

# Synthesis and Thermal Properties of Bismaleate and Bisfumarate Telechelic Oligomers from Hydroxytelechelic Polybutadienes

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**ABSTRACT:** The preparation of original telechelic bismaleate and bisfumarate polybutadienes and their thermal properties are presented. These functional oligomers were synthesized by the esterification of a hemiester of maleic anhydride and methanol or an ethyl hemiester fumarate with hydroxytelechelic polybutadiene (HTPBd) in 94 and 63% yields, respectively. The thermal and thermomechanical properties of the materials obtained from the radical copolymerization of these telechelic bismaleate and bisfumarate polybutadienes with hexane-1,6-dimethacrylate (HDDMA) were investigated and compared to those of a classic polyurethane (PU) resin prepared from HTPBd and hexamethylene diisocyanate. Calorimetry identified only one glass transition temperature of  $-75^{\circ}\text{C}$  assigned to the polybuta-

dienic backbone for all three resins, while a second transition at  $48^{\circ}\text{C}$  attributed to the methacrylate network and was noted by thermomechanical analysis. Both bismaleate and bisfumarate oligomers led to materials having a slightly better thermal stability than that of the PU resin. Thermomechanical analyses indicated that the elastic moduli of the materials achieved from bismaleate and bisfumarate oligomers are higher than that of the PU resin, whatever the temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 72–79, 2003

**Key words:** telechelics; polybutadiene; thermal properties; polyurethane; radical polymerization

## INTRODUCTION

Thermoset soft resins that exhibit low or very low glass transition temperatures and good thermal stability have been the subject of extensive investigation. The wider the range of use, the higher their performances and their price.

In this series, by decreasing order of price and thermal stability, are fluorinated polymers<sup>1–3</sup> and silicone resins,<sup>4</sup> but they are too expensive for numerous applications. Polyurethane resins from either polyethers or from hydroxy telechelic polybutadiene are relevant and widely used because of the versatility of their performance. However, their poor thermal stability (mainly due to urethane links<sup>5</sup>) and toxicity from diisocyanates<sup>6</sup> have directed researchers to use other crosslinking agents and chain extenders.

Finally, and this is the subject of our study, several resins involve unsaturated telechelic oligomers with reactive diluents that enable crosslinking by a radical method.

Using this method, various authors<sup>7–15</sup> have introduced reactive double bonds as end-groups in tele-

chelic hydroxy polybutadiene (HTPBd). The oldest surveys were carried out by Pinazzi et al.,<sup>7</sup> who reported the chemical change of HTPBd by phosgene and methacryloyl chloride. In 1984, Kimura et al.<sup>8</sup> used such reactive oligomer-type materials after dilution in an acrylate to study UV-curing optical fibers and compared them to acrylate silicone resins. In another investigation, the same authors<sup>9</sup> compared the dynamic mechanical properties of the same diacrylate polybutadiene oligomers in formulation with a series of reactive diluents, corresponding polyether and epoxy acrylate resins.

The Arco Company<sup>10</sup> patented the transesterification of HTPBd by methyl methacrylate to obtain reactive oligomers by means of radicals.

However, the most often-used method of modifying HTPBd involves the addition of diisocyanate and of an acrylate bearing a hydroxyl group. This reaction can be realized directly in batch [mixing HTPBd, diisocyanate, and 2-hydroxyethyl acrylate<sup>11</sup> (HEA)] or in a two step-procedure<sup>12</sup> (HEA can be added onto the product obtained from the reaction of HTPBd with diisocyanate).

Because of the increase in viscosity after the addition of HTPBd onto diisocyanate (linked to a hydroxy functionality usually higher than 2), other authors<sup>13</sup> have carried out an addition that is 'reversed,' by reacting diisocyanate onto HEA to synthesize an ac-

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rylate-type molecule bearing an isocyanato endgroup. This compound is then reacted onto HTPBd.

In addition, Pascault et al.<sup>14</sup> have reported the kinetics of reaction in two 'reversed' steps involving HTPBd, HEA and hexamethylene diisocyanate (HDI). They deduced the amounts of gels versus the reaction parameters, and concluded that the gels formed after the semi-crosslinking of HTPBd segments with HDI.

As a matter of fact, chemical changes of HTPBd have already been achieved by *m*-isopropenyl- $\alpha,\alpha'$ -methyl benzyl isocyanate (TMI) that enabled us to obtain original telechelic polybutadienes bearing  $\alpha$ -methyl styrene end groups.<sup>15</sup> Interestingly, such a procedure minimizes the number of urethane groups (decreased by a factor 2) and avoids the formation of gels that may occur in the course of these reactions (involving HTPBd, HDI, HEA) that were previously reported.

Regarding the chemical change of carboxy telechelic polybutadiene, Geetha and Prabha-Karan<sup>16</sup> have used this oligomer to open succinic anhydride, followed by reacting glycidyl methacrylate to synthesize  $\alpha,\omega$ -dimethacrylate polybutadienes.

