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Low molar mass polybutadiene made crosslinkable by silane moities introduced via addition of thiol to double bond: 4. Crosslinking study

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Abstract

The effect of the number of triethoxy silane functions introduced onto low molar mass hydroxy telechelic polybutadiene was investigated by using swelling measurements and mechanical properties (storage modulus E' at the rubbery plateau and maximum of tan δ). These triethoxy silane functions were distributed all along the polymer chain by the addition of mercapto propyl triethoxy silanes to vinyl double bonds. Influence of catalyst, temperature, moisture and time were studied. The best experimental conditions correspond to 80°C under moisture with dibutyl tin dilaurate as catalyst. A large increase in T_g (from -70 to -20°C) and E' (6.5–130 MPa) was observed from 1.05 to 7.9 triethoxy silane groups per chain. These results are due to a decrease of the average molar mass per crosslinked unit ($\overline{M_c}$) which was not observed when the modification was performed essentially at chain extremities (hydroxy functions) via urethane linkage. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polybutadiene; Silane; Crosslinking

1. Introduction

Crosslinking of a low molar mass polyol is usually carried out by using di or poly isocyanates. On account of the toxicity of these compounds, new crosslinking routes are required. In our case, the polyol used is a low molar mass polybutadiene (Poly Bd R45 HT®) which 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 $\overline{f_{OH}} = 2.4$. 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.

One of the ways to avoid the use of isocyanates is to modify the hydroxy functions of the polyol to lead to new crosslinkable functions. For this purpose, alkoxy silane moities are often used [1–17] because they allow to obtain three-dimensional networks only by moisture with an appropriate catalyst. Thus, the modified polymer exhibits the advantage of being free isocyanate and, therefore, limits the environmental and human health problems generally associated with isocyanates. In previous studies [18,19], synthesis and crosslinking study was performed on HTPB modified by using isocyanato propyl triethoxysilane. As a result of the hydroxy functionality, this method allows 2.4 alkoxy silane groups to the maximum. A second way consists of a radical addition of thiol to the vinyl double bonds [20–31]. Thus, the alkoxy silane groups are grafted along the polymer chain and the rate of modification may be higher. In our case, 1.05–7.9 mercapto propyl triethoxysilane groups was added to HTPB chain, which contains up to 10 vinyl double bonds per chain [32], according to Scheme 1.

In this article, it is the crosslinking study of this last type of modified HTPB which is investigated.

2. Experimental

2.1. Materials

Polybutadiene (Poly Bd R45 HT®) was kindly supplied by Elf Atochem. Immobilization of triethoxy silane moities on polybutadiene by using mercapto propyl triethoxy silane (Hüls) at 75°C in the presence of AIBN as initiator was described elsewhere [32].

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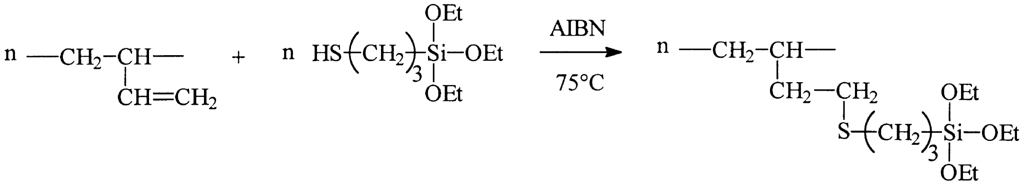


Scheme 1.

2.2. Crosslinking conditions

Modified polybutadiene (PBS,*n*Si with n = number of silane group per polymer chain), with and without catalyst, was casted in PTFE mould (2 mm depth) and placed into an oven at different temperatures. For crosslinking under moisture, a vessel containing water was introduced in the oven.

2.3. Measurements

Crosslinking was studied by two methods.

