PII: S0032-3861(97)10244-0

Low molar mass polybutadiene made crosslinkable by silane moities introduced via addition of thiol to double bond: 3. Synthesis and kinetic study

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Low molar mass polybutadiene was made crosslinkable under moisture by the addition of mercapto propyl triethoxy silane to double bonds. The reaction was carried out at 75°C in the presence of AIBN as initiator. AIBN concentration and time showed that triethoxy silane groups were introduced quantitatively in the range of 1.05 to 7.9 per chain. A ^1H n.m.r. study showed clearly that only vinylic units reacted at low modification rates. Volumetric titration of the remaining thiol was used to follow the reaction. A new mechanism is proposed here to lead to a kinetic relation, similar to the one already used by several authors, but kinetically provable. Moreover, it has been pointed out that there is probably an evolution of kinetic constants with the progress of the reaction due to, among other reasons, a local steric hindrance at the level of vinyl sequences and/or a variation in chain conformation. © 1998 Published by Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Over the past 15 years, several authors[1–13] have been greatly interested in radical addition of thiols to double bonds of polybutadienes in order to synthesize new materials. In most cases, the work has dealt with addition mechanisms or the relative reactivity of the different kinds of microstructure (1,2 or 1,4) to high molar mass polybutadienes or low molar mass derivatives either hydroxy-terminated (PBHT) or carboxy-terminated (PBCT). Thus, De La Campa and Pham[1] studied, by ^1H and ^{13}C n.m.r. and by titration of fluor, the grafting rates of fluorinated thiols on two commercial PBHTs of different structures: Arco 45 M (20% 1,2 and 80% 1,4) and Nisso G 2000 (88% 1,2 and 12% 1,4). They carried out their experiments with AIBN at 60°C and a large excess of thiol with respect to overall double bonds. It has been clearly shown that the reaction occurs faster with double bonds in 1,2-butadiene than in 1,4-butadiene, and secondly that the kinetics are very dependent on the chemical structure of thiols. For example, complete addition is observed for n-butanethiol whereas partial addition with slower kinetics is reported for 2,2-dimethyl propanethiol. Moreover, addition of 4-methyl benzenethiol leads to an isomerization of cis 1,4 unit to trans 1,4 one with a conversion which does not exceed 3–4% after 30 h of reaction. Likewise, the use of models of low molecular weight leads to the same conclusion, namely double bonds in 1,2-butadiene are more reactive than in 1,4-butadiene either by thermal or photochemical initiation[12,13].

Most of the time, an excess of thiol with respect to overall

unsaturations is used because the overall aim of the research is to modify the maximum number of double bonds. In our case, only a moderate addition of a functionalized thiol (mercapto propyl triethoxy silane, MPTS) is considered to allow polymer crosslinking, by hydrolysis of ethoxy silane groups, while preserving polymer properties.

The low molar mass polybutadiene used in this work (Poly Bd R45 HT®)[14] is a commercial hydroxy telechelic polymer (HTPB) synthesized by radical polymerization. Its main characteristics are an average molar mass $\overline{M_n} = 2800$ and an average hydroxy functionality $f_{OH} = 2.4$. Many commercial uses of this polymer stem from its low glass transition temperature ($T_g \sim -75°C$), good mechanical properties and strong resistance to chemical attacks. In a previous work[15], triethoxy silane moities (less than or equal to 2.4 per chain) were introduced onto HTPB by using hydroxy–isocyanate reaction leading to urethane linkage. In this work, the synthetic route allows the modification rate to increase since there are about 50 double bonds per chain with 11.5 of 1,2 type.

EXPERIMENTAL

Materials

Polybutadiene (Poly Bd R45 HT®) was kindly supplied by Elf Atochem. Mercapto propyl triethoxy silane (MPTS) (Hüls) and 2,2'-azobis (2-methyl propionitrile) (AIBN) (Acros) were used without further purification.

Synthesis

First, 0.01 mole (30 g) of HTPB was introduced into a 250 ml round bottom flask equipped with a mechanical stirrer (300 rpm), a switchable inlet for nitrogen and a

vacuum connector. HTPB was first degassed for 15 h by a graduated vacuum up to 10^{-1}–10^{-2} mmHg at 60°C. Then, the reactor temperature was raised to 75°C under nitrogen. MPTS was added in variable amounts (see text) with AIBN dissolved in the minimum amount of methyl ethyl ketone. The reaction was allowed to proceed until entire consumption of thiol functions. Colourless and transparent polymers were obtained. An increase in viscosity was observed with regard to modification rate.

Measurements

The different syntheses were monitored by two analytical methods.

