Synthesis and Use of Hydroxyl Telechelic Polybutadienes Grafted by 2-Mercaptoethanol for Polyurethane Resins

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ABSTRACT: The grafting of hydroxy telechelic polybutadienes (HTPBD) by 2-mercaptoethanol to saturate 1,2-double bonds which enabled an increase of the —OH functionality of HTPBD is presented. The functionalities of the virgin and grafted HTPBD were characterized both by ^{1}H-NMR after silylation of the hydroxy end groups and the consumption of the mercaptan was determined by iodine titration. The radical addition of 2-mercaptoethanol to HTPBD was not complete, which is not acceptable for an industrial application. Hence, the excess of mercaptan was reacted to allyl alcohol, leading to a new short telechelic diol able to be incorporated in the polyurethane (PU) network as a chain extender. This PU was prepared by addition of hexamethylene diisocyanate to both these diols. The thermal (glass transition, T_g, and decomposition temperatures), physical (gel time and viscosity), and mechanical (Shore hardness) properties were assessed. It was noted that the higher the hydroxyl functionality, the greater the Shore hardness, the viscosity, and the modulus but the lower the gel time and the break elongation. However, no improvement of the thermal stability was observed with the use of grafted HTPBD in PU resins. Their T_g's were observed to undergo a slight increase (of 4°C) in the case of PU prepared from Poly BD R45 HT® in contrast to that noted from Poly BD 20 LM® (20°C), showing a lower phase segregation in that latter case. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1655–1666, 2000

Key words: telechelic diol; polybutadiene; mercaptan; radical addition; polyurethane; thermal properties; functionality

INTRODUCTION

The industry of polyurethanes (PU) requires the use of different types of diols or polyalcohols according to the searched applications. Actually, macromolecular diols called "long diols" are able to regulate the softness properties, whereas "short diols or chain extenders" allow one to increase the length of the hard segments. Our interest was focused on macromolecular diols and especially on polyols used in crosslinked PU resins which exhibit good mechanical properties. In this case, triols based on propylene oxide are commercially available[1–3] and so are hydroxy telechelic polybutadienes (HTPBD) with functionalities usually higher than 2.0. HTPBD are quite interesting for their exceptional softness (their glass transition temperature is ca. −75°C), which opens up applications mainly as binders for liquid propellants,[4] but also as protective agents for electronic devices. However, their average hydroxyl functionalities are rather low (2.3 eq

Table I   Graftings of HTPB by Different Thiols

Nature of Thiol	Initiation	Applications	Reference
C_4H_9—SH	Thermal	Additives for composites	6,7
HO—$(CH_2)_2$—SH	Photochemical	Paints and coatings	8,9
HOOC—CH_2—SH	Photochemical	Photocrosslinkable oligomers	10
C_nF_{2n+1}—$(CH_2)_2$—SH	Photochemical,	Coatings for optical fibers	11
(n = 6 and 8)	thermal		12
$(EtO)_3Si$—$(CH_2)_3$—SH	Thermal	Adhesive materials	13
$(EtO)_2P$—$(CH_2)_3$—SH	Photochemical, thermal	Flame-retardant PU	14
$\parallel$			
O			

mol^{-1}) and also their hydroxyl contents depend upon the different lengths of the macromolecular chain,[5] but are usually low (2–2.7 eq mol^{-1}). Further, all HTPBD possess reactive 1,2-double bonds, especially in the presence of radicals which make these PU materials unstable to aging.

For all these reasons, we found it noteworthy to graft a thiol bearing a hydroxyl end group (e.g., 2-mercaptoethanol) to HTPBD to both increase the hydroxyl functionality and to saturate the 1,2-double bonds. Numerous graftings of various mercaptans to HTPB (including our investigations) were achieved by radical or photochemical ways (Table I). Such a reaction can also be carried out without any solvent to allow an industrial scale up. These new polyols with an improved functionality are interesting precursors of crosslinked PU resins, which was the objective of this study.

EXPERIMENTAL

Materials

HTPBD was kindly given by the Elf Atochem Co. (France). Two types are commercially available: Poly BD R45 HT® and Poly BD 20 LM® with an average molecular weight in number and hydroxyl indexes of 2800 and 1250 g mol^{-1} and 0.81 and 1.89 meq g^{-1}, respectively. The hydroxyl functionality is 2.3 eq mol^{-1} for Poly BDR 45 HT®, whereas it is 1.6 or 2.1 eq mol^{-1} for Poly BD 20 LM®. 2-Mercaptoethanol, an iodine solution (0.1029N), and bis(trimethyl silyl acetamide) (Aldrich, Saint Quentin Fallavièr, France), 2,2′-azobisisobutyronitrile (Merck, Paris, France), and t-butyl peroxypivalate (TBPP) (kindly supplied by La Chalonaise des Peroxydes, Chalons s/ Saône,

France) were used without further purification and the solvents were of analytical grades.

Analysis

Molecular weights (MW) and molecular weight distributions (MWD) of the polymers were determined by size-exclusion chromatography (SEC) with a Spectra Physics SP 4270 apparatus equipped with an integrator M730, a differential refraction detector SP8810, and four Ultrastyragel columns, the diameters of the pores of which were 500, 10^3, 10^4, and 10^5 Å. THF was used as the eluent at a rate of 1 mL min^{-1}, using polybutadiene standards.

The products were characterized by ^{1}H- and ^{13}C-NMR spectroscopies at room temperature. They were recorded on a Bruker AC-200 or AC-250 instrument, using deuterated chloroform as the solvent and TMS as the reference. The infrared spectra of the virgin or grafted HTPBP obtained were scanned by an FTIR Nicolet 510 P apparatus with an accuracy of ±2 cm.