2.3.1. Swelling measurement

From polymer casting, samples ($8 \times 8 \times 2\ \mathrm{mm}^3$) were cut off during crosslinking process and swollen in toluene for 24 h. Later, samples were first weighed (m_s) then dried under vacuum for 24 h at room temperature and weighed again (m_d). Swelling (Q) is calculated as:

$$Q = \frac{m_s - m_d}{m_d}.$$

2.3.2. Mechanical properties

Storage modulus (E') and loss tangent ($\tan \delta$) were measured by using dynamic mechanical analysis (DMA 7 Perkin–Elmer) in the compression mode with stainless steel parallel plate probe (1 mm diameter), at 1 Hz, on small samples ($3 \times 3 \times 2\ \mathrm{mm}^3$) regularly taken from a polymer plate. Static and dynamic (80% of static force) forces were chosen according to crosslinking progress and physical properties of materials. For example, these forces were, respectively 300 and 240 mN at the beginning of the reaction and 1000 and 800 mN for high crosslinked materials. Measurements were carried out in the range −125–50°C, at a rate of $5°\mathrm{C\ min}^{-1}$. Standard calibration was performed with *n*-decane ($T_m = -50$°C) and indium ($T_m = 156.6$°C).

3. Results and discussion

Firstly, we studied mechanical properties of the initial modified polybutadiene PBS,*n*Si (with n = number of silane group per polymer chain), before crosslinking, by using d.m.a. measurements. As a matter of fact, measurement is very delicate because of a liquid–liquid transition ($T_{l,l}$) at

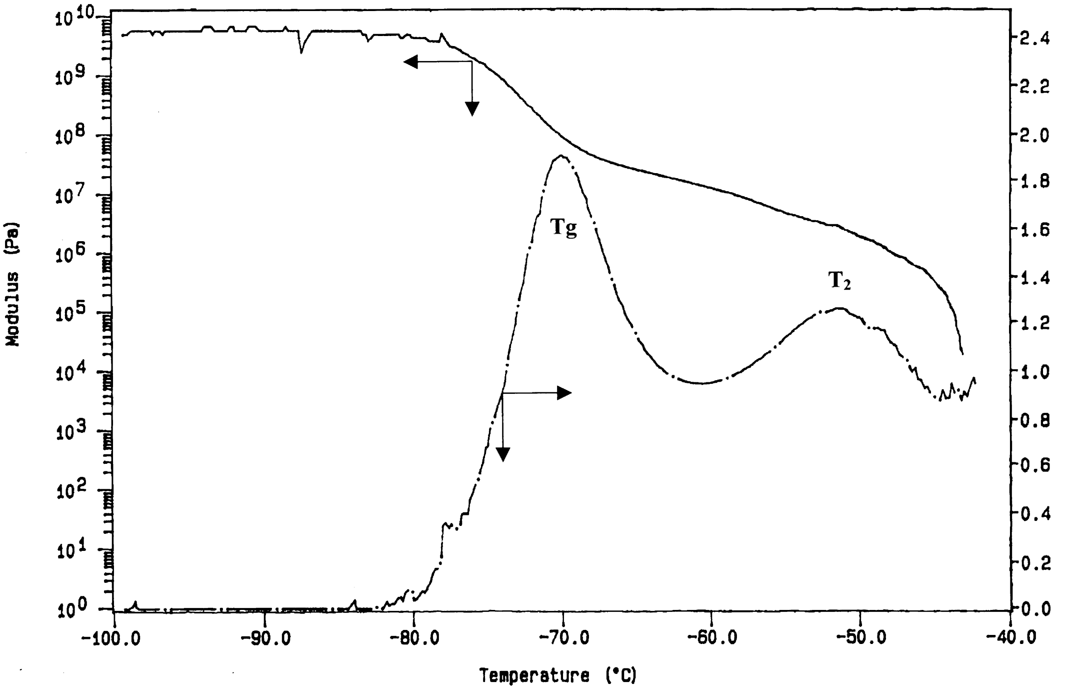
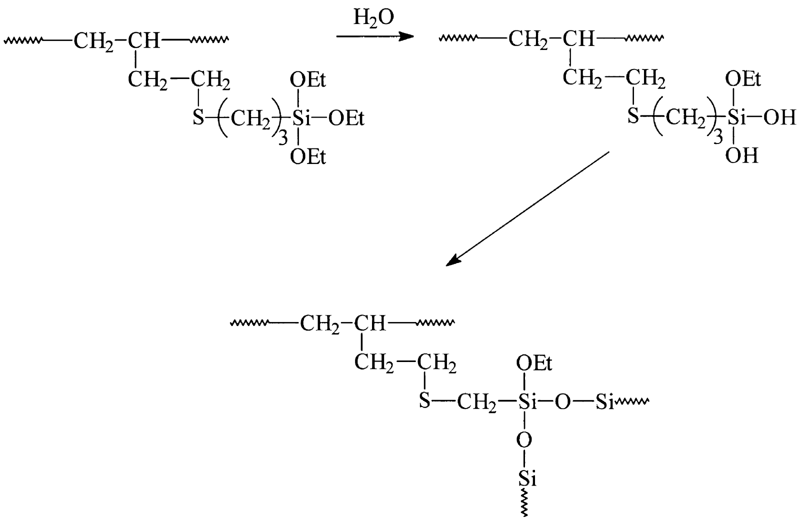