Hence, according to the literature, telechelic polybutadienes bearing various unsaturations have been synthesized. However, to our knowledge, those exhibiting maleate or fumarate end groups have never before been reported; this is the goal of the present article.

Introducing novel unsaturations (e.g., maleate or fumarate types) onto polybutadienes is interesting and original, and we have chosen a simple method that requires inexpensive reactants. The reactive diluent used in this work was hexane-1,6-dimethacrylate (HDDMA), because it is quite reactive about maleic and fumaric unsaturations, it is not volatile and it exhibits a low viscosity that enables the oligomers to be diluted easily.

We have studied the thermal and thermomechanical properties of these materials by differential scanning calorimetry, thermogravimetric analysis and dynamical thermal analysis. They have been compared to those of a classic polyurethane resin obtained from HTPBd and hexamethylene diisocyanate (HDI).

## EXPERIMENTAL

### Reactants

Hydroxytelechelic polybutadiene was kindly offered by Atofina Company (Serquiny, France). We used the R45HT-type (average molecular weight of 2800 g/mol for an average hydroxyl functionality of 2.3 eq/mol).

Maleic anhydride, methanol, the hemiester of fumaric acid, but-2-ene-1,4-diol and hexane-1,6-dimethylacrylate (HDDMA) were supplied by Aldrich. Tert-butyl peroxyvalate, used as initiator, was kindly given by La Chalonnaise des Peroxydes Company (Chalons sur Saône, France). It was 75% pure in a solution of dodecane.

### Apparatus

#### Chemical analyses

The synthesized products were characterized by <sup>1</sup>H-NMR Spectroscopy at room temperature by means of a Bruker AC 250 spectrometer using deuterated chloroform as the solvent and TMS as the reference ( $\delta$  represents a singlet).

FTIR spectra were recorded on a Nicolet 510 P apparatus with an accuracy of  $\pm 2$  cm<sup>-1</sup>.

#### Thermal analyses

Glass transition temperatures of the materials were assessed by means of a Perkin Elmer Differential Scanning Calorimeter (Pyris 1). The samples were heated under nitrogen for measurements of  $T_g$  above room temperature (RT) and under helium when  $T_g$  measurements were below RT. In these latter conditions, the scan started from  $-125^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . The decomposition temperatures were achieved by a thermal gravimetric analyzer under nitrogen or air from RT to  $600^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$ .

#### Dynamic mechanical analyses

These analyses were carried out with a Perkin Elmer DMA 7 under helium using a thermal scan ranging from  $-150^\circ\text{C}$  to  $100^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ . These measurements enabled us to determine the  $\alpha$  transition temperatures associated with the glass transition temperature of different materials and the evolution of the elastic moduli versus the temperature.

### Experimental procedures

Synthesis of hemiester of maleic anhydride and methanol.

A quantity of 10.0 g (0.1 mol) of maleic anhydride and 60 mL of methanol were placed in a two-necked round bottom flask equipped with a condenser and magnetically stirred under nitrogen atmosphere. Then, the mixture was refluxed ( $65^\circ\text{C}$ ) for two hours and, after cooling of the solution, methanol was evaporated. The obtained liquid was characterized by <sup>1</sup>H-NMR spectroscopy and evaporated. <sup>1</sup>H-NMR spectroscopy confirmed the total conversion of the reactants into the hemiester of maleic anhydride.

$^1\text{H-NMR}$  (ppm) : 3.85 (s,  $\text{OCH}_3$ ); 6.30 (s,  $\text{CH}=\text{}$ ); 11.20 (broad s,  $\text{CO}_2\text{H}$ )

#### Synthesis of 1,4-bismaleate-but-2-ene

A quantity of 5.0 g ( $5.7 \times 10^{-2}$  mol) of 2-butene-1,4-diol, 7.4 g ( $5.7 \times 10^{-2}$  mol) of the hemiester of maleic anhydride prepared above and 40 mL of toluene were stirred in a two necked-round bottom flask equipped with a Dean Stark and a condenser. This mixture was heated to  $80^\circ\text{C}$  and 0.27 g ( $2.84 \times 10^{-3}$  mol) of methane sulfonic acid (MSA) were added to the solution. Then, the reaction medium was subjected to reduced pressure (160 mm Hg) to obtain the reflux of an azeotropic toluene-water mixture for 6 h. After reaction, the total product mixture was worked up as follows: extraction of residual organic acids with a NaOH solution (0.5N), drying of the organic phase ( $\text{Na}_2\text{SO}_4$ ), filtration and evaporation of toluene. The reaction was monitored by IR and  $^1\text{H-NMR}$  spectroscopy, and the latter analysis enabled us to assess the conversion of diol or modified polyol. The yield was 80%.