Thermogravimetric analyses of the copolymers were monitored on a DuPont 2000 analyzer from 25 to 600°C at a heating rates of 5°C min^{-1}, under nitrogen or air. Glass transition temperatures were determined from a Perkin–Elmer differential scanning calorimeter equipped with a TADS microcomputer. The apparatus was calibrated with indium and with n-decane. After its insertion into the DSC apparatus, the sample was first cooled to −110°C for 15 min. A first scan was made at a heating rate of 20°C min^{-1}, up to 100°C, where it stayed for 2 min. Then, it was quenched to −110°C at a cooling-rate of 320°C min^{-1}. It was again left for 10 min at that temperature before a second scan at a heating rate of 10°C min^{-1} gave the

values of T_g reported herein, taken at the half-height of the heat-capacity jump of the glass transition.

Synthesis

Grafting in Solution of 2-Mercaptoethanol to HTPBD

In a 100-mL three-necked round-bottom flask equipped with a condenser and a nitrogen inlet were introduced 10.00 g (8×10^{-3} mol) of Poly BD 20 LM® and 0.940 g (12×10^{-3} mol) of 2-mercaptoethanol; then, the volume was completed to 50 mL by toluene. Under stirring, the mixture was saturated with nitrogen for 10 min. At the required temperature [which influences the decomposition rate (k_d) of AIBN], 0.020 g (10^{-3} mol) of AIBN was added to the solution. A second addition of AIBN, identical to the first one, was done at time t to maintain a constant radical concentration.

The reactional times (t_{RX}) of grafting were calculated as follows:

(a) For toluene at 85°C:

$$k_d = 1.58 \times 10^{15} \exp[-128900/(8.31 \times 358)]$$
$$= 2.41 \times 10^{-4} \text{ s}^{-1}$$

$$t_{1/2} = \text{ Ln } 2/k_d = 0.8 \text{ h} = 48 \text{ min}$$

$$t_{RX} = 5t_{1/2} = 4 \text{ h}$$

(b) For toluene at 100°C:

$$k_d = 1.4 \times 10^{-3} \text{ s}^{-1} \text{ and } t_{RX} = 5t_{1/2} = 42 \text{ min}$$

The thiol consumption was monitored by titration in the presence of iodine (described below). The pale yellow solution was then decolored in the presence of sodium thiosulfate; the organic phase was dried with sodium sulfate and toluene was evaporated under reduced pressure.

Bulk Grafting of 2-Mercaptoethanol to HTPBD

As above, 10.00 g (8×10^{-3} mol) of Poly BD 20LM® and 1.00 g (12.8×10^{-3} mol) of 2-mercaptoethanol were degassed under nitrogen for 10 min. When the temperature of the solution reached 85°C, 0.020 g (10^{-4} mol) of AIBN was added, followed by a second similar addition after

4 h. When the reaction time was 8 h, the residual thiol was titrated to determine the grafting rate, which enabled us to calculate the amount of allyl alcohol to introduce into the mixture. This was followed by the addition of AIBN, the amount of which was determined from the grafting rate. After 2 h, the 2-mercaptoethanol was titrated to be sure of its complete consumption. Finally, the excess of allyl alcohol was distilled (bp = 96°C).

The different syntheses were monitored by two analytical methods:

Volumetric Titration of Free Thiol Function

This concerns an oxidation–reduction process as follows:

$$2 \text{ RSH} + \text{I}_2 \rightarrow \text{RS—SR} + 2\text{HI}$$

$$\text{I}_2 + \text{HI} \rightarrow \text{H}^+ + \text{I}_3^-$$
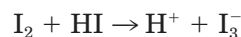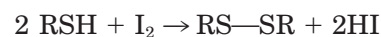
After sampling a known amount of the mixture, the mercaptan was titrated by an aqueous solution of iodine 0.1 mol L^{-1} (prepared from a tritisol ampule) under vigorous stirring until the change of color from colorless to pale yellow (presence of I$_3^-$). Then, the mol number of the free thiol can be calculated from the following formula:

$$n_{\text{thiol}} = N_{\text{I}_2} \times V_{\text{I}_2}$$

where N_{I_2} and V_{I_2} represent the normality and the volume of iodine, respectively.

Silylation of HTPBD

In a 50-mL two-necked round-bottom flask equipped with a condenser, a solution composed of 1.00 g of the oligomer and 15 mL of THF was refluxed. Then, 0.5 mL of bis(trimethylsilyl) acetamide (BSA) was added, and after 5 h, the mixture was cooled to room temperature. The excess of BSA was reacted with 5 mL of methanol. After evaporation, the total product mixture became a paste containing silylated oligomers and acetamide. A hexane/water extraction was performed to get rid of the by-products. The organic phase was dried under magnesium sulfate and evaporated.

Synthesis of PU

In a one-necked round-bottom flask, 30.00 g (1.07×10^{-2} mol) of Poly BD R45 HT® was vigorously

stirred at room temperature with 2.14 g (2.7 $\times 10^{-2}$ mol) of hexamethylene diisocyanate (HDI) and the mixture was quickly poured into an aluminum flask which was then put in an oven (100°C) for 30 min. The required amount of HDI (m_b) was determined from the following equation:
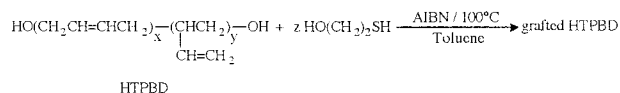
$$m_b = \sum (m_a E_{q_{OH}}) M_b \times 1.05/2$$

were m_a represents the amount of polyol (HT-PBD, propylene glycol, or chain extender) and M_b = 168.1 g mol^{-1}.
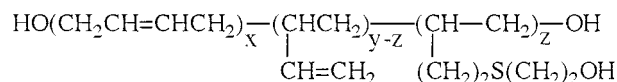
RESULTS AND DISCUSSION

