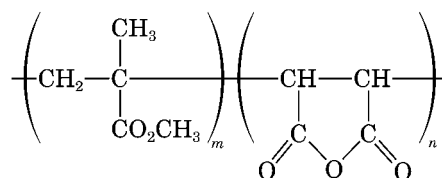


poly(methacrylic-co-glutaric anhydride)

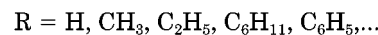
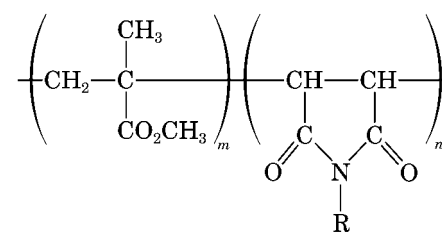


poly(methacrylic-co-glutarimide)

The second technique is the copolymerization of MMA with various cyclic comonomers such as maleic anhydride or *N*-substituted maleimides. This technique requires the reactivity ratio of the reacting comonomers. The respective structures of the copolymers are presented here:



MMA/maleic anhydride copolymer



MMA/*N*-substituted maleimide copolymer

We considered, more particularly, the polyglutarimide type compounds obtained through imidization of PMMA by aminolysis in a solvent medium.

The third route to incorporate the imide comonomer is by cyclopolymerization.<sup>4-6</sup> There is also a fourth pathway, the hydrolysis of adjacent nitrile and acid polymers,<sup>7</sup> which evidently proceeds through rearrangement of the isoimide in a reaction called the Gauthier reaction.<sup>8</sup> This reaction was actually used by Röhm and Haas GmbH to prepare foamed polyimides commercially.<sup>9</sup>

## EXPERIMENTAL

### Analysis Methods

#### FTIR

The FTIR analyses were performed on a Perkin-Elmer 1760X apparatus with a 7700 data station (20 scans, resolution 2, velocity 0.2, interleaved mode).

#### Elemental Analysis

Elemental analyses were performed at the Central Service for Elemental Analysis at the ENSC

Montpellier and at the GRL Elemental Analysis Service.

### **Gel Permeation Chromatography (GPC)**

Chromatograms were obtained on a Spectra Physics SP 4270 apparatus equipped with "Phenomenex" columns of various limited permeabilities ( $10^4$ ,  $10^3$ , 500, and 100 Å) and with a differential refractometer type SP 8810 detector; the eluent was tetrahydrofuran (THF), and the flow rate was 1.5 mL/min. PMMA standards were used for the apparatus calibration.

### **Differential Scanning Calorimetry Analysis (DSC)**

DSC analyses were performed on a Perkin-Elmer DSC 4 apparatus at the ENSC Montpellier and on a Perkin-Elmer DSC 7 at the GRL. The sample was heated in air from 50 to 250°C at 20°C/min.

### **Acid Titration**

The acid titrations on samples of aminolysed polymers were performed by titration with a 0.1N sodium hydroxide aqueous solution in the presence of phenolphthalien as an indicator in a THF medium.

### **Amine Titration**

The amine titrations were performed on aminolysed polymers by titration with 0.05N perchloric acid ( $\text{HClO}_4$ ) in dioxane in the presence of bromocresol green in a chloroform medium.

### **FTIR Titration of Various Functions in Modified Telomers**

For each sample of known concentration the three species (ester, amide, and imide) titration was performed according to a method of cascade subtraction of the different bands on the sample spectrum from the spectra of each standard for which the real concentrations  $C_i$  are known.

This consists of the subtraction of the NH amide band at  $3451\text{ cm}^{-1}$  [obtained from the poly(*N*-cyclohexylmethacrylamide) (PMCMIDE) standard spectrum] from the spectrum of the analyzed sample. The computer then calculates the multiplying factor  $f_1$ , which should be applied to this standard spectrum to remove this band. In a similar manner, the  $f_2$  and  $f_3$  multiplying factors to be applied to imide and ester standard spectra were calculated in order to remove the imide C=O and ester C=O bands.

These multiplying factors obey the following equation:

$$C_{\text{sample}} \times l - f_1 \times C_{1\text{PMCMIDE}} \times l - f_2 \times C_{2\text{PCGLUT}} \times l - f_3 \times C_{3\text{PMMA}} \times l = 0$$

where  $l$  is the width of the analysis cell and PCGLUT is poly(*N*-cyclohexylglutarimide).

We verified that the final spectrum is reduced to a flat base line after subtraction of the previous vibration bands.

The calculated concentration  $x_i$  for each species is then given by the formula

$$x_i = \frac{f_i \times C_i}{C}$$

where  $f_i$  is the multiplying factor for the spectrum of standard  $i$ ,  $C_i$  is the weight concentration of standard  $i$ , and  $C$  is the weight concentration of the sample.

## **Syntheses and Aminolysis Reactions**

### **PMCMIDE 2 Synthesis**

A 5-g sample ( $5.04 \times 10^{-3}$  mol) of MCMIDE, diluted in 150 mL of THF, was placed in a 250-mL three-necked flask fitted with a condenser, a nitrogen inlet, and a dropping funnel. The reaction mixture was heated at 69°C; then 0.08 g ( $5.04 \times 10^{-4}$  mol) of AIBN prediluted in THF was added dropwise during 10 min. The reaction lasted for 16 h.

The crude reaction mixture was then concentrated to 100 mL and precipitated into 1 L of diethyl ether. The precipitate was filtered and dried in an oven at 70°C for 16 h, and 3.65 g of a heavy white homopolymer was obtained. The remaining part was high homopolymers and unreacted MCMIDE.