#### Synthesis of 1,4-bisfumarate-but-2-ene

The same procedure was repeated starting with 5.002 g ( $5.7 \times 10^{-2}$  mol) of 2-butene-1,4-diol, 8.201 g ( $5.7 \times 10^{-2}$  mol) of the hemiester of fumaric acid and methanol. The same treatment as above was carried out, and 2-butene-1,4-bisfumarate was obtained in 92% yield.

#### Preparation of telechelic polybutadiene with maleate end groups

With the same procedure and work-up as above, starting from 10.010 g (8.1 mmol) of HTPBd and 1.052 g (8.1 mmol) of synthesized maleic-type hemiester,  $\alpha,\omega$ -dimaleate polybutadiene was obtained in 94% yield.

#### Synthesis of bisfumarate telechelic polybutadiene

Similarly, starting from 10.005 g (8.1 mmol) of HTPBd and 1.170 g ( $8.1 \times 10^{-3}$  mmol) of fumarate-type hemiester,  $\alpha,\omega$ -difumarate polybutadiene was obtained in 63% yield.

#### Preparation of polyurethane resins

20.003 g (7.6 mmol) of HTPBd and 1.562 g (9.3 mmol) of HDI were vigorously stirred at room temperature, under atmospheric pressure, and the mixture was placed in an oven at  $80^\circ\text{C}$  for 1 h to allow crosslinking.

#### Synthesis of crosslinked resins from bisfumarate and bismaleate modified HTPBds

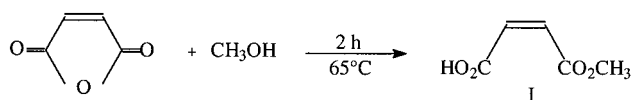
In a flask, a mixture composed of 16.0 g (5.6 mmol) of modified HTPBd, 4.00 g (17.7 mmol) of hexane-1,6-diacrylate, 0.100 g (0.25 mmol) of cobalt naphthenate and 0.100 g (0.43 mmol) of tert-butyl peroxy-pivalate was stirred at room temperature for 5 min. Then, the reaction medium was poured into an aluminum pan and left at room temperature for one hour to enable adequate curing.

## RESULTS AND DISCUSSION

Several methods can be used to achieve the synthesis of functionalized (e.g. fumarate and maleate) oligobutadienes. The first one, which is the simplest, concerns the direct opening of maleic anhydride by HTPBd, leading to a telechelic oligomer bearing maleate and carboxylic end groups. This process requires a further isomerization to obtain its fumarate homologue. The second alternative deals with the preparation of the hemiester of maleic anhydride and methanol, and the hemiester of fumaric acid and ethanol and the azeotropic esterification of HTPBd acido-catalyzed by methane sulfonic acid with these two precursors.

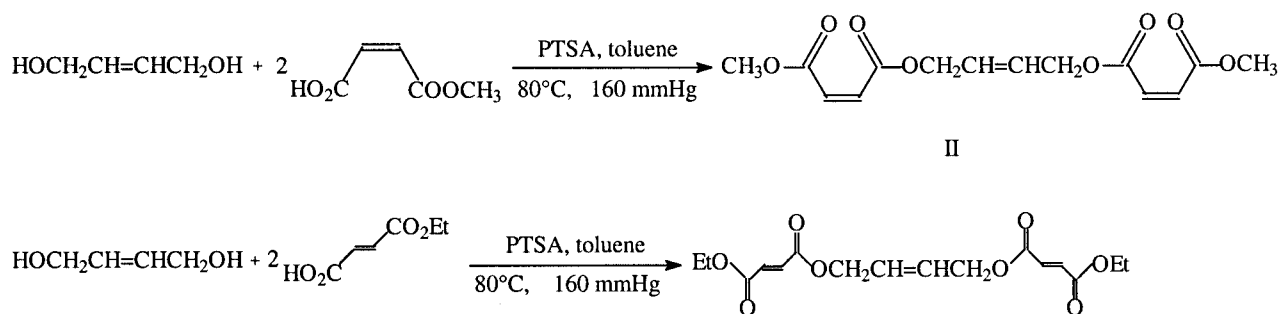
Both these methods were applied to HTPBd. The first one has shown that the opening of maleic anhydride by unsaturated polyols such as HTPBd was achieved in poor yields in contrast to the latter method, which led to encouraging results. In addition, the obtained diacid oligomers had to be esterified by a simple alcohol that could be easily gotten rid of. This was required to avoid the thermal retrogradation (into alcohol and anhydride) evidenced by Engle and Wagener.<sup>17</sup> Moreover, the presence of carboxylic acids contributes to an increase in the viscosity of the product that represents a key factor in its processing.

Hence, the second alternative was used from commercially available HTPBd and ethyl fumarate and from the hemiester of maleic anhydride and methanol synthesized by the direct addition of methanol onto maleic anhydride. This is summarized in the following scheme:



Furthermore, to better characterize the modified oligomers, we have achieved a model reaction from a molecular diol (e.g. 2-butene-1,4-diol), whose reactivity by esterification is close to that of HTPBd.