Grafting in Solution

As shown above, the addition of 2-mercaptoethanol to HTPBD can be performed either photochemically or chemically. We have chosen this latter way since it is simpler and it can easily be scaled up. Toluene was used because it solubilizes all reactants and it allows the reaction to be carried out at 100°C. 2,2′-Azobisisobutyronitrile (AIBN) was used as the solvent for a reactional time of about 1 h (i.e., five half-lives). The reaction was as follows:

HO(CH₂CH=CHCH₂)ₓ—(CHCH₂)ᵧ—OH + z HO(CH₂)₂SH $\xrightarrow[\text{Toluene}]{\text{AIBN / 100°C}}$ grafted HTPBD

CH=CH₂

HTPBD

The grafted HTPBD exhibits the following formula:

HO(CH₂CH=CHCH₂)ₓ—(CHCH₂)ᵧ₋z—(CH—CH₂)z—OH

CH=CH₂   (CH₂)₂S(CH₂)₂OH

Both commercially available HTPBD (R 45 HT® and R 20 LM®) were involved in such grafting. To explain our methodology, the reaction describing the radical addition of this mercaptan to Poly BD 20 LM® is detailed below.

Such a telechelic polydiene has an average number of 1,2 double bonds of y = 4.23 per mol. A 1.5-fold molar excess of 2-mercaptoethanol about the butadienic oligomer was used to get a lower amount of mercaptan about the 1,2 double bonds. The calculated theoretical functionality was 3.6 equiv per mol of grafted HTPBD (z = 1.5).

The grafting rate, τ, is defined as the ratio of the mol number of grafted 1,2 double bonds to the total number of mol of 1,2 double bonds as follows:

$\tau_{th} = z/y \times 100 = 1.5/4.23 \times 100$

= 35.5% as the maximum of grafting about

1,2 double bonds

$\tau_{real} = z'/y \times 100,$

where z' represents the real number of

grafted 1,2 double bonds.

After evaporation of toluene, the grafted HT-PBD was characterized by ^{1}H-NMR [Fig. 1(b)] compared to that of the virgin HTPBD [Fig. 1(a)]. Interestingly, the ^{1}H-NMR spectrum of the grafted HTPBD shows the presence of a signal centered at 2.8 ppm (proton 7) assigned to methylene groups adjacent to the sulfur atom. In addition, the integration of the peak of the methylene group adjacent to the hydroxy function (proton 8) centered at 3.5 ppm (1,2 double-bond units) increased because of the aliphatic CH₂OH group of the graft.
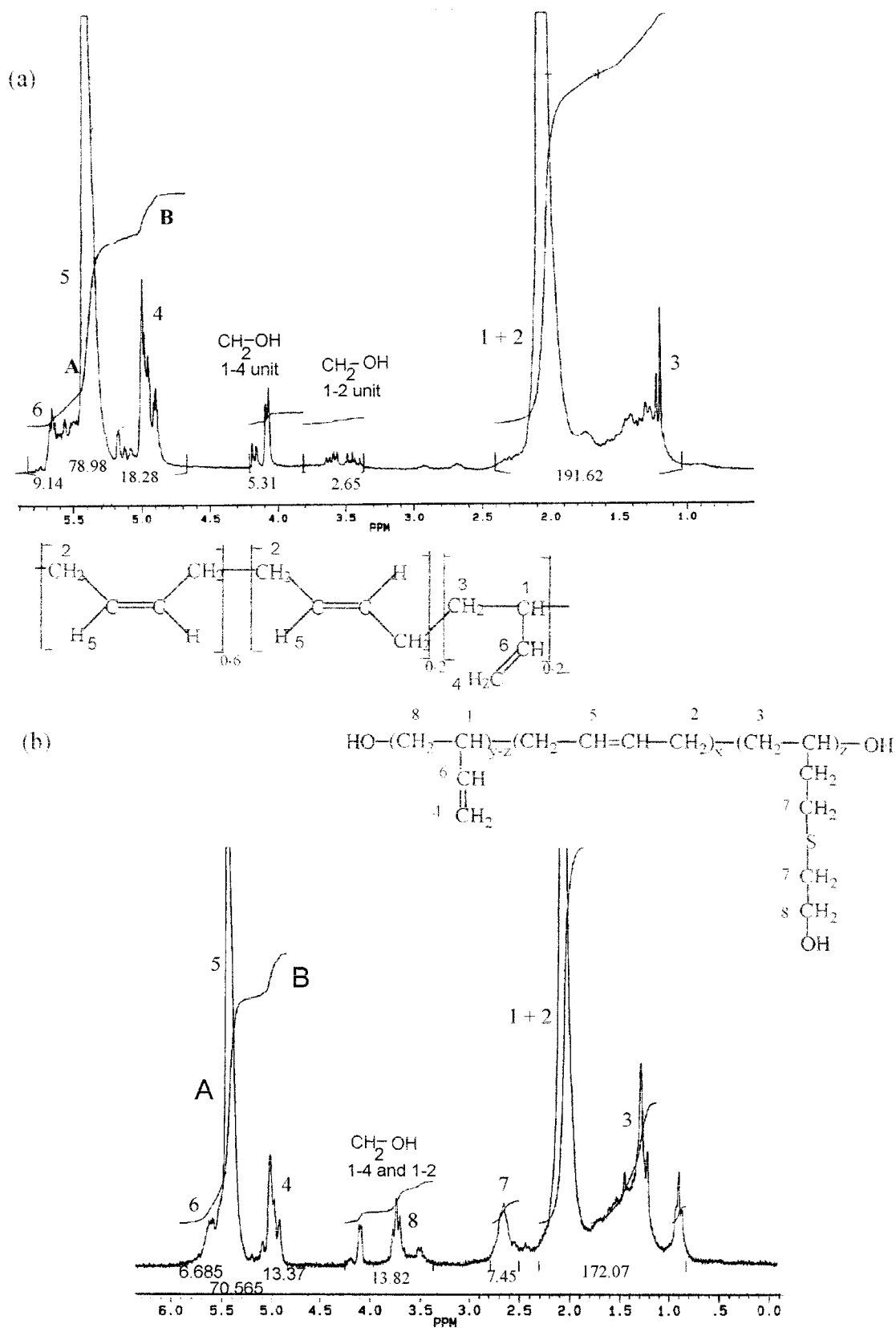
From this spectrum, the determination of the real grafting rate about the 1,2 double bonds was possible. Let us consider z' as the number of 1,2 units which have reacted with the mercaptan, and x and y, the values corresponding to the number of 1,4 and 1,2 double bonds of the Poly BD R20 LM®, respectively. Assuming that the grafting occurred to 1,2 double bonds only[14] (they were shown to be more reactive than the 1,4-ones), the ratio of integrations of the characteristic signals allowed us to determine the z' value as follows:
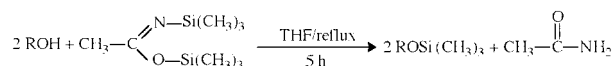
$$\frac{4z'}{2x} = \frac{7.45}{70.565},$$