Anal. Calcd for:  $\text{C}_{10}\text{H}_{17}\text{N}$  C, 71.86%; H, 10.18%; N, 8.38%. Found: C, 72.08%, H, 10.36%, N, 8.33%.

### **PMCMIDE 2 Thermal Treatment in Xylene**

One gram of homopolymer was introduced in a Pyrex tube with 5 mL of xylene. The tube was sealed, placed in an autoclave, and heated at 250°C for 3 h. The crude reaction mixture was diluted with a minimum of THF in order to solubilize the polymer into the xylene phase. The polymer was then precipitated in 150 mL of diethyl ether and dried in an oven at 70°C for 10 h.

### PMMA Aminolysis by Cyclohexylamine in Xylene

PMMA was dissolved in xylene at 80°C to adjust its concentration to about 30% by weight in xylene.

The different reaction mixtures were prepared as follows: 20 g of 32.8% PMMA solution in xylene ( $6.56 \times 10^{-2}$  mol ester) was placed in an inox tube of about 80-mL capacity; 6.51 g ( $6.56 \times 10^{-2}$  mol) of pure cyclohexylamine was added with two steel balls to insure the stirring. The tubes were hermetically closed and placed on a longitudinal axis system, which was placed in a thermostable oil bath heated at the desired temperature. The rotation speed was fixed at 30 rpm/min. Kinetics were carried out at 190, 210, 230, 240, and 250°C. Samples were taken every 30 min for 3 h, then after 4, 5, 7, and 23 h.

The reaction mixtures were diluted in a chloroform volume corresponding to 10 times the total volume. Polymers were dried for 24 h at 60°C in a vented oven, then for 10 h at 80°C under a vacuum. They appeared as white powders, except for a few.

### Stoichiometry Influence on PMMA Aminolysis by Cyclohexylamine

A 33.7% PMMA solution in xylene was used. In each inox tube were placed the product amounts summarized in Table I. The tubes were introduced into the oil bath at 250°C for 2 h. Samples were treated as previously described.

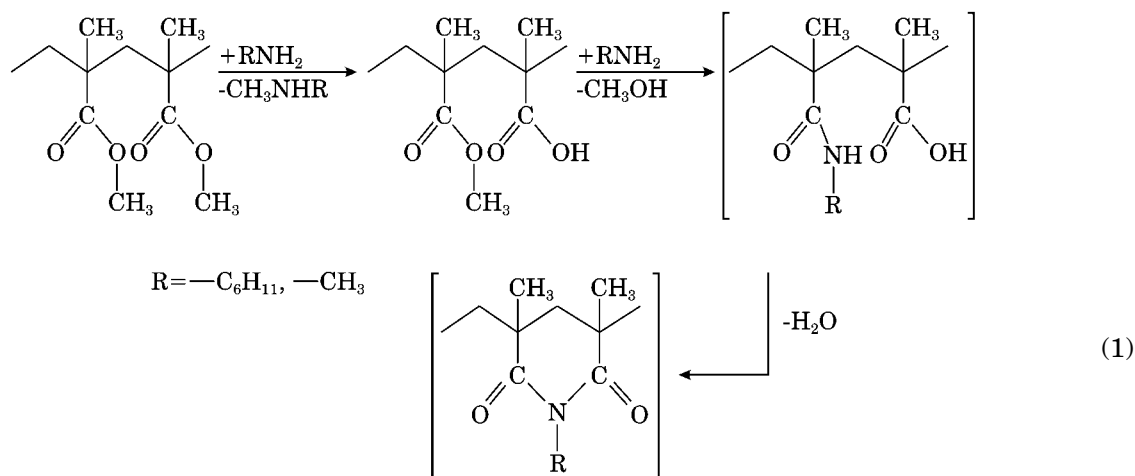
### RESULTS AND DISCUSSION

The polyglutarimide structure has been known for a long time. In 1929 Staudinger and Urech<sup>10</sup> discussed the preparation of cyclic glutarimide by intramolecular condensation of polyacrylamides. In 1936 the first patent was submitted by Dupont de Nemours<sup>11</sup>; it concerned the synthesis of *N*-substituted polyglutarimides by treating methacrylic PMMA polymers or MMA/methacrylic acid (MAA) copolymers with ammoniacs, primary amines, or ammoniac generators such as ureas.

Since then an important series of patents has been developed to optimize the process of making these polyglutarimides while controlling their imidization degree. Among these companies, the main ones to be mentioned are Röhm and Haas<sup>12–20</sup> and Röhm,<sup>21–26</sup> which commercialized a whole range of acrylic glutarimide copolymers (with a variable ratio of imide and acid) under the name Kamax; and Mitsubishi Rayon Co. Ltd.,<sup>27–31</sup> the main competitor to the previous company on the worldwide market for thermostable methacrylic polymers.

From a mechanistic point of view, a mechanism of the aminolysis reaction of PMMA with a primary amine at 200–250°C was proposed by Schröder<sup>32</sup> in 1965. More recently, a mechanism concerning the chemical modification of PMMA in an extruder was developed by Röhm and Haas.

The *N*-alkylation reaction takes place as the first step, then an amidization reaction occurs as the second step. The resulting amide–acid intermediate leads to *N*-methyl glutarimide by cyclodehydration:



These intermediate species were demonstrated for the first time by Ziegenberg and Klesper<sup>33,34</sup> in the MAA/dimethacryloylamine copolymers.