Fig. 1. Storage modulus and tan δ versus temperature of a modified polybutadiene (PBS,2Si; $n = 2$ silane groups per chain) before crosslinking.



Scheme 2.

Table 1
Crosslinking time versus molar ratio $[H^+]/[Si]$ and temperature with triflic acid as catalyst

H^+/Si	5×10^{-4}	10^{-3}	7.5×10^{-3}	10^{-2}	2.5×10^{-2}	5×10^{-2}
20°C	v. v.[a]	v. v.[a]	24 h	6 h	2 h	1 h
40°C	v. v.[a]	v. v.[a]	12 h	3 h	1 h	30 min

[a] v. v.: very viscous after 30 d.

low temperature which disturbs the results. For this purpose, we were obliged to use a parallel plate probe of 10 mm diameter. Indeed, it is necessary to apply dynamic and static forces sufficiently high in the glassy state and sufficiently weak in the liquid state so that the measurement can be possible. The compromise is very difficult to find, and many experiments were carried out in order to obtain acceptable results. Storage modulus and tan δ are reported in Fig. 1 for PBS,2Si.

Two mechanical transitions can be observed. The first one (−70°C at the maximum of tan δ) is connected to T_g in our experimental conditions. This transition is assigned to mainly 1,4 repeating units [33]. The second transition (T_2) which was assigned to short vinyl sequences [19], correspond to a very weak variation of E' immediately followed by a drop of modulus due to the liquid–liquid transition. As the modified rate increases, from 1.05 to 7.9 vinyl double bond per chain, the intensity of T_2 decreases rapidly. Likewise, one may expect a disappearance of T_2 with the progress of the crosslinking as we have previously observed for HTPB modified via urethane linkage [19].

Table 2
Crosslinking time versus molar ratio $[H^+]/[Si]$ and temperature with acetic acid as catalyst

H^+/Si	2.5×10^{-2}	5×10^{-2}	7.5×10^{-2}	7.5×10^{-1}
40°C	v. v.[a]	v. v.[a]	v. v.[a]	15 d
80°C	15 d	15 d	10 d	4 d

[a] v. v.: very viscous after 30 d.

One can consider two steps for the crosslinking mechanism (see Scheme 2).

A total or partial hydrolysis of ethoxy silane groups, in the first step, is followed by the condensation of the resulting silanols. Thus, these reactions, and consequently the ultimate properties of materials, depend on many parameters such as absence or presence of catalyst, nature of catalyst, concentration of catalyst, temperature, moisture content, reaction time, number of silane functions per chain and sample thickness.

A preleminary study, on PBS,2Si was investigated in order to determine the best experimental crosslinking conditions:

Without catalyst: Samples were kept at ambient atmosphere and room temperature. After 30 d, no modification was observed and the samples were always liquid and soluble in various solvents (toluene, acetone, methyl ethyl

Table 3
Crosslinking time versus molar ratio [DBTL]/[Si] and temperature

[DBTL]/[Si]	1.5×10^{-3}	3×10^{-3}	5×10^{-3}	6.5×10^{-1}
40°C	5 d	3 d	2 d	24 h
80°C/humidity	24 h	18 h	8 h	5 h