leading to z' = 0.965 grafted 1,2 base unit

where 7.45 and 70.565 represent the integrations assigned to methylene groups adjacent to the sulfur atom (4H by 1,2 unit; proton 7) and to ethylenic protons (1,4 units; proton 5). Consequently, the z' value allowed us to assess the functionality f as follows: $f_{NMR} = f_{OH}$ (HTPBD 20 LM®) + z' = 3.07 eq mol^{-1}. Hence, the grafting rate was 23% and the molar consumption rate of thiol was 65%.

The functionality in the hydroxyl groups of virgin and grafted HTPBD was determined by silylation[15] as explained in the Experimental section. This method enables us to have a total silylation of the hydroxyl function as follows:

Figure 1 ^{1}H-NMR of (a) HTPB R20LM and (b) grafted HTPB R20LM.

$$2\,ROH + CH_3-C\begin{matrix} N-Si(CH_3)_3 \\ O-Si(CH_3)_3 \end{matrix} \xrightarrow[\text{5 h}]{\text{THF/reflux}} 2\,ROSi(CH_3)_3 + CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH_2$$

That reaction was evidenced by ^{1}H-NMR, and the spectrum shows the presence of methyl groups centered at 0.15 ppm assigned to the trimethylsilyl group.

The average functionality can thus be assessed by the following formula:

$$\bar{f}_{OH} = \frac{S(3-x)\bar{M}_n}{9(A+B)54.09}$$

where x represents the amount of 1,4 base units [i.e., $x = (2A - B)/(2A + B)$]; S, A, and B designate the integrations of the methyl groups of the trimethylsilyl endgroup, of the vinylic protons centered at 5.40 ppm, and of the vinylic protons centered at 5.00 ppm, respectively. Figure 2 represents the ^{1}H-NMR spectrum of the silylated virgin and grafted HTPBD.

According to that method of determination of functionality, we found $\bar{f}_{OH} = 2.1$ and 3.0 eq mol^{-1} for the starting and grafted HTPBD. That functionality is lower than that of the theoretical one (3.6) and we may assume that the grafting reaction was not total. These results are in very good agreement with the previous ones calculated from NMR.

Hence, it is observed that at the end of the reaction a total thiol conversion has not been reached, which is not acceptable from industrial application taking the environment problems into account. To be sure of this uncomplete reaction, the colorimetric titration of free thiol was performed as the addition reaction occurred, by the following oxidation–reduction process:

$$2RSH + I_2 \rightarrow RSSR + 2HI$$

$$HI + I_2 \rightarrow H^+ + I_3^-$$
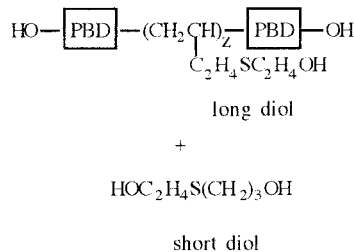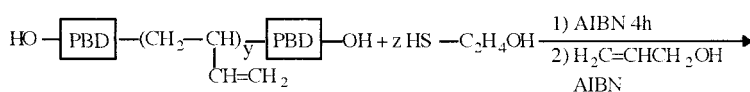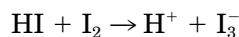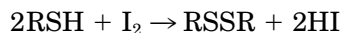
Such a grafting was performed on Poly BD R45 HT® and on other samples of Poly BD 20 LM® in similar conditions as above. The results obtained for each reaction, that is, the titration of the remaining thiol and the values of the grafting rate and of z', are listed in Table II.

In all cases, it is observed that the grafting of the mercaptan is incomplete (from 70 to 95%) in contrast to the results mentioned by Schapman et al.[13] who noted a total conversion of the thiol. The same method was applied for the grafting reaction involving Poly BD R45® and the results observed are similar to those above. Hence, we have been able to propose a method of control of the reaction on both the grafting rate and the determination of the functionalities. However, it is noted that a nonnegligible amount of 2-mercaptoethanol has not reacted (ca. 30% of unreacted mercaptan remained after grafting to Poly BD R45 HT®). Hence, it was of interest to investigate a process that improves the synthesis of a polyol in bulk with a chemical change of the free thiol, as below.