In order to better understand the polyglutarimide synthesis, we studied the imidization reaction from kinetic and mechanistic points of

**Table I Influence of Stoichiometry on PMMA Aminolysis by Cyclohexylamine (Experimental Conditions)**

$\frac{[\text{Amine}]_0}{[\text{Ester}]_0}$	33.7% PMMA Solution in Xylene (g)	Cyclohexylamine (g)
0.25	20.04	1.67
0.5	20.04	3.34
0.75	20.04	5.01
1.0	20.04	6.68
1.25	20.04	8.35
1.50	20.04	10.02
1.75	20.04	11.69
2.0	15.0	10.01
2.5	15.0	12.51
3.0	15.0	15.01

view. It seemed to us that it would be more judicious to work on the aminolysis of PMMA in a solvent medium to achieve a parallel and comparative study with the Röhm and Haas one.

In this study we are more particularly interested in the kinetic aspect of this reaction but also in the influence of chemical modification on the thermal properties of polymers, working with high molecular weight PMMA.

The selected amine was cyclohexylamine, because of its high reactivity and its interesting physical characteristics (liquid at room temperature), which facilitate the reaction processing. Moreover, we considered that the steric hindrance of the six carbon cycloaliphatic chain should not induce a large decrease of the  $T_g$ .

We developed an analytical method that allows the observation of the potential intermediate species formed during the aminolysis reaction such as ester, amide, imide, amine, and acid.

#### Analytical Monitoring of Various Species Formed during Aminolysis

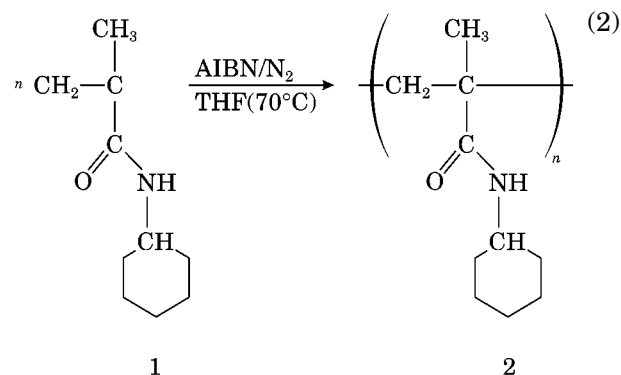
The characterization and quantification of ester, amide, and imide species formed during the

PMMA aminolysis by cyclohexylamine were performed through FTIR spectrometry. Acid and amine function monitoring was achieved by volumetric titration.

#### Ester, Amide, and Imide Species Monitoring

In order to test a titration method for these different functions, it was necessary to synthesize pure model compounds based on CGLUT moieties. Two macromolecular models were synthesized where the spectrometric answer accounts for the polymer environment.

PMCMIDE **2** was prepared by radical polymerization of MCMIDE monomer **1** according to the following reaction:



The GPC analysis of the polymer (Table II) leads to a low average molecular weight polymer. This may be due to the transfer reaction to the cyclohexyl group, particularly to the hydrogen atom in the  $\alpha$  position to the nitrogen atom.

Then, following the works of Crauwels and Smets,<sup>35</sup> we performed the deamination reaction of compound **2** in xylene, leading to *N*-cyclohexylmethacrylamide/CGLUT copolymer **3**:

**Table II General Characteristics of Model Macromolecular Compounds before and after Thermal Treatment at 255°C**

Polymer	<sup>1</sup> H-NMR		$T_g$ (°C)	$\bar{M}_n$	$I = \frac{\bar{M}_w}{\bar{M}_n}$
	Amide (mol %)	Imide (mol %)			
HomoPMCMIDE <b>2</b>	100	—	146.8	2900	1.8
<b>2</b> Pyrolysis	91	9	155.5	2800	1.7