- Volumetric titration of free thiol functions. An assay sample of about 2 g of the reactive medium was dissolved in 10 ml of THF and 50 ml of ethanol. The resulting solution was titrated with an aqueous solution of iodine (0.1 N) until stable coloration appeared.
- n.m.r. spectroscopy. ^{1}H n.m.r. experiments were recorded at room temperature on a Brucker AC (200 MHz) spectrometer using C_6D_6 as solvent and locking agent.

RESULTS AND DISCUSSION

According to De La Campa and Pham[1], the ^{1}H n.m.r. spectrum of HTPB leads to 23% of 1,2-butadiene units and 77% of 1,4-butadiene units.

In order to obtain hydrolysable crosslinking, we chose to introduce ethoxy silane moities onto HTPB via the addition of thiols to double bonds by using mercapto propyl triethoxysilane (MPTS) as reactant, according to the following scheme:
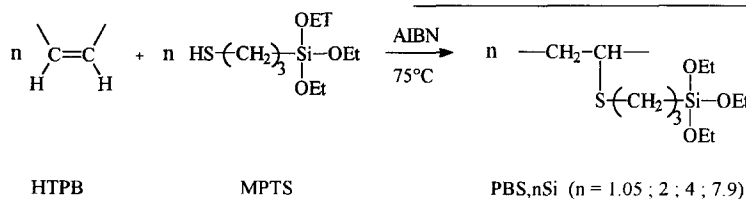
The modified HTPB is called PBS,nSi where n is the number of triethoxysilane groups per chain. The reaction was carried out in bulk, owing to the low viscosity of HTPB and the good solubility of MPTS in the polymer. AIBN was used as initiator at 75°C.

Influence of the concentration of thiol

The progress of the reaction was studied by using titration of residual thiol *versus* time, for variable ratios [thiol]/[DB], where [DB] is the concentration of overall double bonds. The experimental conditions were chosen to obtain a maximum number of triethoxysilane per chain, n_{max}, in the range 1.05 to 7.9 with an initial concentration of AIBN defined as $C_0 = $ [AIBN]/[DB] $= 0.2 \times 10^{-2}$. The number of silane groups introduced on HTPB *versus* time is reported in *Figure 1*.

The initial slopes of the curves show that the reaction rate logically increases with n_{max}. For low values of n_{max} (1.05 and 2), a plateau is rapidly reached and a quantitative addition is observed after 4 to 6 h whereas 24 h are required for $n_{max} = 4$. Nevertheless, conversion reached the ceiling of 82% after 24 h for $n_{max} = 7.9$. This result cannot be due to steric hindrance but probably to a gradual decrease of radical concentration with the consumption of AIBN as the reaction proceeded.

Influence of initiator concentration

For the same values of n_{max} (1.05 to 7.9), the reaction was carried out with a concentration of AIBN, $C_0 = $ [AIBN]/[DB], in the range 0.2×10^{-2} to 0.8×10^{-2} at 75°C for 48 h. For $n_{max} = 1.05$ to 4, reaction rates increased with C_0 and quantitative yields were obtained in a shorter time. In

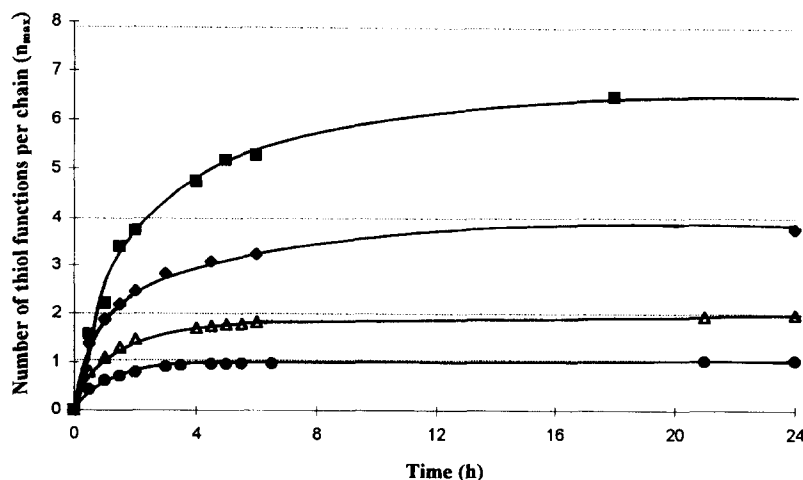HTPB   MPTS   PBS,nSi (n = 1.05 ; 2 ; 4 ; 7.9)