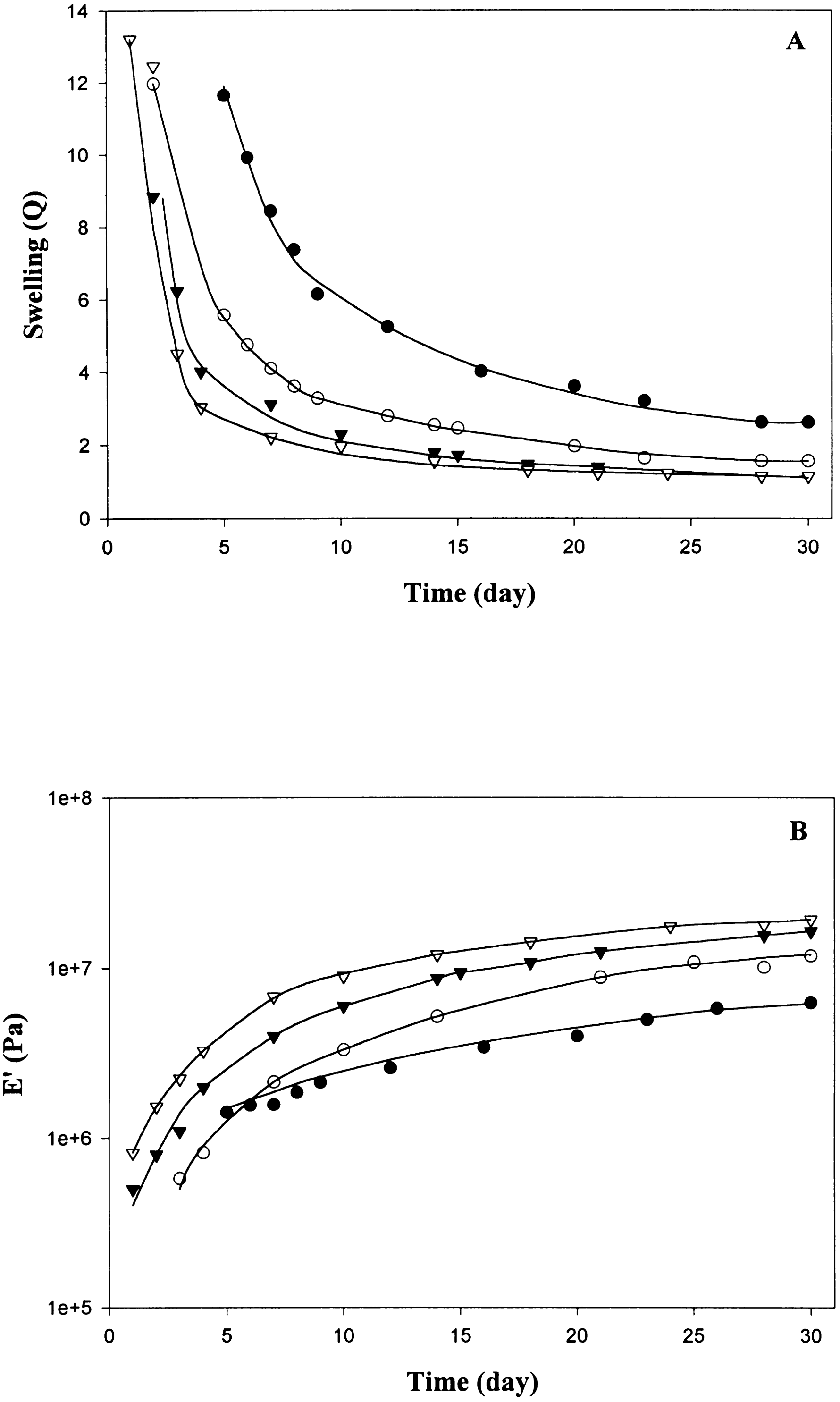


Fig. 2. Swelling (A) and storage modulus at the rubbery plateau (B) versus crosslinking time of PBS,2Si at 40°C and various 10^3 [DBTL]/[Si]: (●) 1.05; (○) 3; (▼) 5; (▽) 6.5.

ketone). The diffusion of water from the surrounding medium is not sufficient to lead to crosslinking. The same result was obtained at 40°C. This observation is very important from an industrial point of view because it shows that the modified polymer has a great stability and a long pot-life.