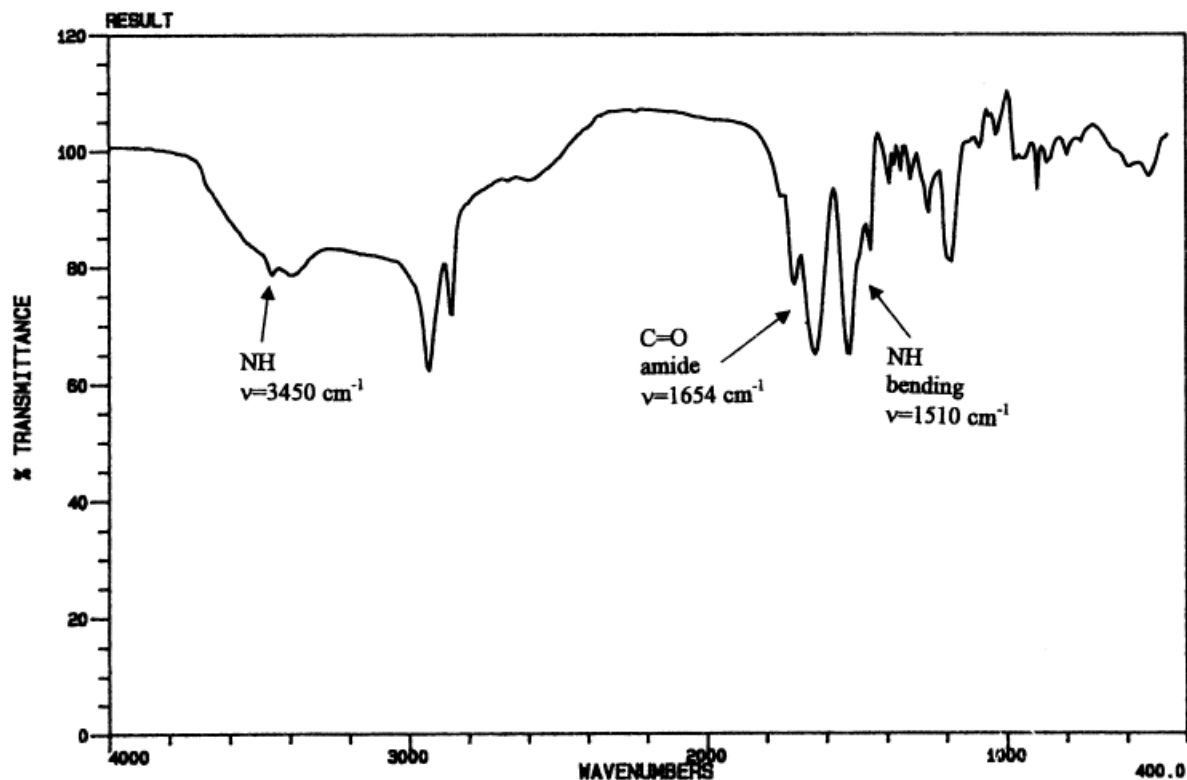


Figure 2 PMCMIDE 2 FTIR spectrum ( $\text{CHCl}_3$ ).

bands are observed for the two symmetrical and asymmetrical vibration harmonics of glutarimide function. The spectral data of the different macromolecular models in  $\text{CHCl}_3$  are given in Table III.

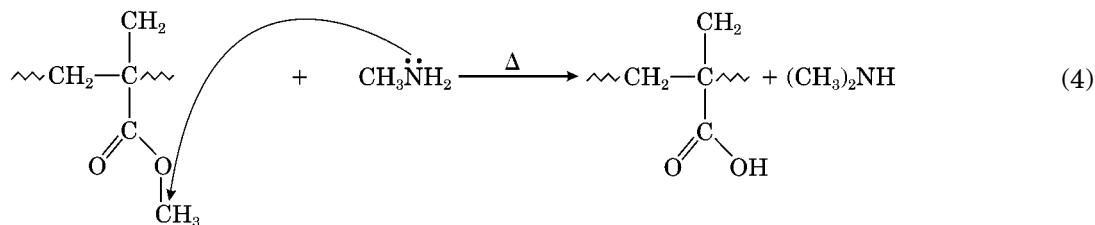
### Principle

The three species (ester, amide, and imide) analysis for each sample was performed according to a "cascade" subtraction of the different bands in the sample spectrum from the spectrum bands of

each standard. The calculation method is detailed in the Experimental section.

### Amine Function Monitoring

The most recent articles about PMMA imidization by methylamine account for the presence of acid functions inside the imidized polymers.<sup>20</sup> These functions originate from methylamine *N*-alkylation reactions by methyl esters at elevated temperatures. The proposed reaction is the following:



In the same manner we could observe the presence of *N*-methylcyclohexylamine in our reaction mixtures with cyclohexylamine, which supports the previous reaction.

Indeed, a titration with perchloric acid in dioxane showed the presence of primary amines in very low amounts, which were "trapped" by the aminolysed polymer acids as alkyl ammonium salts.

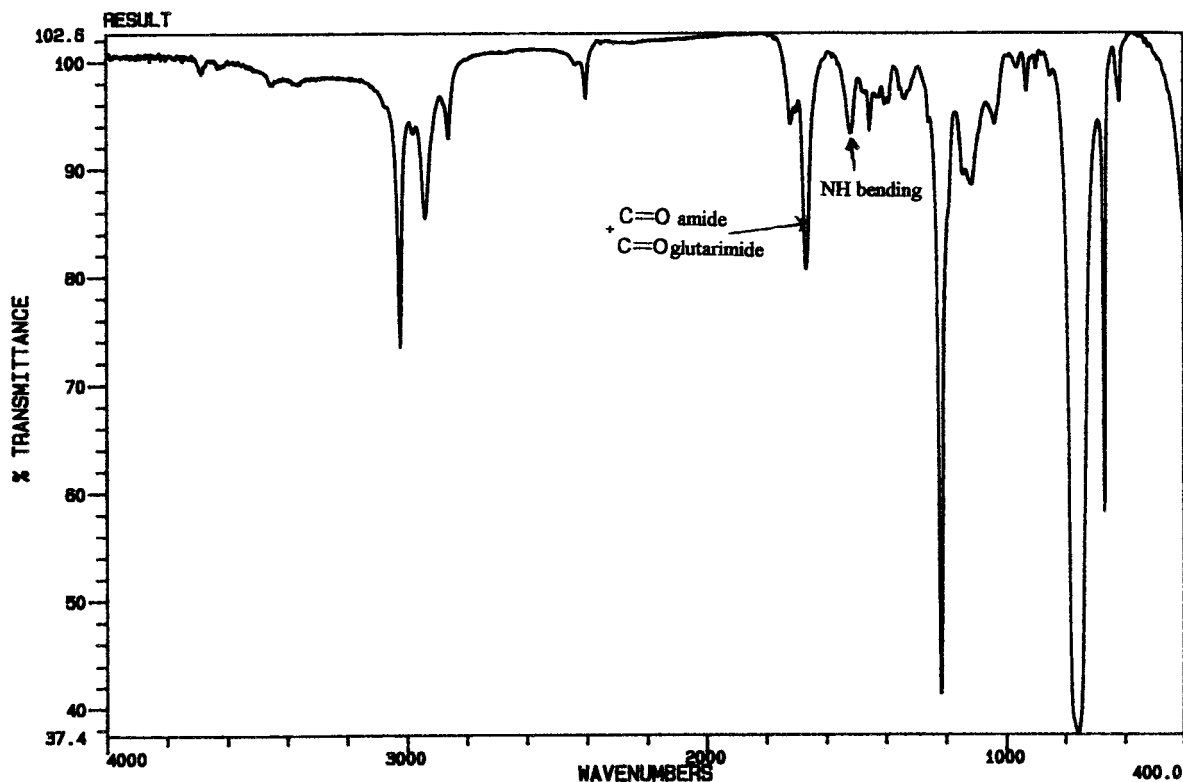


Figure 3 Thermally modified PMCMIDE 3 FTIR spectrum ( $\text{CHCl}_3$ ).