Hence, the procedure is as follows:

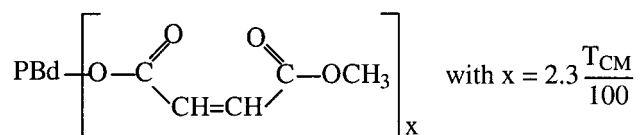


These reactions were monitored by FTIR spectroscopy, which mainly shows the disappearance of all OH-vibration bands (from the alcohol and the acid). However,  $^1\text{H-NMR}$  spectroscopy was a more accurate method of observing the conversion rate of the reactants. The characteristic chemical shifts are shown in Table I.

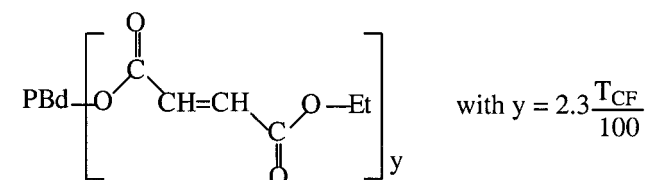
Furthermore, the results show that, under moderated conditions ( $80^\circ\text{C}$  for 6 h), in the presence of methane sulfonic acid,  $\alpha,\omega$ -bisfumarate molecules cannot be obtained from the isomerization of  $\alpha,\omega$ -bismaleate. Indeed, the 1,4-bismaleate or 1,4-bisfumarate-but-2-ene molecules keep the same configuration as that of the precursor (methyl hemiester maleate or ethyl hemiester fumarate).

Higher temperatures (e.g. at least  $160^\circ\text{C}$  under acido catalysis) are required to reach the isomerization point.<sup>18</sup> However, such drastic conditions are not possible for HTPBD and methyl maleate, especially for HTPBD, which is likely to be degraded by thermal crosslinking.

Hence, direct functionalization in the presence of ethyl fumarate was preferred without performing isomerization of the previous maleate-functionalized oligomers. This was achieved by using the above procedure, and both obtained oligomers have the following formulae:



and



where  $T_{\text{CM}}$  and  $T_{\text{CF}}$  represent the conversion rates of reactants into maleate and fumarate groups.

The  $^1\text{H-NMR}$  spectra of HTPBD, maleate-functionalized PBd and fumarate-functionalized PBd are



shown in Figures 1–3, respectively. The absence of signals centered at 3.5 and 4.1 ppm, assigned to allylic and vinylic methylene groups adjacent to hydroxyl end groups of 1,4- and 1,2- units, respectively, can be noted in Figure 1, and their low field shifts toward 4.1 and 4.6 ppm can be noted in Figures 2 and 3. This is evidence that these methylene groups are located in a position adjacent to ester functionalities. The chemical shifts of the methylene groups are characteristic of maleate and fumarate forms.