Figure 1 Number of silane groups introduced per chain of HTPB *versus* time for $n_{max} = 1.05$ (•), 2 (△), 4 (◆), 7.9 (■)
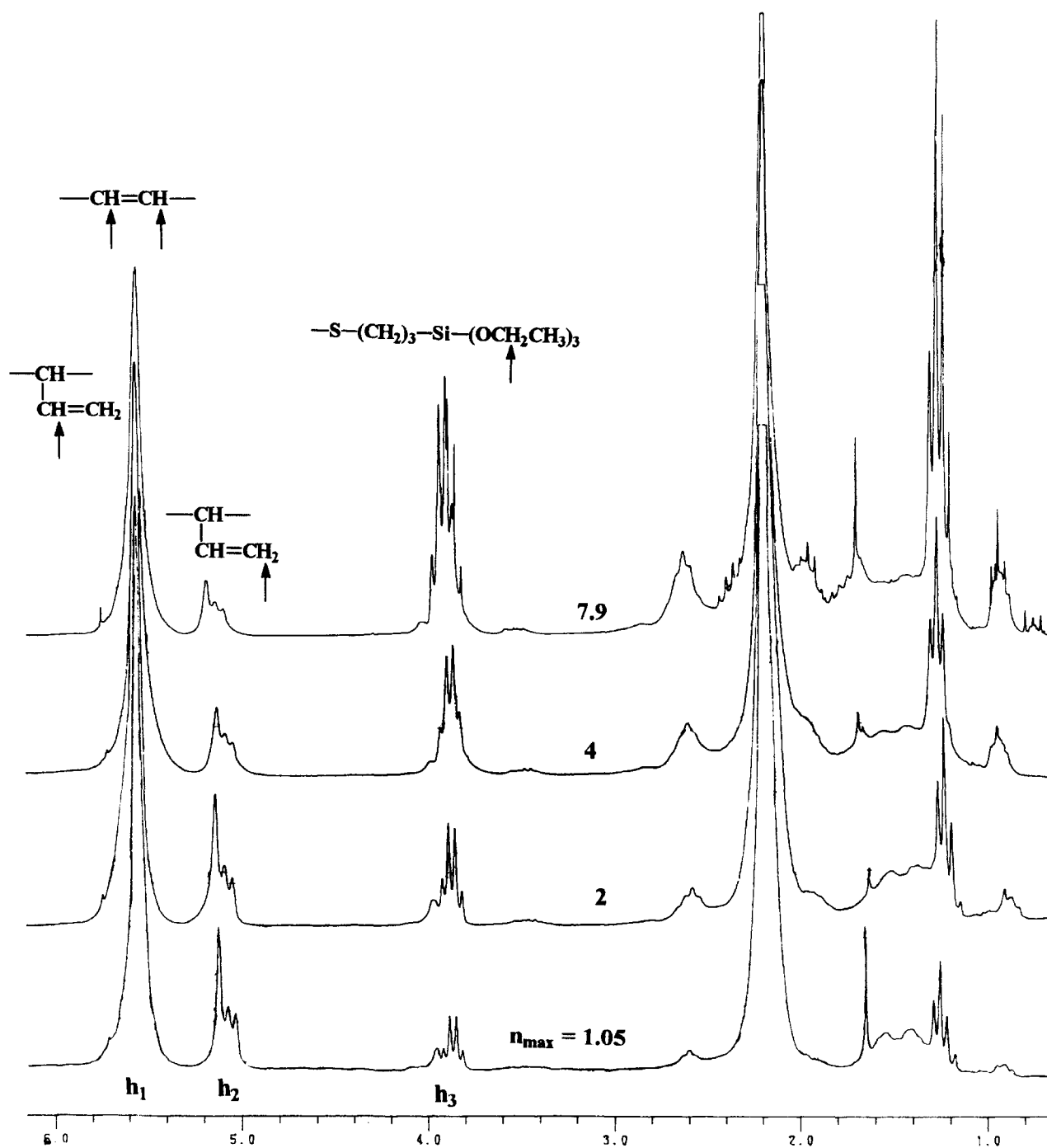
Figure 2 ^{1}H n.m.r. spectra of modified HTPB, after 24 h with $C_0 = 0.2 \times 10^{-2}$ at 75°C, for various values of n_{max}, the maximum number of triethoxysilane per chain

the case of $n_{max} = 7.9$, a quantitative addition was observed only after 48 h when $C_0 = 0.8 \times 10^{-2}$.