#### Study of PMMA Aminolysis by Cyclohexylamine in Solvent Medium

The PMMA chosen for this study was a polymer synthesized via a radical route, which was provided by Elf-Atochem, and had a weight average molecular weight ( $\bar{M}_w$ ) of 125,000 and a  $T_g$  of 113°C. Aminolysis reactions by cyclohexylamine were performed in perfectly hermetic inox reactors (specially designed for this study) under pressure and in xylene; the polymer concentration prediluted in xylene was set at 30% by weight. The different parameters studied are approached in turn in this part.

#### Amine/Ester Stoichiometry Influence on Imidization Reaction

In order to optimize the imidization reaction conditions and to better understand its mechanism, we studied the starting amine/ester stoichiometry's influence on the imidization ratio and on the polymer thermal resistance. Thus, we operated at 250°C for a 2-h period. The ratio of  $[\text{cyclohexylamine}]_0/[\text{ester}]_0$  was varied from 0.25 to 3 (Table I).

The various species present in the polymer were followed by FTIR. As indicated in Figure 6, the formation of the glutarimide structure is fa-

vored for a stoichiometry ratio close to 1; indeed, the imide group curve reaches a maximum at this value. It slowly decreases for values higher than 1. On the contrary, if the stoichiometry ratio is low ( $<0.75$ ), the formation of acid functions is favored rather than amide functions.

Whatever the stoichiometry, the imidization ratio is limited by the presence of amide and acid functions in the polymer. From the DSC study of the thermal behavior of the different samples (Fig. 7) it can be seen noticed that the  $T_g$  gradually increases with the starting stoichiometric ratio, then it reaches a stage level at 193°C when the stoichiometric ratio is equal to 1 and above 1.

#### PMMA Chemical Modification Kinetics at Various Temperatures

These kinetic studies were performed in optimal stoichiometry conditions for imidization (i.e., using equimolar amounts of esters and amines).

At each studied temperature the samples from the same initial reaction mixture were taken over time, and the polymers were purified by precipitation in hexane.

FTIR and volumetric titrations performed for each sample allow the observation of the



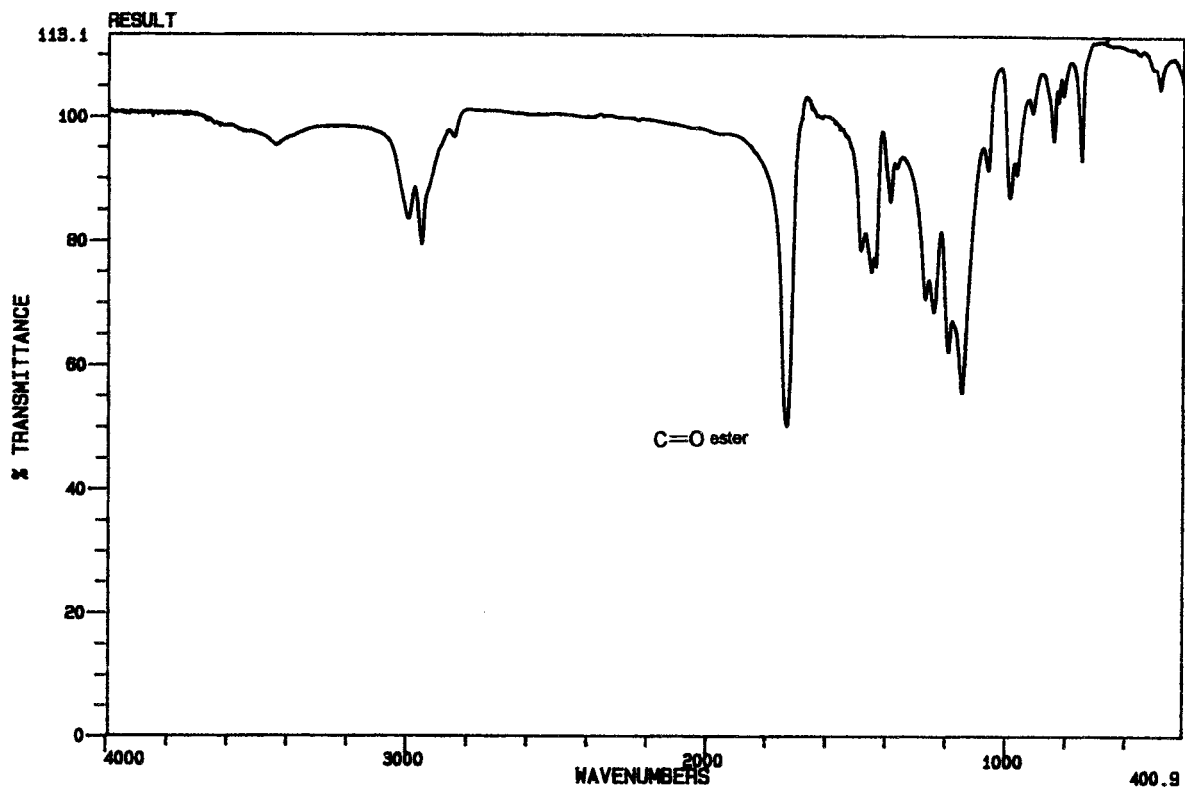


Figure 4 PMMA FTIR spectrum (CHCl<sub>3</sub>).

evolution of the different functionalities with time.