Another experiments were carried out by adding a small amount of water (molar ratio $[H_2O]/[Si] = 3$) directly into the liquid polymer under quick stirring. A whitish mixture was obtained which became transparent few hours after casting in the moulds. After a week, whatever the temperature (room temperature, 40 and 80°C), the sample remained

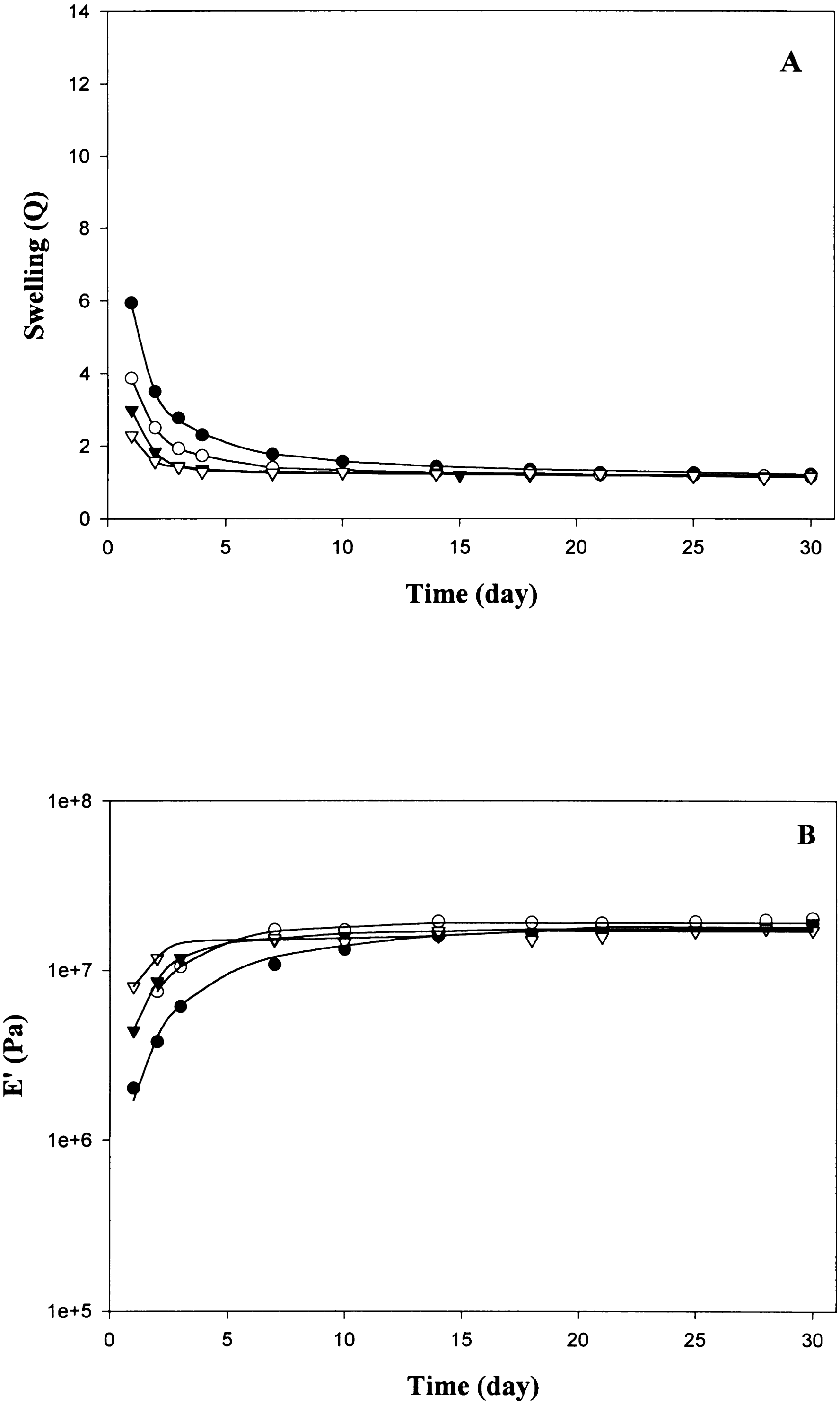


Fig. 3. Swelling (A) and storage modulus at the rubbery plateau (B) versus crosslinking time of PBS,2Si at 80°C under humidity and various 10^3 [DBTL]/[Si]: (●) 1.05; (○) 3; (▼) 5; (▽) 6.5.

liquid and more or less viscous. Introduction of water is always insufficient to induce crosslinking.