^{1}H n.m.r. analysis

The PBS,nSi values obtained after 24 h with $C_0 = 0.2 \times 10^{-2}$ were analyzed by ^{1}H n.m.r. and compared with the initial HTPB spectrum. The spectra (*Figure 2*) show clearly the appearance of a triplet at 1.25 ppm and a quadruplet at 3.85 ppm assigned to ethoxy groups which increase with n_{max}. Similarly, a broad triplet at 2.6 ppm, corresponding to $-S-CH_2-$, shows thiols addition to double bonds. Concurrently, a variation of the ratio h_2/h_1 is noticed with a faster decrease of h_2. Since there are 50 double bonds per chain ($\overline{X}_n = 50$), it may be seen that HTPB has 38.5 double

bonds of 1,4 type (77%) and 11.5 of 1,2 type (23%). Thus, if we consider the three integrations h_1, h_2, h_3, we can calculate the number of double bonds, resulting from 1,2 units (x) and 1,4 units (y), which have reacted.

Indeed, $n = x + y$ and three expressions may be found:

$$h_1 = k[2(38.5 - y) + (11.5 - x)]$$

$$h_2 = k[2(11.5 - x)]$$

$$h_3 = k6n$$

where k is a constant of proportionality. Combining these

expressions gives:

$$x = 11.5 - \frac{300h_2}{6h_1 + 3h_2 + 2h_3}$$

and

$$y = 38.5 - \frac{150(2h_1 - h_2)}{6h_1 + 3h_2 + 2h_3}$$

In each case, it was found that $y = 0$, i.e. there is no addition to 1,4 units in our experimental conditions. Moreover, a complete agreement is observed between x and n, viz. $x = 1.05, 2, 4$ and 6.5 (82% of 7.9).

Kinetic study

Theoretical considerations. The classical scheme reported in the literature[8,9] for addition of thiol (RSH) to double bond (M) in the presence of radical initiator (A–A) is shown below and consists of a sequence of three steps:

• initiation

$$A - A \xrightarrow{k_d} 2A^\bullet \qquad (1)$$

$$A^\bullet + RSH \xrightarrow{k_a} RS^\bullet + AH \qquad (2)$$

• propagation

$$RS^\bullet + M \xrightarrow{k_1} RSM^\bullet \qquad (3)$$

$$RSM^\bullet + RSH \xrightarrow{k_2} RSMH^\bullet + RS \qquad (4)$$

• termination

$$RS^\bullet + RS^\bullet \xrightarrow{k_t} RSSR \qquad (5)$$

Expression (1) leads easily to

$$[A - A] = [A - A]_0 e^{-k_d t}. \qquad (6)$$

Moreover, reaction (2) is always considered as instantaneous and therefore, the steady-state assumption yields

$$2fk_d[A - A] - 2k_t[RS^\bullet]^2 = 0 \qquad (7)$$

hence,

$$[RS^\bullet] = \left(f\frac{k_d}{k_t}\right)^{1/2} [A - A]_0^{1/2} e^{-\frac{k_d}{2}t} \qquad (8)$$

where f is the initiator efficiency. The rate of double bond disappearance is given by

$$-\frac{d[M]}{dt} = k_1[RS^\bullet][M] \qquad (9)$$

Substituting for $[RS^\bullet]$ from equation (8) in equation (9) and taking into account that at $t = 0$, $[M] = [M]_0$, gives after integration

$$Ln\frac{[M]_0}{[M]} = 2k_1 \left(\frac{f}{k_d k_t}\right)^{1/2} [A - A]_0^{1/2} \left(1 - e^{-\frac{k_d}{2}t}\right) \qquad (10)$$

Experimentally, only [RSH] is measured and therefore it is necessary to connect this concentration to [M]. Several assumptions are expressed[8,9] in order to obtain the

following relation

$$Ln\frac{[RSH]_0}{[RSH]} = A \left(1 - e^{-\frac{k_d}{2}t}\right) \qquad (11)$$

where A is a constant. Nevertheless, in each case it is assumed either that $[RS^\bullet] = [RSM^\bullet]$ or that $[A^\bullet]$ and $[RSM^\bullet]$ are constant during the reaction, which is not verified, or that we always have $Ln[M]_0/[M] = Ln[RSH]_0/[RSH]$ which is only true when $[M]_0 = [RSH]_0$. However, equation (11) fits the experimental results very well. Therefore, how is it possible to justify this expression?

Our interpretation requires some preliminary remarks. First of all, in classical theories reported in the literature, the crossed recombination of $A^\bullet$ and $RSM^\bullet$ with $RS^\bullet$ is never considered and we have retained this assumption. Consequently, only reaction (5) is considered, even if experimentally the recombination of $RS^\bullet$, which leads to formation of disulfide, was not observed[12]. Thus, we assumed that the $RS^\bullet$ radicals prefer to react on double bonds, which are in high concentration, rather than undergo (5). Secondly, we think that reaction (4) had to be slow due to a lack of accessibility of the bulky reactant RSH to the radical $RSM^\bullet$ formed (*Scheme 1*).