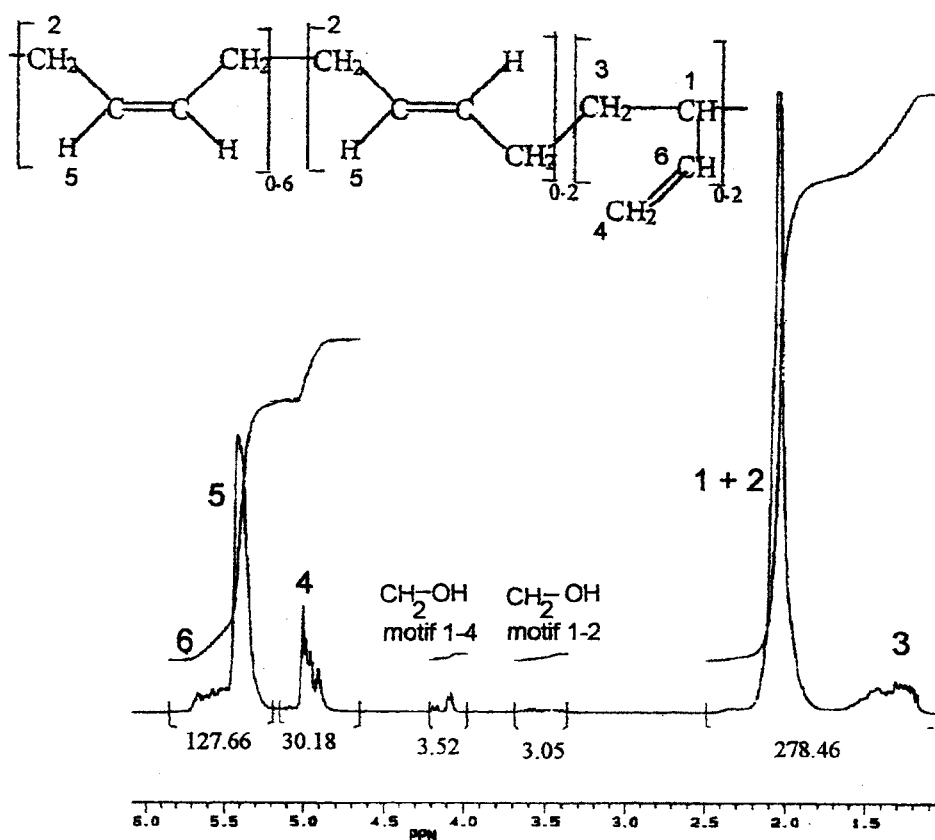
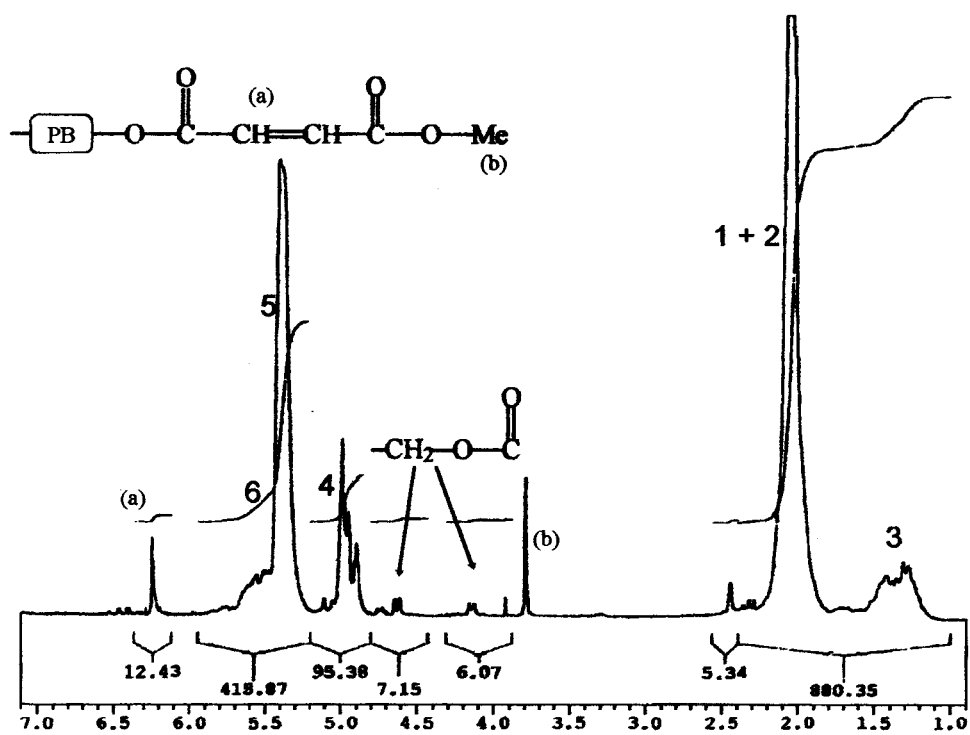
Regarding the maleate structure, the protons of unsaturation are centered at 6.25 ppm, while those of the methyl groups of the maleic ester appear at 3.8 ppm.

The  $^1\text{H-NMR}$  spectrum of the telechelic bisfumarate PBd shows a multiplet centered at 6.8 ppm, assigned to the protons of the double bond, which distinguishes them from the maleate structure. Through such a reaction, the isomerization can be investigated, if it occurs. In the same way, the signals at 4.2 and 1.3 ppm are characteristic of methylene groups adjacent to the ester functionality and to the methyl end group in the ethyl group, respectively. Comparing the integrals of methylene groups in the  $\alpha$  position to ester groups and those of the maleate and fumarate protons enables one to calculate the conversion rates, named  $T_{\text{CM}}$  and  $T_{\text{CF}}$ .

The functionalization rates were assessed from comparing the integrals of the inner protons in the oligomeric chain in the ester position with those of CH of unsaturations. The results obtained from 1,4-diol-but-2-ene and HTPBD are summarized in Table II.

TABLE I  
 $^1\text{H-NMR}$  Chemical Shifts of But-2-ene-1,4-bismaleate and But-2-ene-1,4-bisfumarate.

Functionality	Chemical Shift (ppm)
	6.3
	6.8
$\text{O}-\text{CH}_3$	3.8
$\text{O}-\text{CH}_2-\text{CH}_3$	4.3
$\text{O}-\text{CH}_2-\text{CH}_3$	1.3

Figure 1  $^1\text{H-NMR}$  spectrum of HTPBd.Figure 2  $^1\text{H-NMR}$  spectrum of bismaleate modified HTPBd.