Bulk Grafting

After the bulk reaction, allyl alcohol (used in a slight excess) was reacted with the free mercaptan. Indeed, this olefin exhibits a more reactive double bond than the 1,2 ones of HTPBD (regarding this radical addition). Thus, such a reaction led to an aliphatic telechelic diol, called a "short diol," useful as a chain extender for the synthesis of PU resins. The excess of allyl alcohol can be easily gotten rid of by distillation because of its low boiling point (96°C).

Scheme 1 represents the overall reaction of the synthesis, starting from a Poly BD R20 LM® type (with a functionality of 1.6) and the bulk grafting can be summarized as follows:
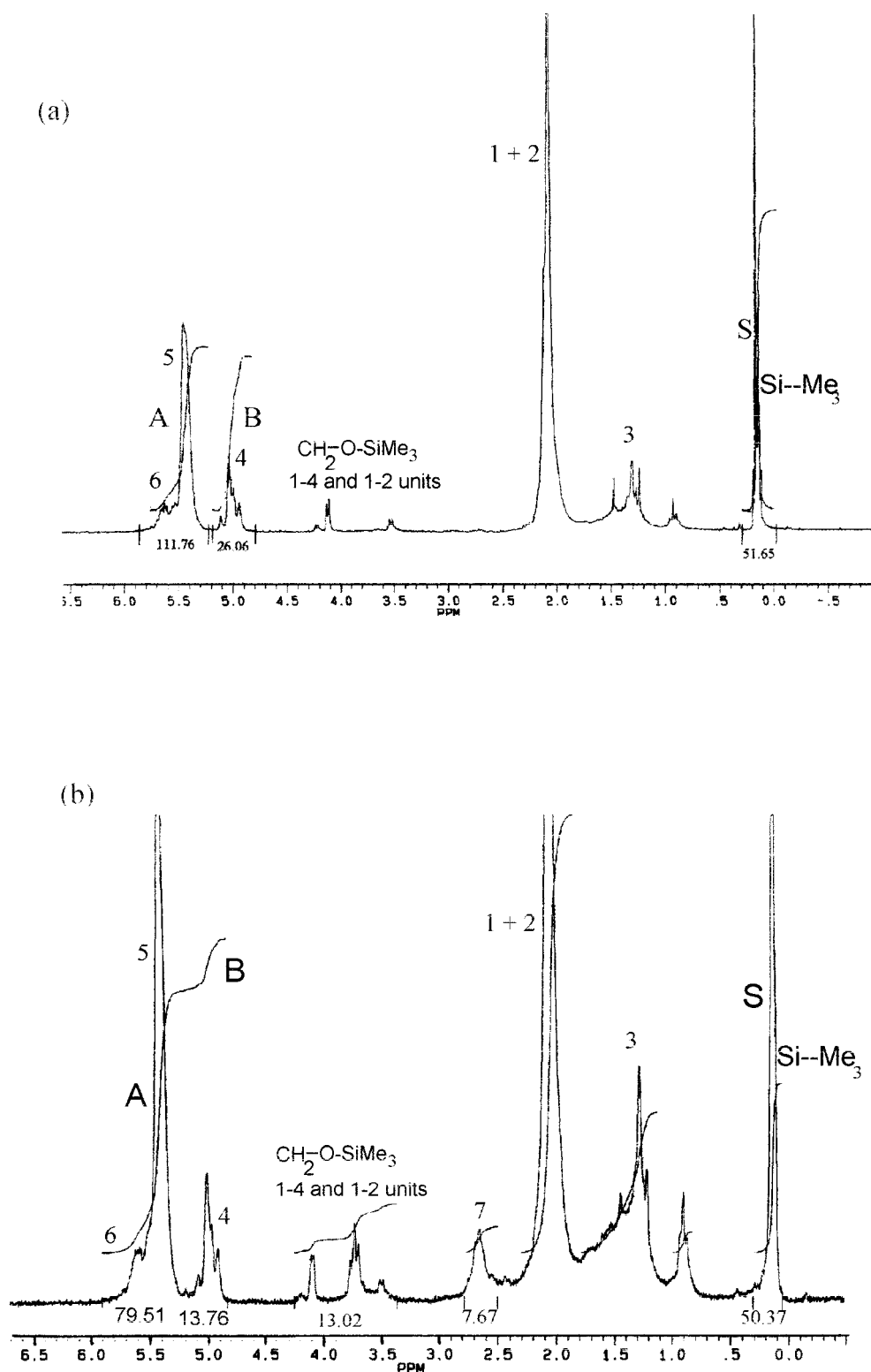
$$HO-\boxed{PBD}-(CH_2-CH)_y-\boxed{PBD}-OH + z\,HS-C_2H_4OH \xrightarrow[\substack{2)\,H_2C=CHCH_2OH \\ AIBN}]{1)\,AIBN\,4h}$$

with CH=CH$_2$ substituent

$$HO-\boxed{PBD}-(CH_2\,CH)_z-\boxed{PBD}-OH$$
$$\underset{C_2H_4SC_2H_4OH}{}$$

long diol

+

$$HOC_2H_4S(CH_2)_3OH$$

short diol

Figure 2 ^{1}H-NMR of (a) silylated HTPB R20LM and (b) silylated grafted HTPB R20LM.