The good agreement between nitrogen percentages calculated by FTIR (imide + amide), titra-

tion (ammonium salt), and elemental analysis, and the final mass balance being at  $100 \pm 8\%$  are indications showing the reliability of the analysis method employed. This residual error is probably

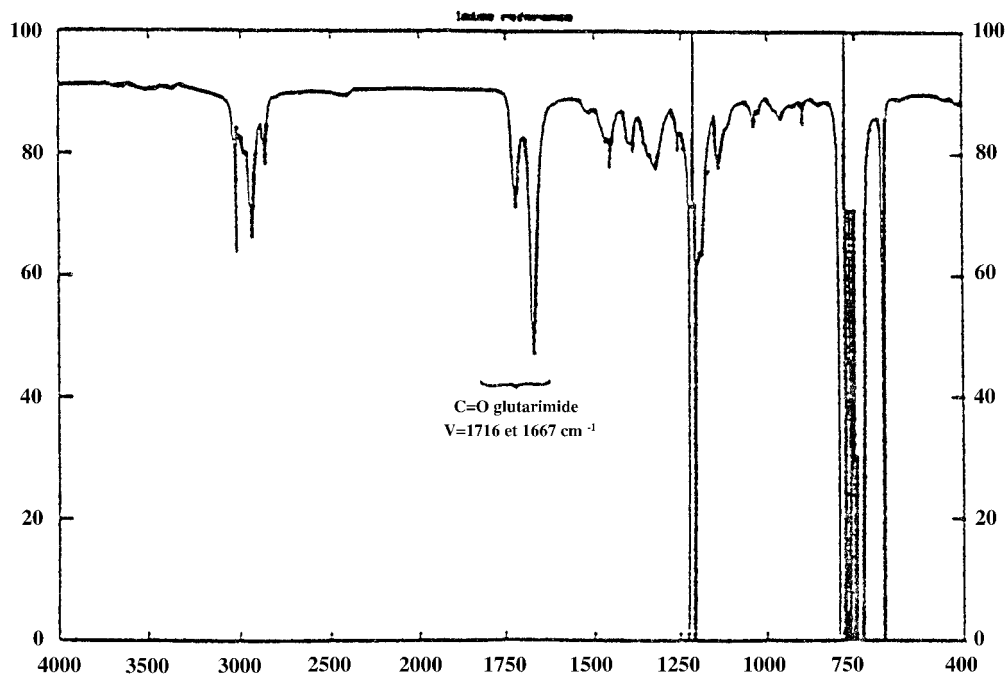


Figure 5 Poly(N-cyclohexylglutarimide) (PCGLUT) FTIR spectrum (CHCl<sub>3</sub>).

**Table III FTIR Standard Spectral Data**

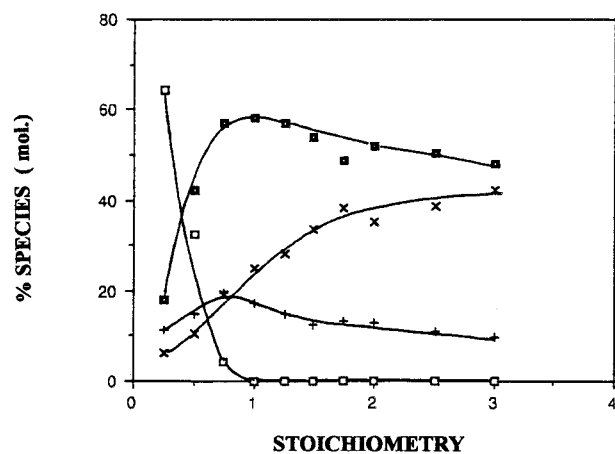
Standard	Absorption	
	Type	$\nu$ (cm <sup>-1</sup> )
PMMA	C=O	1729
PMCMIDE	C=O	1654
	NH Stretching	3451
	NH Bending	1510
PCGLUT	(C=O)asym	1716
	(C=O)sym	1667

due to cumulated errors coming from the various titration techniques used.

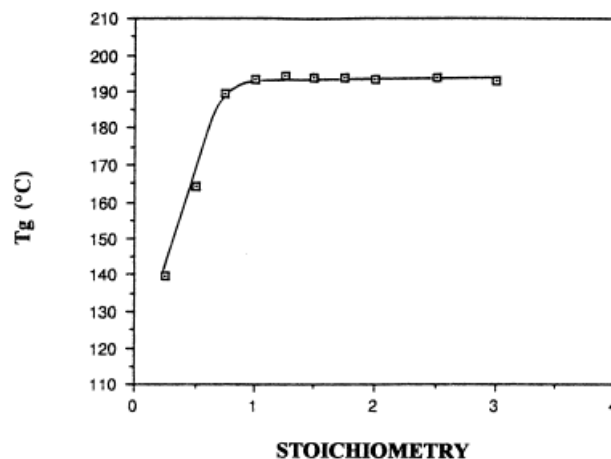
All the mass percentages were converted into molar percentages and the results are given as curves in Figure 8 to better visualize the evolution of each species with the treatment temperature. The schemes in Figure 8 clearly indicate that all the amide, acid, and imide forms coexist, whatever the treatment temperature studied.