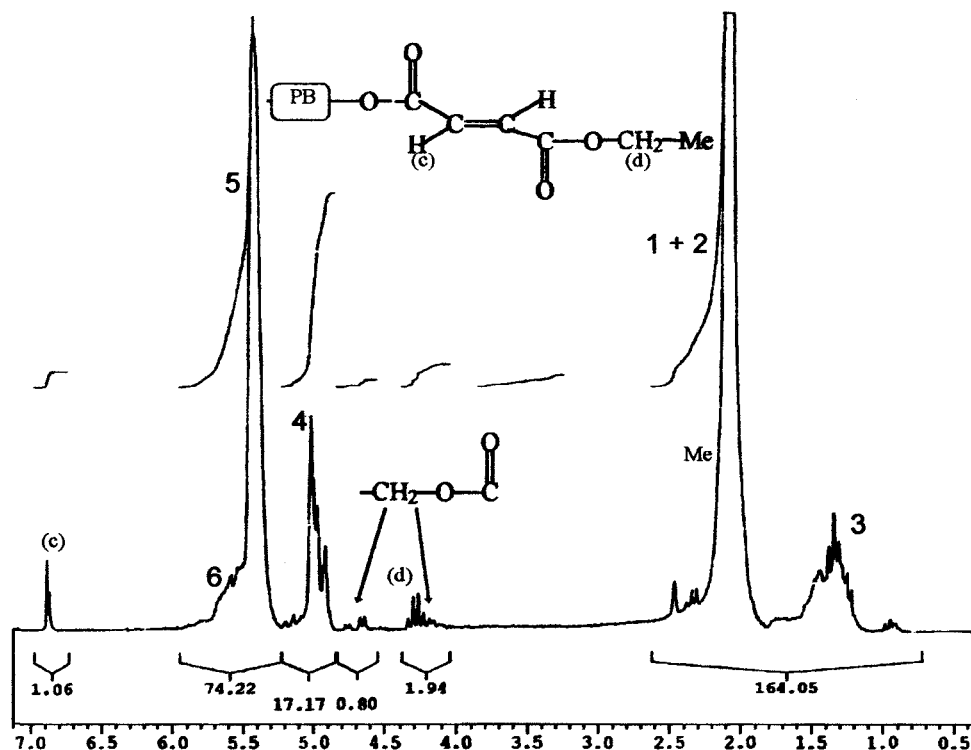


Figure 3  $^1\text{H-NMR}$  spectrum of bisfumarate modified HTPBd.

Then, formulations of these reactive oligomers were carried out, involving hexane-1,6- dimethacrylate (HDDMA) as reactive diluent, tert-butyl peroxyvalerate as the initiator and cobalt naphthenate as cocatalyst to enable the crosslinking of the resin at room temperature. The composition in the reactive oligomer was about 70% of maleate or fumarate-functionalized HTPBd, including 30 wt % of HDDMA. These resins, initially in a visquous liquid state, were cured at 80°C for 2 h.

In addition to the synthesis of these new elastomers, a polyurethane was synthesized from HTPBD and HDI, since PU, as presented above, showed the best compromise in the choice of the reactants (including polyalcohol and diisocyanate) and for its thermal stability.<sup>19</sup> Thus, the properties of these materials were investigated and compared.

### Thermal analyses

First, calorimetric analyses were conducted on both materials obtained from modified oligomers and from

TABLE II  
Conversion Rates into Maleate or Fumarate

Products	$T_{\text{CM}}$ or $T_{\text{CF}}$ (%)
But-2-ene-1,4-bismaleate	80
But-2-ene-1,4-bisfumarate	92
Maleized HTPBd	94
Fumarized HTPBd	63

the PU resin. For these three elastomers, the presence of a glass transition temperature ( $T_g$ ) was observed at  $-75^\circ\text{C}$ , characteristic of the soft phase formed by the soft backbone of polybutadiene. Except for this  $T_g$ , no other transition was noted, as expected and characteristic of an acrylic network of both modified materials.

Regarding thermogravimetric analysis (TGA), Figure 4 shows the superposition of the thermograms of three materials. As for the PU resin, a first loss of weight (approx. 8%) was noted from 260 to 300°C,

