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Grafting phosphonated thiol on hydroxy telechelic polybutadiene

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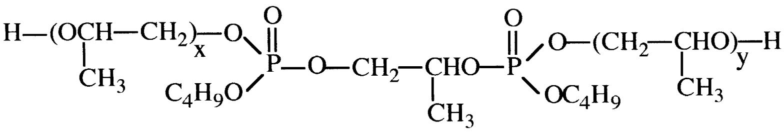
Summary

An hydroxytelechelic polybutadiene (PBHT) of 1200 molecular weight has been modified by the phosphonated thiol $HS-(CH_2)_3-PO(OC_2H_5)_2$ (I). The thiol (I) was prepared in three steps: phosphonation of allyl bromide, addition of thioacetic acid and hydrolysis. The grafting rate of (I) on PBHT has been calculated by sulfur analysis and by ^1H NMR. The results confirmed that the 1,2 double bonds are 10 times more reactive than the 1,4. The method led to new macromolecular polyols containing between 3 and 5 % in weight of phosphorous. These new long polyols should be very interesting in order to prepare fire retardant polyurethane networks.

Introduction

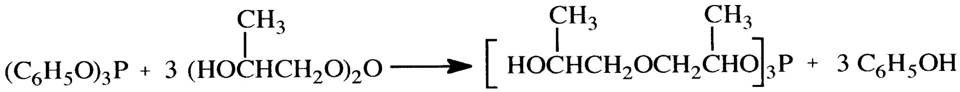
Improved fire resistance of polymers is a very important challenge. In this purpuse various additives (1), (2) or many halogenated reactants (diols (3), (4), triols (5)) have been prepared and used particularly in the synthesis of polyurethanes (PU) (6). However the environmental problems of the halogenated products either in gaseous phase (CFC) or in aromatic solid phase (PCB) have stopped their uses in polymer formulation.

As a result, mineral additives (aluminium or magnesium hydrates) or organic additives (tri (2-chloroisopropyl) phospate, TCPP) are used at present in PU, and their mechanical properties are obviously decreased. Consequently polyols containing phosphorus atoms have been prepared ; for instance we can cite the Vircol 82 (Mobil) (7) which is a phosphate with 11.3 % phosphorus weight content :



x + y = 3.5

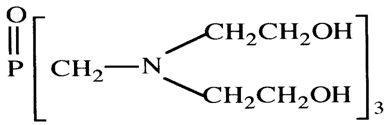
Others molecular or macromolecular polyols as phosphite have been successfully prepared by reaction of triphenyl phosphite with dipropylene glycol (8):



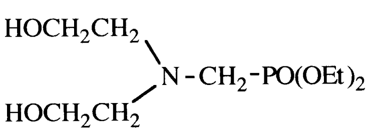
$$(C_6H_5O)_3P + 3\ (HO\underset{}{\overset{\substack{CH_3\\|}}{C}}HCH_2O)_2O \longrightarrow \left[\ HO\overset{\substack{CH_3\\|}}{C}HCH_2OCH_2\overset{\substack{CH_3\\|}}{C}HO\right]_3P + 3\ C_6H_5OH$$

Though, phosphate and phosphite polyols lead to poor physico-chemical properties of polyurethanes because they have (P - O) - C bonds which are particularly sensible to hydrolysis.

In order to avoid this inconvenient, Sivriev et al have developped the synthesis of phosphine oxide (9) which have, for example, the following structure:



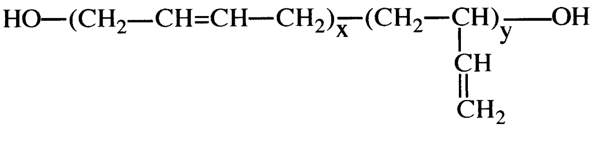
The efficiency of these polyols is often compared to the one of a low molecular weight amino phosphonate as FYROL (STAUFFER CHEMICAL) (10):



In this paper we described the synthesis of new phosphonated hydroxy telechelic polybutadienes by grafting with a thiol bearing phosphorus atoms.

Results and discussion

The hydroxy telechelic polybutadiene PBHT 20 LM provided from ATOCHEM has the random structure shown below:



$$HO{-}(CH_2{-}CH{=}CH{-}CH_2)_x{-}(CH_2{-}\underset{\substack{|\\CH\\\|\\CH_2}}{C}H)_y{-}OH$$

Their main caracteristics obtained by NMR ^1H studies and hydroxyl titration are summarised in Table 1.

$\overline{M_n}$	Eq_{OH} meq/g	$\bar{f}_{OH}$	x	y
1250	1.63	2	17.1	5.4

Tab.1. Caracteristic data of PBHT 20 LM.

Many thiols have been grafted on PBHT in the past either by the Pascault team (functional thiol) (11) or by our team (fluorinated thiol) (12), but the thiols used do not contain phosphorus moities. The only work in this area is the grafting of $HPO(OEt)_2$ onto PBHT by the Brosse team (13). In this case, the increase of the grafting rate leads to a systematic rise of the interchain linkage to give a gelled fraction then a total gel.