For these above syntheses, t-butyl peroxypivalate, more reactive than AIBN, was also used as another initiator. However, this latter was added

4 h after the reaction started in order to ensure a constant concentration of the initiating radical. To monitor the reaction (i.e., consumption of

Table II   Results of Graftings of 2-Mercaptoethanol to HTPBD in Solution and in Bulk

Type of Grafting	z (unit)	z' (unit)	Process	Graft Rate (%)	Consumption Rate of Thiol (%)	f_{OH}	f'_{OH}
Grafted HTPB R20LM[a]	1.50	0.97	Solution (toluene)	23	65	2.10	3.07
Grafted HTPB R20LM[b] and short diol	1.60	1.52	Bulk	36	95	1.60	3.00
Grafted HTPB R45HT[b] and short diol	2.20	2.00	Bulk	42	90	2.30	4.00

f_{OH} and f'_{OH} are the functionalities of virgin and grafted HTPB.
[a] After getting rid of unreacted thiol.
[b] Total product mixture containing the short diol.
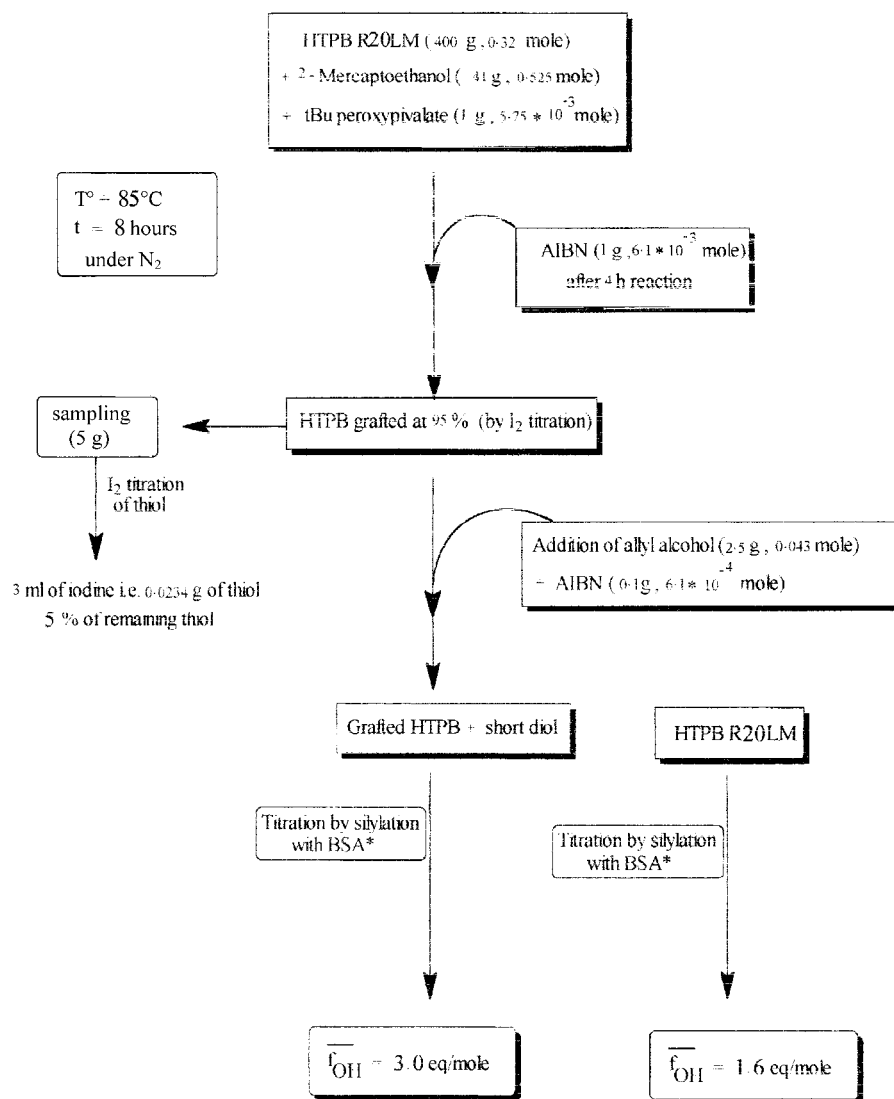
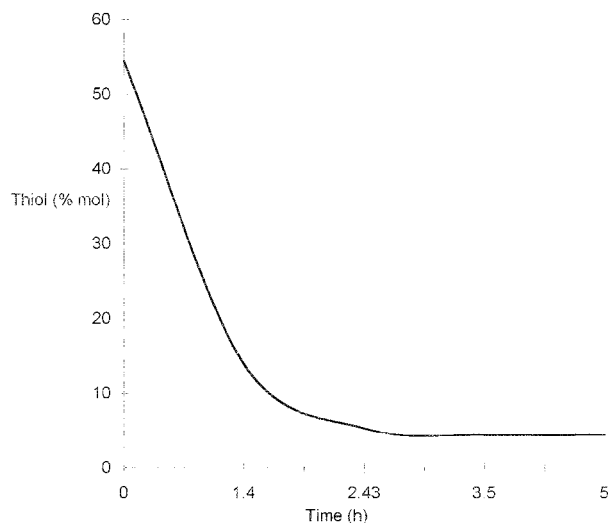**Scheme 1**   Bulk grafting of Poly BD R20LM® by 2-mercaptoethanol.

Figure 3 Consumption of 2-mercaptoethanol versus time in the grafting of Poly BD R20LM® (mol % deduced from SEC).