Concerning imidization, the more the reaction temperature increases, the faster the glutarimide links are formed and in increasing amounts. Thus, at 190°C the imidization process begins only after 4 h and the imide ratio hardly reaches 30% after 23 h; at 250°C the imidization occurs very rapidly, reaching a 60% ratio after 2.5 h.

The lower the treatment temperatures (190–210°C), the more important amidization and *N*-alkylation processes are compared to imidization. Even at the very beginning of the treatment, we observed that the acid forms dominate until 30–45



**Figure 6** Species evolution versus C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>/starting ester stoichiometry (conditions: T = 250°C, T = 2 hours): (+) Acid, (×) Amide, (■) Imide, (□) Ester.



**Figure 7**  $T_g$  evolution versus C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>/starting ester stoichiometry (conditions: T = 250°C, t = 2 hours).

min. Then the amide level overtakes the acid level and tends to stabilize at around 30–35%.

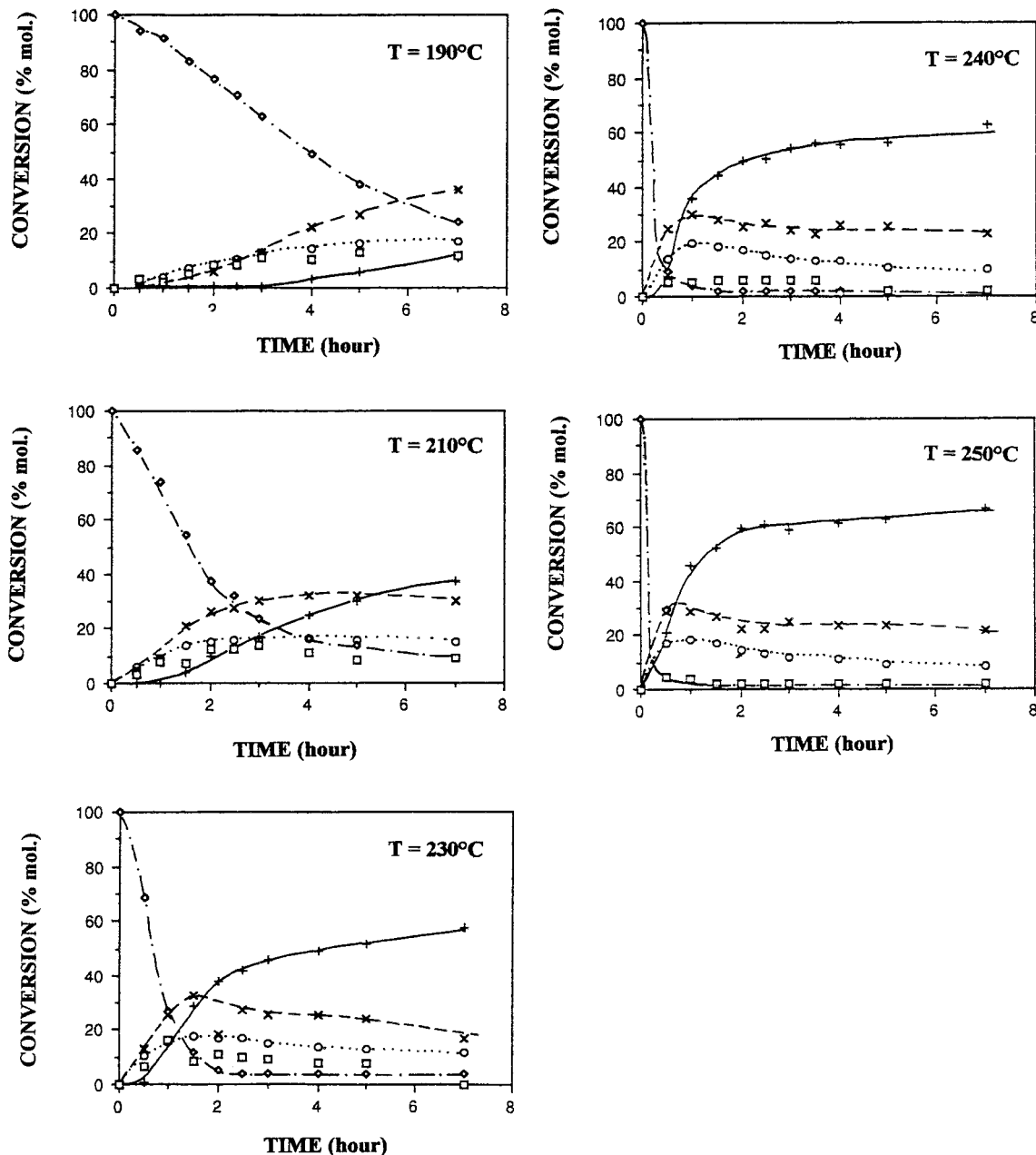
At elevated temperatures (240–250°C) the amidization process predominates at the very beginning of the reaction and then decreases with time and stabilizes at around 20–25%. It is replaced by the imidization process, which increases very rapidly. It should be noted that amidization is always preponderant over *N*-alkylation at these temperatures.

#### **Influence of Treatment Temperature on PMMA Thermal Behavior**

The evolution of the PMMA thermal behavior was observed at the different treatment temperatures by performing a DSC analysis for each sample to measure its  $T_g$ . From Figure 9 one can notice that the polymer  $T_g$  increases as the reaction temperature increases and reaches a plateau at 190°C. At high treatment temperatures this level tends to slightly decrease with time. This phenomenon may be explained by a possible degradation of the polymer or by a decrease of amide and acid polar functions.