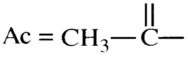
Generally the reactivity order of the double bond (dl) for the grafting is the following (14) :

dl 1.2 > dl cis 1.4 > dl trans 1.4

We have prepared the phosphorus containing thiol by the method previously published by Randall (15) and Putvinski (16) as follows :

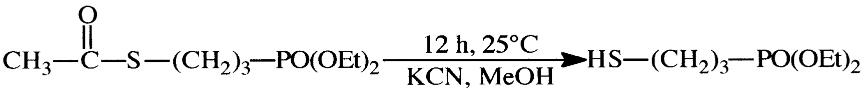
$$CH_2{=}CH{-}(CH_2)_n{-}Br \xrightarrow{P(OEt)_3} CH_2{=}CH{-}(CH_2)_n{-}PO(OEt)_2 \xrightarrow{AcSH}$$

$$AcS(CH_2)_{n+2}{-}PO(OEt)_2 \xrightarrow{HCl} HS{-}(CH_2)_{n+2}{-}PO(OEt)_2 \qquad n = 6, 9$$



$$Ac = CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}$$

We have applied this synthesis to allyl bromide (n=1) and the hydrolysis was achieved using by the Herzig method (17) using a catalytic quantity of KCN in methanol (97% yield):



$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}S{-}(CH_2)_3{-}PO(OEt)_2 \xrightarrow[KCN,\ MeOH]{12\ h,\ 25°C} HS{-}(CH_2)_3{-}PO(OEt)_2$$

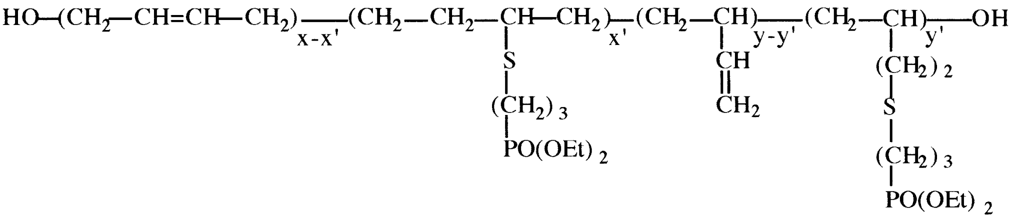
We have given more details of this reaction in another article (18).

The grafting of thiol : $HS—(CH_2)_3—PO(OEt)_2$ (I) was made in THF solution during 6

hours at 70°C with AIBN as initiator (2% molar ratio to dl bonds). After reaction, the grafted PBHT was washed into methanol to eliminate the thiol.

We have used two ratios of thiol related to double bonds : $R_o = (RSH)_o/(dl)_o = 20$ and 30%.

The grafted PBHT can be written :



$$HO\text{—}(CH_2\text{—}CH{=}CH\text{—}CH_2)_{x-x'}\text{—}(CH_2\text{—}CH_2\text{—}\underset{\substack{|\\ S\\ |\\ (CH_2)_3\\ |\\ PO(OEt)_2}}{CH}\text{—}CH_2)_{x'}\text{—}(CH_2\text{—}\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH})_{y-y'}\text{—}(CH_2\text{—}\underset{\substack{|\\ (CH_2)_2\\ |\\ S\\ |\\ (CH_2)_3\\ |\\ PO(OEt)_2}}{CH})_{y'}\text{—}OH$$

x’ and y’ is the number of dl (1.4) and dl (1.2) grafted.

These values were determined by ^1H NMR considering the quintuplet at 4 ppm of $P\text{-}OC\underline{H}_2(h_3)$ and the 1.4 dl (h_1) and 1.2 dl (h_2) in the 5-6 ppm range (Figure 1).

Using the following relationships, we have determined x’, y’, T, $T_{1.4}$ and $T_{1.2}$ (grafting rates).

$$x' = 1/2\ H_{3.2}\ y - y'\ (1/2\ H_{3.2} + 1)$$

$$y' = \frac{\left(H_{3.2} + 2\ H_{1.2}\right)\ y - 2x - y}{H_{3.2} + 2\ H_{1.2} + 1}$$

$$\text{with} \quad H_{1.2} = \frac{h_1}{h_2} \quad \text{and} \quad H_{3.2} = \frac{h_3}{h_2}$$

$$T = 100\,\frac{x' + y'}{x + y} \qquad T_{1.4} = 100\,\frac{x'}{x} \qquad \text{et} \qquad T_{1.2} = 100\,\frac{y'}{y}$$

We have also determined the global grafting rate T by weight analysis of sulfur as follows :

$$\%\,S = 100\,\frac{32 \bullet (x' + y')}{1250 + 212\,(x' + y')}$$

All these results are gathered in Table 2.