2-mercaptoethanol), two kinds of analyses were utilized: The first one concerns the iodometric titration of free mercaptan by oxidation–reduction, while the second one deals with size-exclusion chromatography (SEC) (Fig. 3). That latter one enabled us to monitor the thiol consumption by comparing the relative areas of the peaks corresponding to the mercaptan and to HTPBD, taking into account a calibration curve designed from various amounts of both these reactants (Fig. 3). The remaining quantity of thiol allowed us to assess the amount of allyl alcohol (in excess) to add to the gross. For the reaction involving Poly BD R20 LM® ($\bar{f}_{OH}$ = 1.6 eq mol^{-1}), 5% of the free mercaptan remained after 6 h as observed by SEC, corresponding to a 95% yield of grafting. Such a result is in good agreement with what we observed by titration (Table II). After reaction and then distillation of the excess of allyl alcohol, the obtained polyol mixture had a functionality of 3.0 eq mol^{-1}, with a molar mixture composed of 95% of grafted PBHT R20 LM® (i.e., long polyol) and 5% of short diol. The real grafting rate calculated from ^{1}H-NMR (z' = 1.52 grafted units) was 36%, whereas the theoretical one was 38% (determined from z' = 1.6 units to graft) about 1,2 double bonds.

The same reaction was carried out with the Poly BD R45 HT® and the free thiol content observed after 6 h was about 10% (meaning ca. 90% of grafting yield). The functionality of that polyol mixture was 4.0 eq mol^{-1}, for a molar mixture of 90% of grafted HTPBD and 10% of short diol. The real grafting rate was 42% (i.e., z' = 2 grafted units), whereas the theoretical grafting was 52% about 1,2 double bonds. The analyses of these products, as described above, showed that it was possible to prepare polybutadiene having a chosen functionality from a simple and reproducible method.

Syntheses of PU

They were performed using a bicomponent mixture of a resin containing the polyol and the catalyst (dibutyl tin dilaurate, DBTDL) and the hardener (α,ω-diisocyanate). Such a reaction was conducted in bulk, at room temperature, and at atmospheric pressure.

Four formulations were performed using hexamethylene diisocyanate (HDI) in 5% excess about polyalcohol, Poly BD R45 HT® ($\bar{f}_{OH}$ = 2.3 eq mol^{-1}), Poly BD R20 LM® ($\bar{f}_{OH}$ = 2.1 eq mol^{-1}), and their grafted homologs ($\bar{f}_{OH(graft\ R45)}$ = 4.0 eq mol^{-1} and $\bar{f}_{OH(graft\ R20LM)}$ = 3.0 eq mol^{-1}). Obviously, these are mixtures composed of grafted HTPBD with a short diol.

For each formulation, five kinds of analyses were carried out that concerned mainly the physical, mechanical, and thermal properties. For the first one, viscosity and its monitoring along the polyaddition (i.e., gel times) were investigated.

Then, for mechanical properties, the Shore hardness was assessed and preliminary results about the break modulus and break at elongation, useful for understanding the mechanical behavior of the resins, were obtained. As for the thermal properties, the glass transition and decomposition temperatures were measured by differential scanning calorimetry and thermogravimetric analysis.

The gel times, viscosities, and the Shore hardnesses of the different PU resins are listed in Table III. Concerning the gel times, it is observed that the higher the functionality of the polyalcohol, the lower the gel times. This can be explained by the use of a greater amount of HDI, which led to a more cured network. The viscosities of the polyalcohol/HDI blends are expectively lower than those of the macroalcohol since HDI is a liquid. However, those of the grafted HTPBD increased as the functionality of the polyalcohol increased. As for the Shore hardness, it is clear that the higher the functionality, the higher this value, owing to the density of curing.

In addition, a lower molecular weight of the macroalcohol also led to a higher density of the

Table III   Results of Analyses of PU with HDI

| Polyol | Gel Time (mn) | Viscosity (Pa s) | | T_g (°C) | Shore Hardness PU (A) |
		Polyol	Polyol with HDI		
HTPB R45HT (2.3 eq/mol)	19.39	20	6	−63.5	20 ± 5
Grafted HTPB R45HT (4 eq/mol)	12.44	37	9	−59.2	50 ± 5
HTPB R20LM (2.1 eq/mol)	15.16	10	5	−59.2	30 ± 5
Grafted HTPB R20LM (3 eq/mol)	9.17	22	8	−38.0	52 ± 5

network and, thus, to a higher Shore hardness. Further, the first mechanical measurements showed an increase of both the modulus and the break at elongation, concomitant to a decrease of the break stress (ε_R).

The DSC endotherms exhibited a slight increase of the value of the glass transition temperature (from −63.5 to −59.2°C) of the PU when virgin and grafted PBHT R45 HT® were used. Interestingly, this increase was enhanced for the PU prepared from PBHT R20 LM® and from their grafted homologs (from −59.2 to −38.0°C). This behavior may be assigned to the segregation of rigid (from urethane links and chain extenders) and soft phases. Actually, an increase of the isocyanate rate introduced in the mixture favors a lower dienic phase separation which allows an increase of the T_g. These results confirm Flynn and Petrovic's observations.[16]

The thermal stability of these PU was studied by thermogravimetry (TGA, Table IV). Figure 4 represents the TGA thermograms of a PU prepared from virgin and grafted Poly PB R45 HT® compared to that produced from poly(propylene glycol) (PPG) ($\bar{M}_n$ = 1000 and $\bar{f}_{OH}$ = 2.0 eq mol^{-1}). Two degradations are noted from the thermograms of these elastomers prepared from pure and grafted HTPBD. The first one comes from the degradation of urethane links and roughly corresponds to a weight loss similar to that of the weight of HDI introduced in the PU. In the case of PU obtained from grafted HTPBD, this loss is more important and corresponds to the amounts of HDI and of the short diol, as could be expected. The second weight loss, observed from 430°C, represents the degradation of butadienic network; however, it is worth noting that this temperature value is very high for a hydrocarbonated chain. Interestingly, similar behavior was also observed when the thermodegradation occurred under air (yet being an oxidative medium for these chains).