With catalyst: CF_3SO_3H. As mentioned earlier, a molar ratio $[H_2O]/[Si] = 3$ was chosen with various amount of acid, expressed as molar ratio $[H^+]/[Si]$, at 20 and 40°C. The reaction was followed until crosslinking and the time to obtain a material dry to the touch and easily stripping is reported in Table 1.

One can notice a drop of crosslinking time for catalyst concentration higher than 7.5×10^{-3} $[H^+]/[Si]$. Moreover,

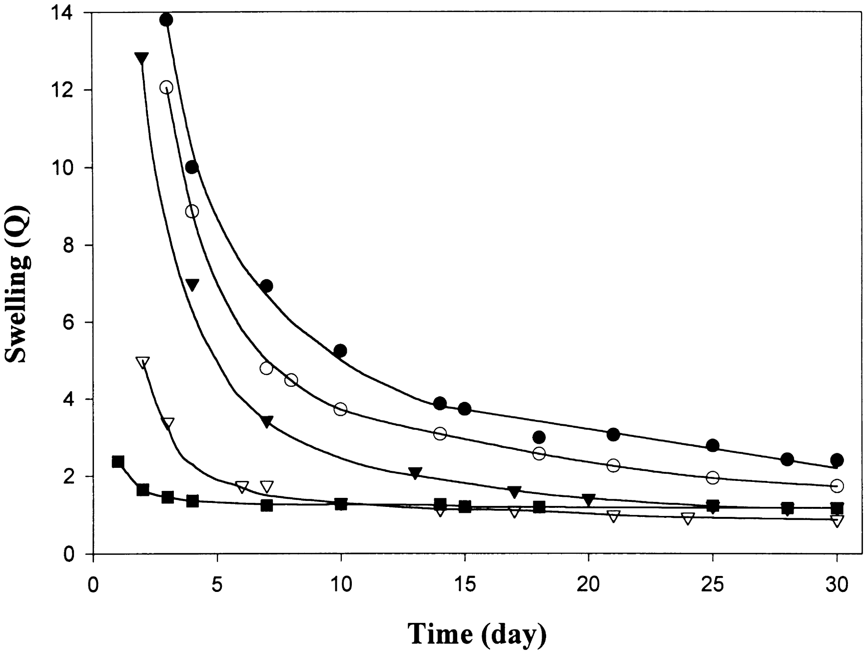


Fig. 4. Swelling versus crosslinking time of PBS,2Si with 10^3 [DBTL]/[Si] = 5, at different temperatures: (●) 20°C; (○) 40°C; (▼) 60°C; (▽) 80°C; (■) 80°C/humidity.

we observe an two-fold decrease of time between 20 and 40°C. Experimentally, from molar ratio of 10^{-2}, the whitish mixture became rapidly viscous and it is necessary to cast it quickly. The crosslinked materials are white, flexible but break under folding.

Acetic acid: The same experiments were carried out with acetic acid as catalyst but at higher temperatures and concentrations (Table 2).

The reaction was much slower and the resulting material remained very soft and brittle.

Dibutyl tin dilaurate (DBTL): DBTL is a usual catalyst for hydrolysis and condensation of silanes [3,6,25]. For example, the gelation of grafted PE with triethoxy silane is obtained after 1000 h at 80°C and only after 10 h with DBTL [3]. Experimentally, the crosslinking was performed at 40 and 80°C under humidity (Table 3).