It is interesting to interpret this  $T_g$  increase from the polymer chemical modification. However, it is difficult to discover a direct correlation between the polymer  $T_g$  and the formation of a particular species, because all the species appear simultaneously.

Figure 10 shows the variation of  $T_g$  with the imide level; a very important increase of the  $T_g$  between 0 and 5 mol % imides is observed. Then, from 10% imides the  $T_g$  reaches a plateau at 190°C.



**Figure 8** Evolution of the PMMA species aminolysed by cyclohexylamine at different temperature: (O) ACID, (X) AMIDE, (I) IMIDE, (◇) ESTER, (□) AMINE.

In fact, this curve is distorted by the presence of amide and acid functions (mainly for low imidization ratios), which participate to a large degree in the  $T_g$  increase, by the increase of the intermolecular forces due to hydrogen bonds. Thus, the synthesized poly(*N*-cyclo/hexylmethacrylamide) that was used for the FTIR calibration exhibits a  $T_g$  at 146°C while PMAA exhibits a  $T_g$  at around 230°C.<sup>36</sup>

We tried to find a correlation with Fox's equation<sup>37</sup> for the  $T_g$  in the function of the various species:

$$\frac{1}{T_g} = \sum_i \frac{\omega_i}{T_{g_i}}$$

where  $\omega_i$  is the mass fraction of the  $i$  species and  $T_{g_i}$  is the  $T_g$  of the  $i$  species homopolymer. How-

ever, the various attempts at calculation showed that these polymers do not obey this type of relation.

From all these results it seems that mainly imide and acid functions exert the greatest influence on the  $T_g$  increase, the former by stiffening the polymer chain, the latter by increasing the chain cohesion.

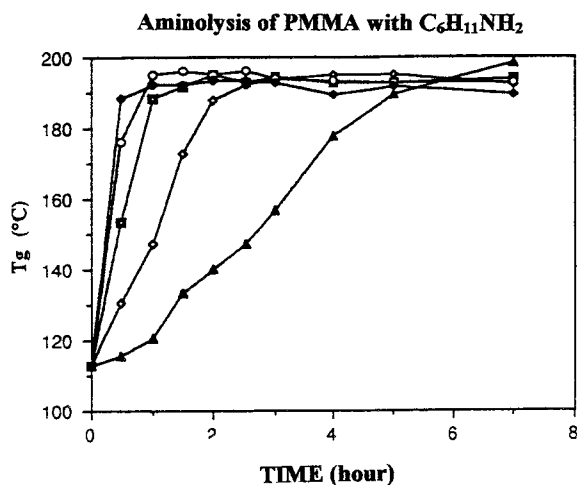
Similarly, we also investigated the aminolysis of PMMA by methylamine,<sup>38</sup> because it is a far more nucleophilic amine and more reactive toward the polymeric methyl esters. Furthermore, it is the amine used by Röhm and Haas to obtain polyglutarimides commercialized as Kamax.

In Figure 10 we show the evolution of  $T_g$  with the *N*-methyl glutarimide level. For the same imide level, the  $T_g$ s obtained with cyclohexylamine are always higher than those obtained with methylamine.

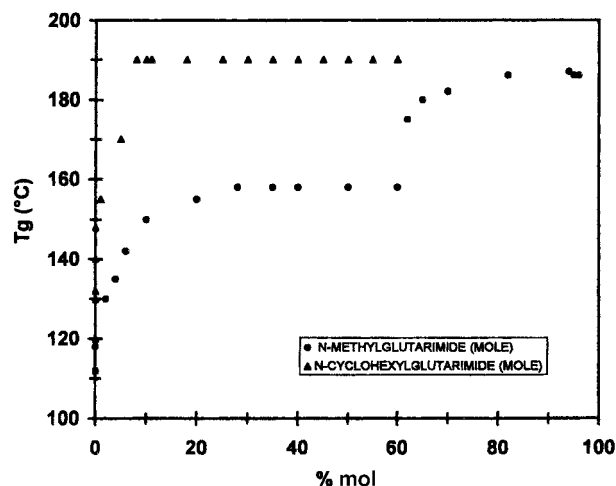
This result may look paradoxical because a cyclohexyl ring, being bulkier than a methyl group, should contribute to a decrease in the  $T_g$  by a plasticizer effect. However, it should be pointed out that the chemistry of these modification reactions is different, because of the additional polar amide functions in the case of cyclohexylamine. For this reason the  $T_g$  values are hardly comparable.

## CONCLUSION

During this study we developed a method to chemically characterize and to determine by



**Figure 9**  $T_g$  evolution versus time at various reaction temperature: (▲) 190°C, (◇) 210°C, (□) 230°C, (○) 240°C, (◆) 250°C.



**Figure 10**  $T_g$  curves versus *N*-cyclohexylglutarimide and *N*-methylglutarimide ratio.

FTIR the functionalities existing in aminolysed PMMAs. Then we used this titration technique for kinetic studies of the chemical modification of radically polymerized PMMAs in the presence of cyclohexylamine. We identified and followed all the species formed along this reaction, and thus the mechanism suggested by Röhm and Haas was confirmed. We stated the specificity of the modification reaction depending on the amine used: cyclohexylamine leads to amide, glutarimide, and acid functions.

From this study it was observed that imidization by cyclohexylamine in a solvent medium is favored when the stoichiometric amine/ester ratio is equal to 1, and this let us assume that the real imidization mechanism takes place with 1 amine for 1 ester.

We succeeded in correlating the glass transition temperature increase of these materials with the stiffening of the polymer chain when glutarimide functions are formed and with interchain cohesion when acid functions are formed.

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