Nevertheless, the overall reaction rate is fast and we suppose that this is the result of a rearrangement of the former $RSM^\bullet$ with a neighbouring unit (1,2- or more probably 1,4- if we take into account its concentration) to produce a new allylic $RSM^\bullet$ (*Scheme 2*: A, B, C, D). This radical is less hindered and can thereby justify the reaction rate observed.

Thus, according to the above-mentioned assumptions for the crossed recombination of $A^\bullet$ and $RSM^\bullet$ with $RS^\bullet$ and for the cancelling of reaction (5), we have assumed that the only reaction of radical recombination, which can be considered as the main termination reaction, was:

$$RSM^\bullet + RSM^\bullet \xrightarrow{k_c} RSM - MSR \qquad (12)$$

The consequences of this coupling are multiple. First, the consumption of radicals enables us to consider the existence of a steady-state. Secondly, this type of recombination can lead to the production of branched polymers. The extent of branching may increase with $RSM^\bullet$ as initial concentration of thiol increases. Experimentally, we did observe that the viscosity of the medium is higher for $n_{max} = 7.9$.

If we consider now equation (12) and steady-state assumption

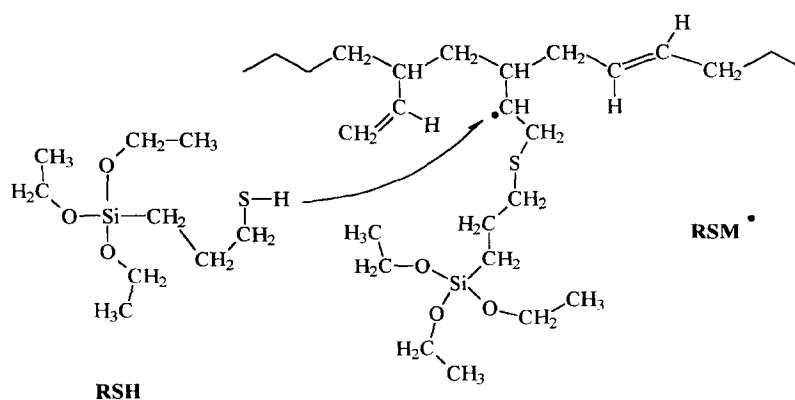$$2fk_d[A - A] - 2k_c[RSM^\bullet]^2 = 0 \qquad (13)$$

hence,

$$[RSM^\bullet] = \left(f\frac{k_d}{k_c}\right)^{1/2} [A - A]_0^{1/2} e^{-\frac{k_d}{2}t} \qquad (14)$$
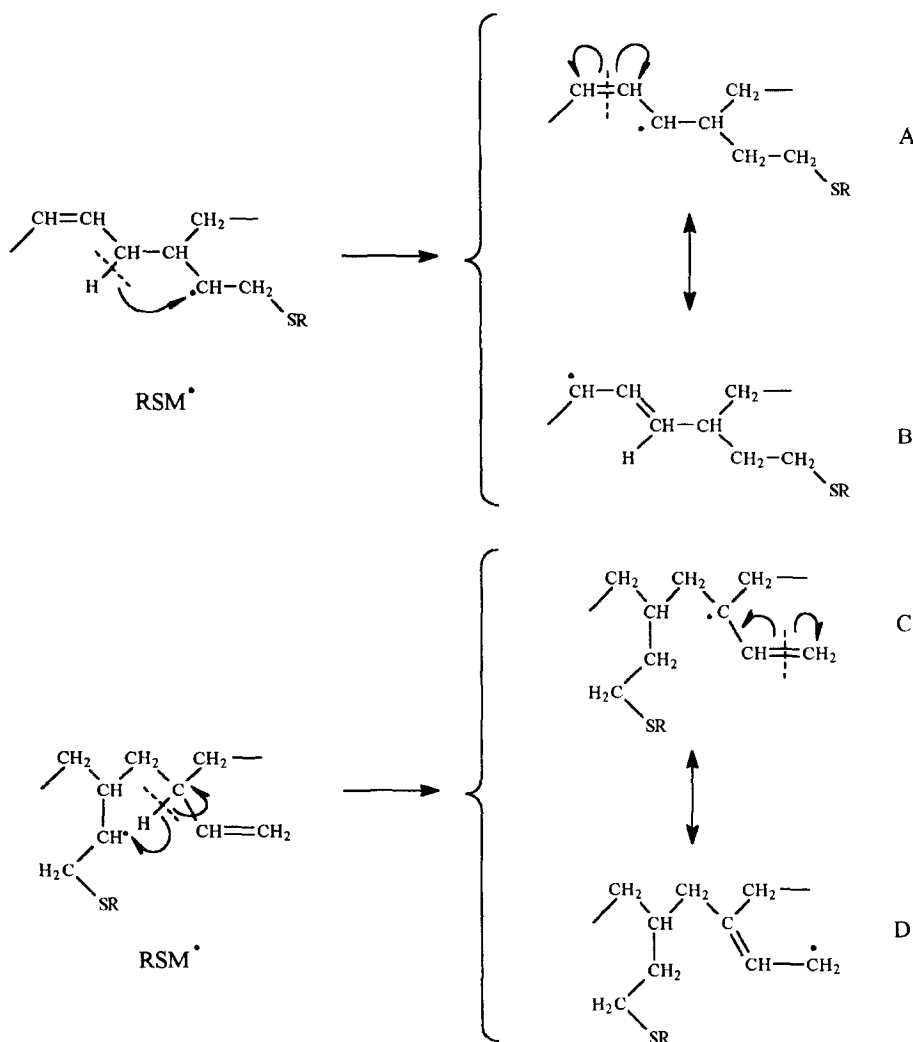
Then, the rate of thiol disappearance is given by