R_o (%)	Sulfur Analysis		NMR						
	x' + y'	T	x'	y'	x' + y'	T	$T_{(1.4)}$	$T_{(1.2)}$	$\frac{T_{(1.2)}}{T_{(1.4)}}$
20	1.92	8.54	0.49	1.73	2.22	9.85	2.85	32.00	11.22
30	2.77	12.29	0.84	2.63	3.47	15.40	4.90	48.67	9.93

Tab.2. Determination of grafting rate obtained by ^{1}H NMR and sulfur analysis.

First the radical addition of thiol (I) on to PBHT gave phosphonated polyols with an increasing phosphorus content which is linked to the quantity of the thiol introduced from the outset of the reaction. The results show that the grafting is never complete (almost the half of introduced thiol). In any cases the 1.2 dl are 10 times more reactive than the 1.4 dl. Finally the sulfur analysis results are in good agreement with ^{1}H NMR. This method led us to prepare, by a simple procedure, new macromolecular diols containing 3.5 et 4.7 % in weight of phosphorus. The main application we expect of these products is their use in the polyurethane synthesis in order to obtain flame retardant properties.

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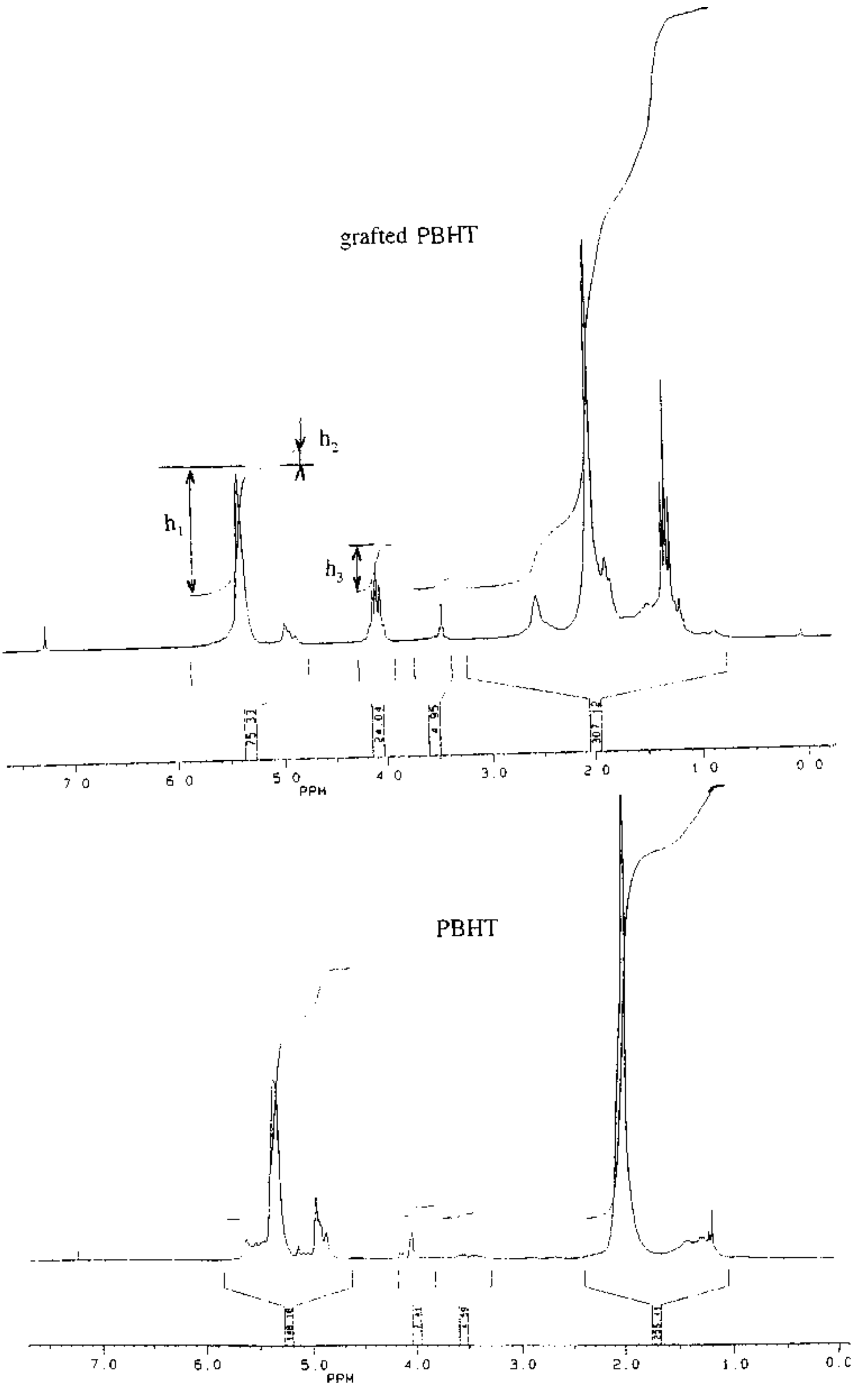

Fig. 1. ^{1}H NMR ($CDCl_3$) spectra of PBHT and grafted PBHT.