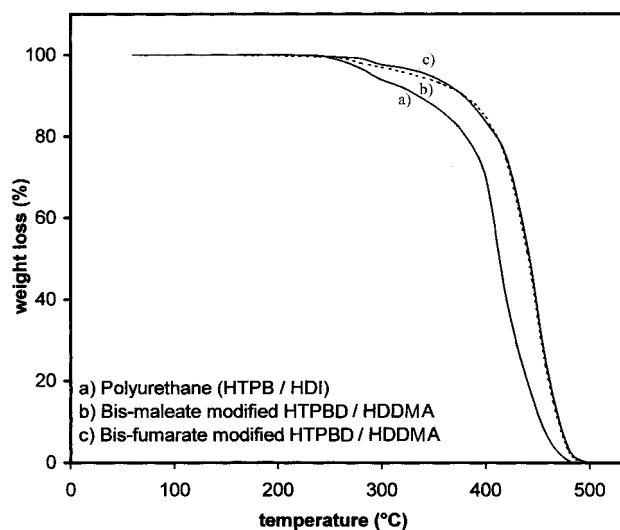
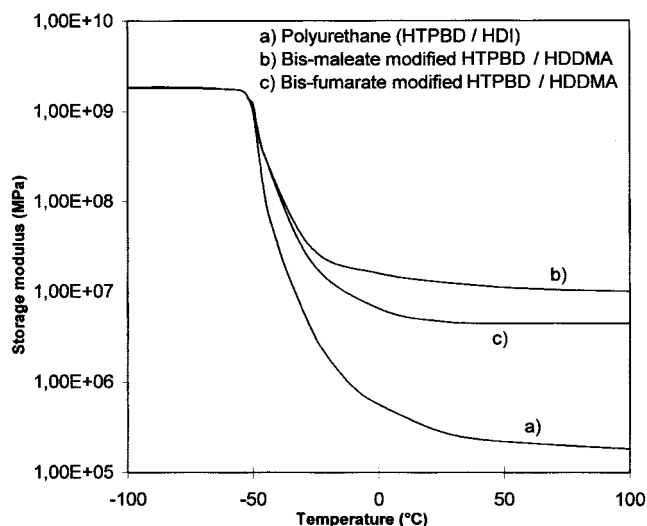


Figure 4 TGA thermograms of PU resin: (a) bismaleate; (b) bisfumarate; (c) modified HTPBd.



**Figure 5** Storage moduli of PU resin: (a) bismaleate; (b) bisfumarate; (c) modified HTPBd.

corresponding to the degradation of urethane links related to the decomposition of the diisocyanate (HDI) introduced in the formulation.

Interestingly, these original resins (especially the telechelic bismaleate and bisfumarate oligomers modified by HDDMA) exhibit similar behavior under thermogravimetric analysis. They start to undergo a degradation from 300°C, more slowly than the PU resin. Hence, these new resins show an improved thermal stability compared to those of conventional PUs.

To assess and compare the thermomechanical behavior of these resins, it was useful to investigate their dynamic mechanical analyses.

### Dynamical mechanical analysis (DMA)

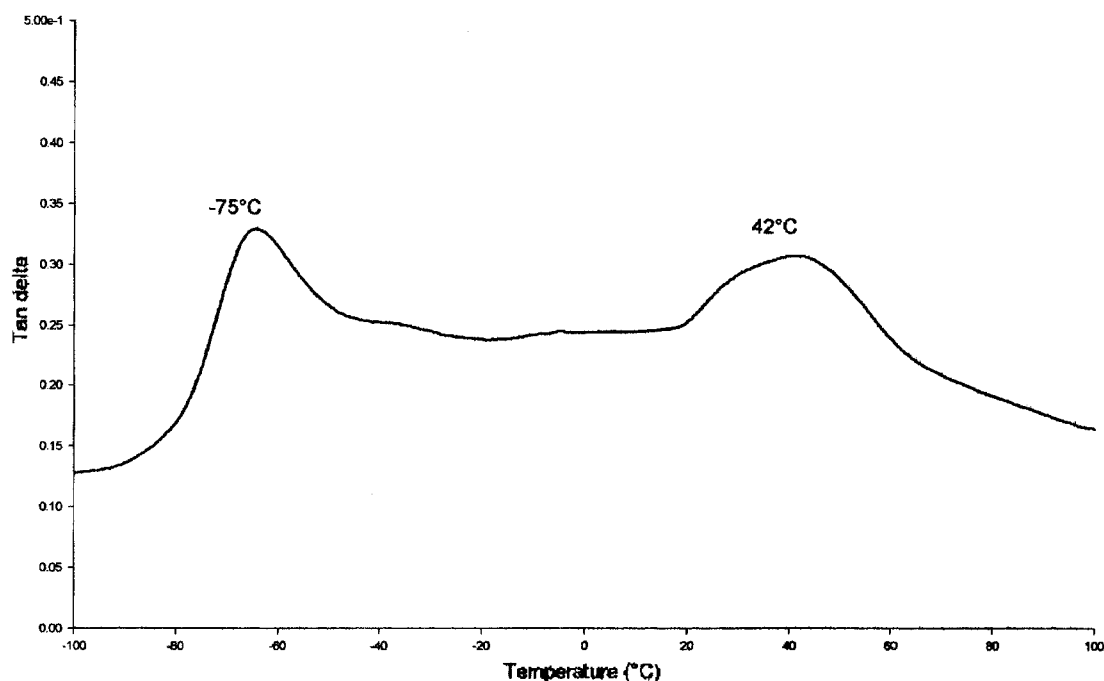
Such an analysis enables one to monitor the evolution of the elastic modulus versus the temperature. Figure 5 represents the modulus-temperature curves of the three resins mentioned above.