$$-\frac{d[RSH]}{dt} = k_2[RSM^\bullet][RSH] \qquad (15)$$

hence, taking equation (14) into account and after integration with $[RSH] = [RSH]_0$ at $t = 0$

$$Ln\frac{[RSH]_0}{[RSH]} = 2k_2 \left(\frac{f}{k_d k_c}\right)^{1/2} [A - A]_0^{1/2} \left(1 - e^{-\frac{k_d}{2}t}\right) \qquad (16)$$

RSH

Scheme 1

Scheme 2

Expression (16) is similar to (10), except that k_2 and k_c are substituted for k_1 and k_t. Moreover, when $t \rightarrow \infty$, the right-hand side of (16) reaches a limiting value which implies that [RSH] $\rightarrow$ [RSH]$_\infty$ and that the reaction cannot be complete and leads to a theoretical maximum conversion Y_∞.

$$\mathrm{Ln}\frac{[\mathrm{RSH}]_0}{[\mathrm{RSH}]_\infty} = 2k_2\left(\frac{f}{k_d k_c}\right)^{1/2}[\mathrm{A-A}]_0^{1/2} \qquad (17)$$

thus, [RSH]$_\infty$ depends on [RSH]$_0$ and [A–A]$_0$. Combining (16) and (17) gives

$$\mathrm{Ln}\frac{[\mathrm{RSH}]_0}{[\mathrm{RSH}]} = \mathrm{Ln}\frac{[\mathrm{RSH}]_0}{[\mathrm{RSH}]_\infty}\left(1 - \mathrm{e}^{-\frac{k_d}{2}t}\right) \qquad (18)$$

Influence of initiator concentration. Equation (16) was applied to experimental results obtained with $n_{max} = 1.05$
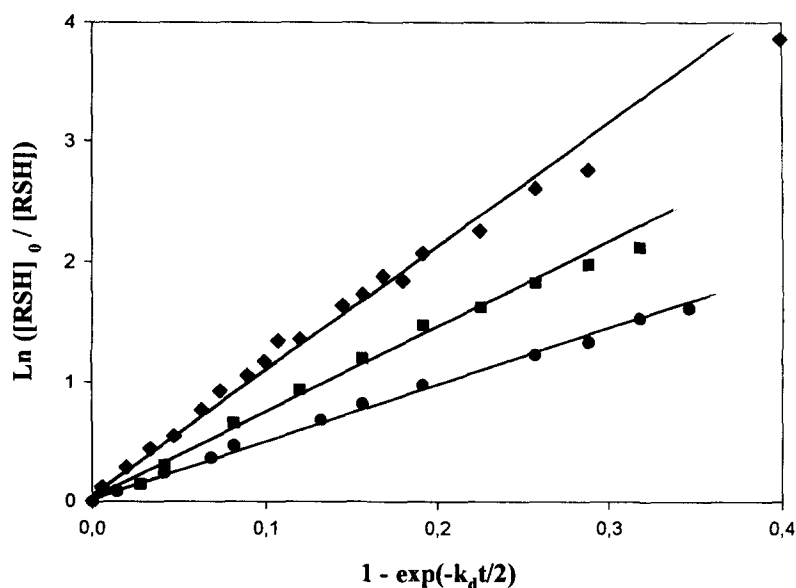
Figure 3 Influence of initiator concentration (C_0) on the addition kinetic for $n_{max} = 1.05$ at 75°C, according to equation (16): •, 0.2×10^{-2}; ■, 0.4×10^{-2}; ♦, 0.8×10^{-2}
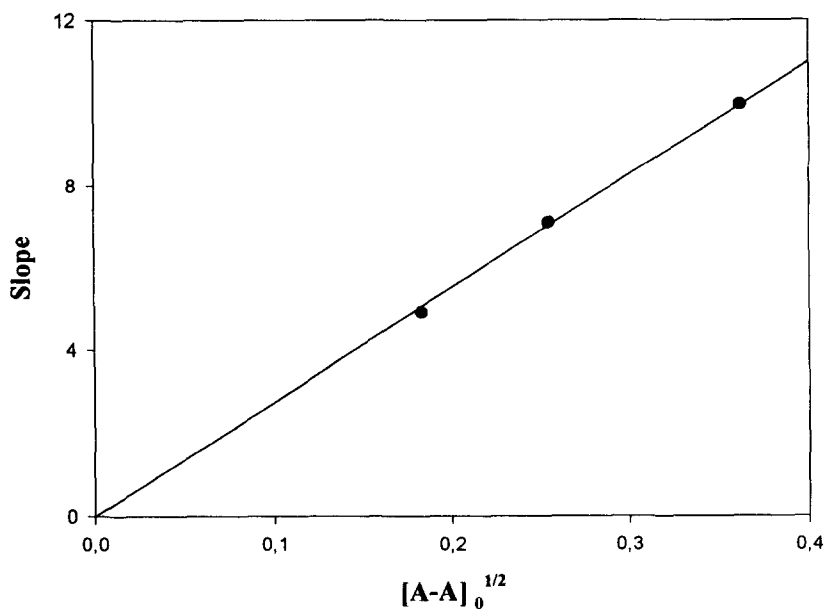