Such a phenomenon may be explained by crosslinking (which takes place at around 300–350°C) of the butadienic chain by the free 1,2 double bonds which thermodynamically stabilize the network up to 430°C. That observation is in good agreement with Chiantore et al.'s works[17] that detailed the mechanism of thermal cyclization of double bonds of HTPBD.

As for the PU obtained from PPG, the degradation occurred at lower temperatures (ca. 280 and 200°C under nitrogen and air, respectively). This is evidence of the thermal and oxidative weak points of polyethers. Petrovic et al.[18] described the decomposition mechanisms of polyethers under air and suggested a thermal increasing reactivity scale:

$$PPG < PEG < PTMG$$

Table IV   Thermogravimetric Analyses of PU

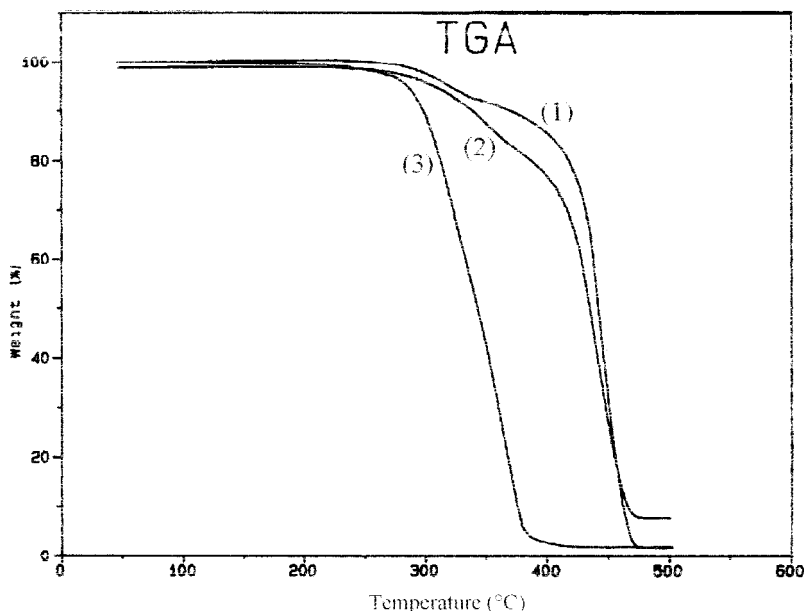| | Hard Segment | | Soft Segment | | Content (wt %) | | |
	T (°C)	Weight (%)	T (°C)	Weight (%)	HDI	PBHT	Grafted Thiol
PU from HTPB R45HT	322.6	7.8	441.9	92.2	6.7	93.3	0
PU from grafted HTPB R45HT	349.2	15.7	436.5	84.3	11.2	82.1	6.7
PU from HTPB R20LM	320.5	19.7	443.7	80.3	12.9	87.1	0
PU from grafted HTPB R20LM	346.0	28.7	441.0	71.3	17.5	74.0	8.5

Figure 4 Thermograms of synthesized PU (under nitrogen, heating rate = 5°C/mn):
(1) PU from HTPB R45HT; (2) PU from grafted HTPB R45HT; (3) PU from PPG 1000).

where PEG and PTMG mean poly(ethylene glycol) and poly(tetramethylene glycol), respectively].

This study shows the rather good thermal stability of PU prepared from HTPBD with yet a hardening noted with time, because of crosslinking of the diene blocks. For example, Scheme 2 represents the weak points involved in the degradation of the corresponding PU.

Aging of these elastomers was assessed at 150°C, and after 200 h, an increase was noted of the Shore hardness on the surface of about 5A units. However, introducing 2-mercaptoethanol does not modify drastically this behavior and we plan to perform a comparative study versus time of different kinds of polyalcohols.

CONCLUSIONS

This study shows that it is possible to chemically modify HTPBD by a controlled grafting of the functional thiol to obtain polyols that exhibit assessable and accurate functionalities. Moreover, the bulk grafting followed by the addition of allyl alcohol enabled us to get rid off the excess of unreacted mercaptan, which is required to solve, mainly, the problems of smell. Furthermore, another advantage of such a reaction is directly linked to the absence of any solvent, which is interesting for the environment. As expected, the overall properties of the obtained polymers are modified because of the increase of the functionality and this is well shown for those of the cor-
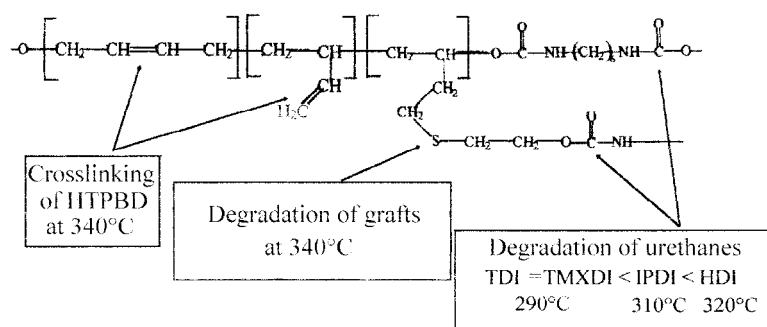
Scheme 2 Thermal degradations (TGA) of PU from grafted HTPB.

responding PU: The viscosity and the Shore hardness increase while the gel time decreases with increase of the functionality. On the other hand, the thermal stability is less upset; however, the value of the T_g can be drastically modified by the grafting rate. Hence, with low average molecular weight in the number of HTPBD, the phase separation is not total and that is clearly evidenced by the increase of the T_g. Thus, control of the grafting rate is crucial. Deeper investigations are in progress.

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