First, it can be observed that the rigidity of the original materials based on modified oligomers and HDDMA is higher than that of PU, whatever the temperature. At 20°C, the elastic moduli of the resins containing maleate-modified polybutadiene, the fumarate resin and the PU resin rose up to 10.0, 7.0 and 0.6 MPa, respectively.

The difference in rigidity between both novel modified HTPBds (telechelic bismaleate and bisfumarate) is attributed to the difference of the HTPBd conversion rate (94% of hydroxyl end groups into bismaleate ones and only 65% into bisfumarate ones). Hence difference of hardness of the networks formed from these modified HTPBd can be explained.

This analysis also enables one to monitor the evolution of  $\tan\delta$  versus the temperature. This method is useful in assessing the  $\alpha$  transition temperature associated with the  $T_g$ 's of these materials.

Figure 6 exhibits the DMA thermogram of a material containing maleate-modified HTPBd and HDDMA where two phase transitions are observed: (1) the one



**Figure 6** DMA thermogram of the material obtained from the copolymerization of bismaleate modified HTPBd and HDDMA.

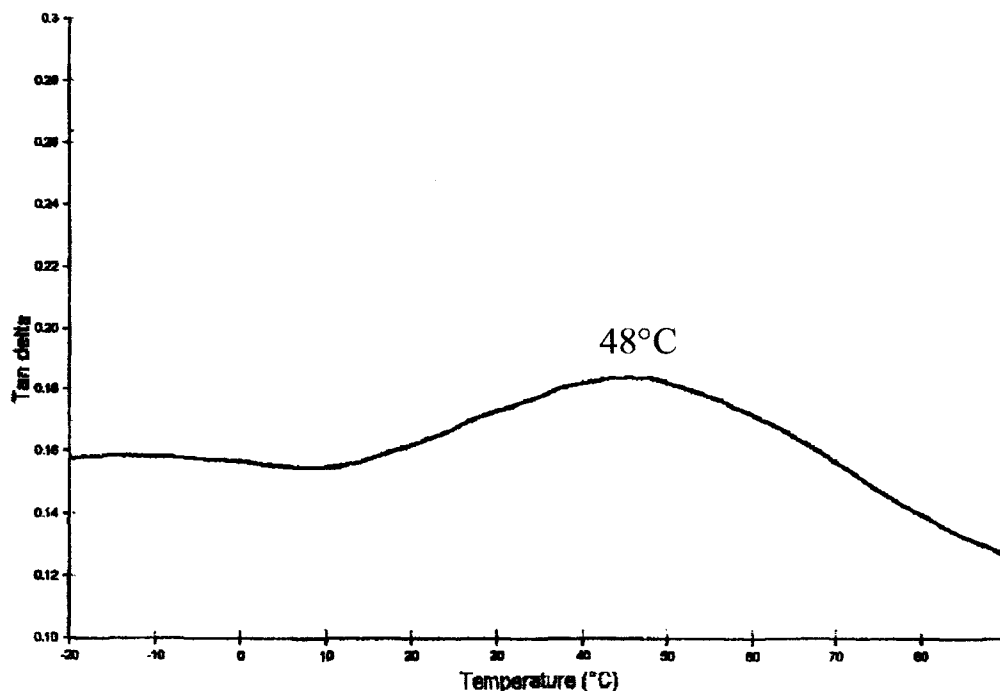


Figure 7 DMA thermogram of poly(HDDMA).

centered at  $-75^{\circ}\text{C}$  is associated with the soft phase characteristic of HTPBd (this was also characterized by DSC); and (2) the second one is attributed to the hard phase of the acrylic functions. Such a transition was also confirmed by the DMA thermogram of the homopolymer of HDDMA, indicating a mechanical glass transition temperature of  $48^{\circ}\text{C}$  (Fig. 7).

### CONCLUSION

Esterification of the hydroxyl end groups of HTPBd with the hemiester of methyl maleate was successfully achieved in good yield, while the conversion rate obtained from the fumarate homologue was lower. Regarding the comparison of these new materials with PU resins, it was noted that the thermostability was improved by about  $40^{\circ}\text{C}$ , especially at the beginning of the degradation, from about  $260^{\circ}\text{C}$ . DMA has shown that these original materials are harder than the corresponding polyurethane resins, but these mechanical behaviors can be modified into those of softer resins by simply changing the nature of the reactive diluent, and of its functionality. Actually, it is possible that a monofunctional reactive diluent containing a fatty ester chain could soften these resins, and such an optimization is under progress. Finally, these new oligomers, which exhibit the same reactivity as those of unsaturated polyester-type resins and can also be used as reactive diluent. As their unsaturations are electron-donating (e.g., vinyl ethers or styrene), they can be involved in acceptor/donor copolymerization.<sup>20–22</sup>

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