Figure 4 Slopes of the curves in *Figure 5 versus* $[A_2]_0^{1/2}$, according to equation (16)

Table 1 Slopes and ultimate yields calculated from *Figures 3, and 5*

n_{max}	$[A-A]_0 \times 10^2$ (mol kg^{-1})	$C_0 \times 10^2$	Slope	$[RSH]_\infty$ (mol kg^{-1})	Y_∞ (%)
1.05	13.1	0.8	10.0	2×10^{-5}	≈ 100
1.05	6.5	0.4	7.1	3×10^{-4}	99.9
1.05	3.3	0.2	4.9	2.7×10^{-3}	99.3
2	3.1	0.2	4.5	6.8×10^{-3}	98.9
4	2.7	0.2	3.4	3.6×10^{-2}	96.7
7.9	2.2	0.2	2.4	2.2×10^{-1}	90.9

$([RSH]_0 = 0.342$ mol kg^{-1}) in the presence of AIBN $(C_0$ in the range 0.2 to 0.8 $\times 10^{-2}$ with $k_d = 0.34$ h^{-1} according to ref. [14]) at 75°C *(Figure 3)*.

Almost straight lines were obtained for conversions up to 95%. Moreover, the slopes of these curves are proportional to $[A-A]^{1/2}$ *(Figure 4)*.

According to equation (18), the slopes enable us to calculate $[RSH]_\infty$ as well as the corresponding theoretical maximum conversion Y_∞ *(Table 1)*.

It should be noted that in our conditions, the limiting value of Y_∞ is very close to 100% in each case, which is in agreement with our experimental results.

Influence of thiol concentration. The results obtained with AIBN, at 75°C, for $C_0 = 0.2 \times 10^{-2}$ and $n_{max} = 1.05$, 2, 4 and 7.9 are reported in *Figure 5*.

Several observations can be made.

(1) Equation (16) is verified and almost straight lines are obtained in each case.

(2) As previously, the slopes of the curves enable us to calculate $[RSH]_\infty$ and the theoretical maximum conversion Y_∞ (*Table 1*). In agreement with experimental results, the values of Y_∞ show that the reaction can be almost quantitative, even for the higher value of n_{max}.

(3) From equation (16), only a single curve would be obtained with a slope equal to $2k_2(\frac{f}{k_d k_c})^{1/2}[A - A]_0^{1/2}$. As a matter of fact, the values of the slopes decrease as the concentration of thiol increases. To explain these results, we have considered that this evolution was due to the variation of kinetic constants k_2 and/or k_c according to the modification rates and the progress

of the reaction. Thus, the evolution of the average values of $2\frac{k_2}{k_c^{1/2}}(\frac{f}{k_d})^{1/2}$ *versus* n_{max}, are reported in *Figure 6*.

Several reasons may be put forward:

• a continuous variation of chain conformation;
• an increase in global steric hindrance;
• an increase in local steric hindrance near vinylic sequences.

In this last case, it is noteworthy that, on average, there are 11.5 vinyl units per chain with a mean length of 2.2 units according to Pham[15]. Therefore, the number of vinyl diads must be the highest and it is reasonable to believe that, on average, the kinetic constant k_2 may vary because of the steric hindrance between the first addition and the second, to the next vinyl group. Likewise, the variations of global steric hindrances or of chain conformations may have the same effect on k_2. The same phenomenon could be observed for termination reaction and may also affect k_c.
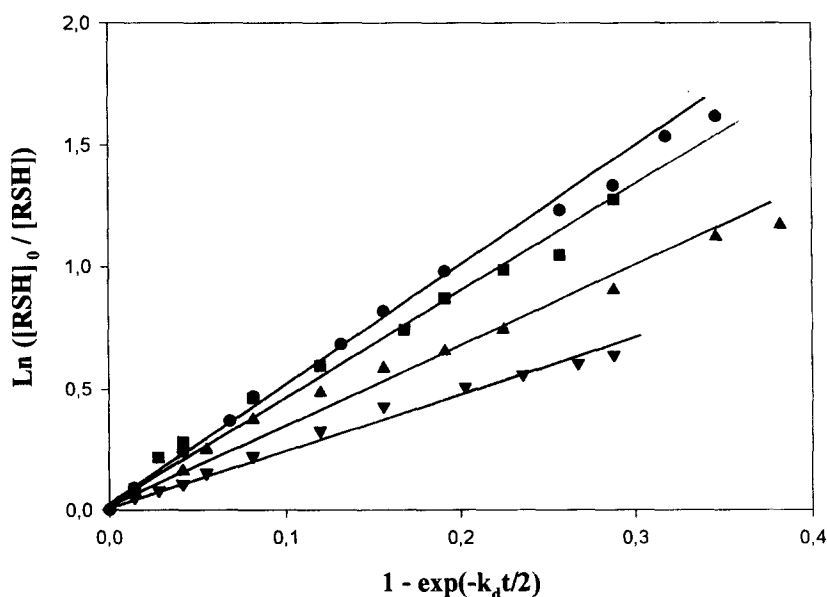

Figure 5 Influence of thiol concentration on the addition kinetic, with $C_0 = 0.2 \times 10^{-2}$ at 75°C, according to equation (16) corresponding to different n_{max}: ●, 1.05; ■, 2; ▲, 4; ▼, 7.9
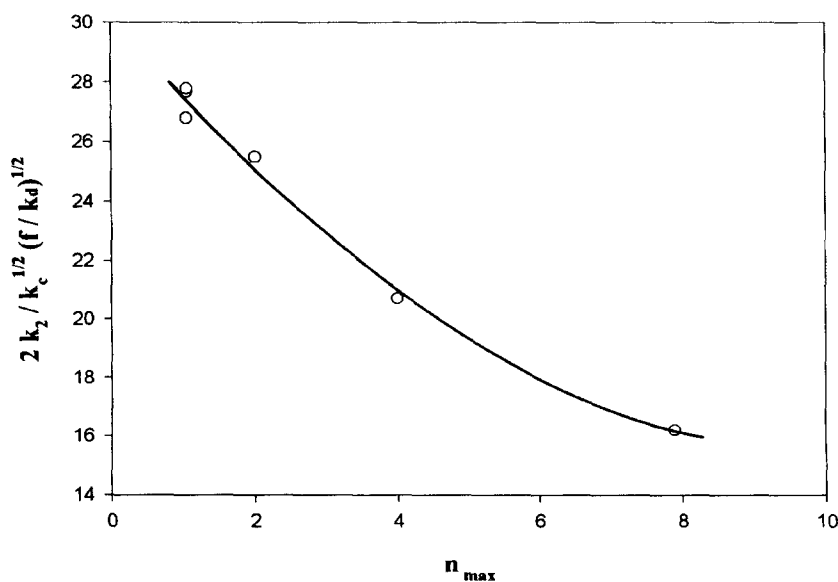

Figure 6 Experimental variations of kinetic constants *versus* n_{max}

CONCLUSIONS

The radical addition of thiol to double bonds is suitable for the introduction of new functions to a polybutadiene backbone. Thus, triethoxy silane groups were quantitatively introduced to low molar mass polybutadiene in the range of 1.05 to 7.9 functions per chain. The kinetic study led us to reconsider some mechanisms and, in particular, to assume that the reaction of termination takes place by recombination of less hindered and more stable radicals of polymer chains. Finally, to justify our experimental results, we also assumed that the kinetic constants varied because of a steric hindrance between neighbouring vinylic double bonds, when one of them is already modified, and/or the evolution of local or global steric hindrance with modification rate.

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