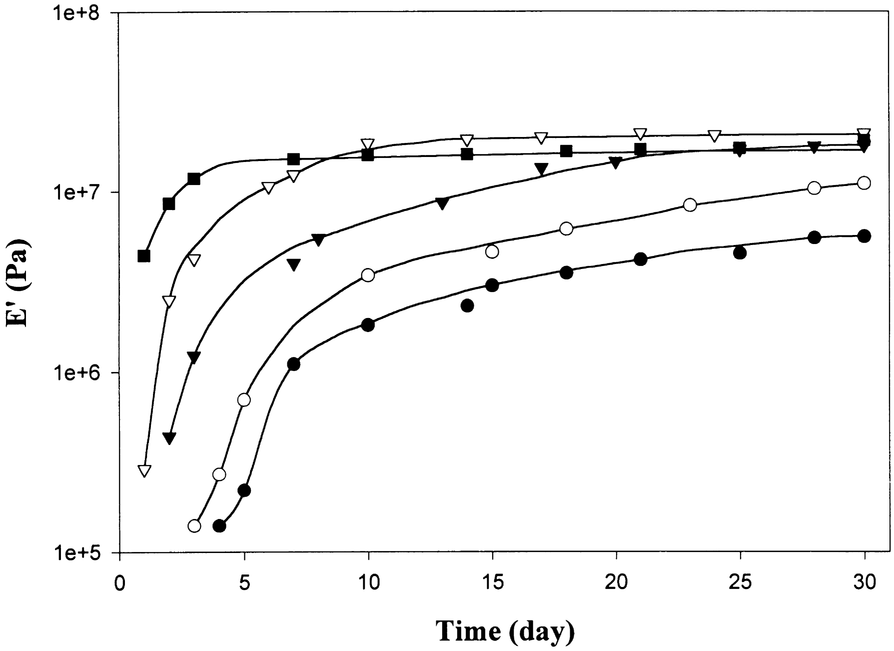


Fig. 5. Storage modulus at the rubbery plateau versus crosslinking time of PBS,2Si with 10^3 [DBTL]/[Si] = 5, at different temperatures: (●) 20°C; (○) 40°C; (▼) 60°C; (▽) 80°C; (■) 80°C/humidity.

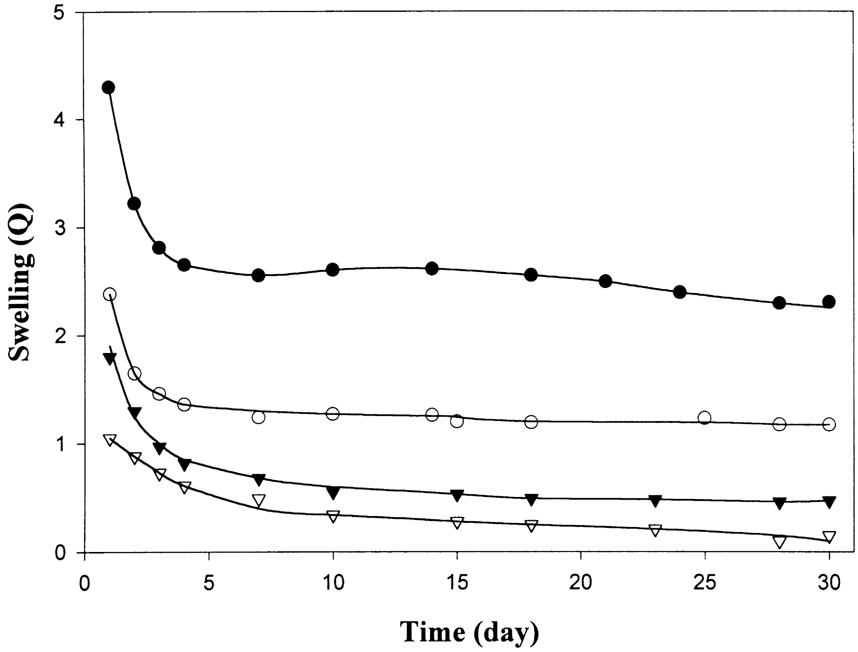


Fig. 6. Swelling versus crosslinking time at 80°C/humidity with 10^3 [DBTL]/[Si] = 5, for different PBS,*n*Si: $n = 1.05$ (●); 2 (○); 4 (▼); 7.9 (▽).

Very interesting results were obtained, even at 40°C, with small amounts of DBTL. There was no increase in viscosity during the process, the crosslinked material was flexible, transparent and very slightly yellow at 80°C. Afterwards, the following studies were carried out with this catalyst.

Influence of [DBTL]/[Si] ratio: Swelling (Q) and storage modulus at the rubbery plateau (E') curves exhibit the same shape at each temperature and show clearly the influence of DBTL concentration (Figs. 2 and 3).

At 40°C, Q and E' are very dependent of DBTL concentration and a minimum value of Q (or a maximum value of E') is only obtained for $[\mathrm{DBTL}]/[\mathrm{Si}] = 6.5 \times 10^{-3}$ (Fig. 2(A) and (B)). However, these optima are reached after 10 d at 80°C under humidity whatever DBTL concentration (Fig. 3(A) and (B)).

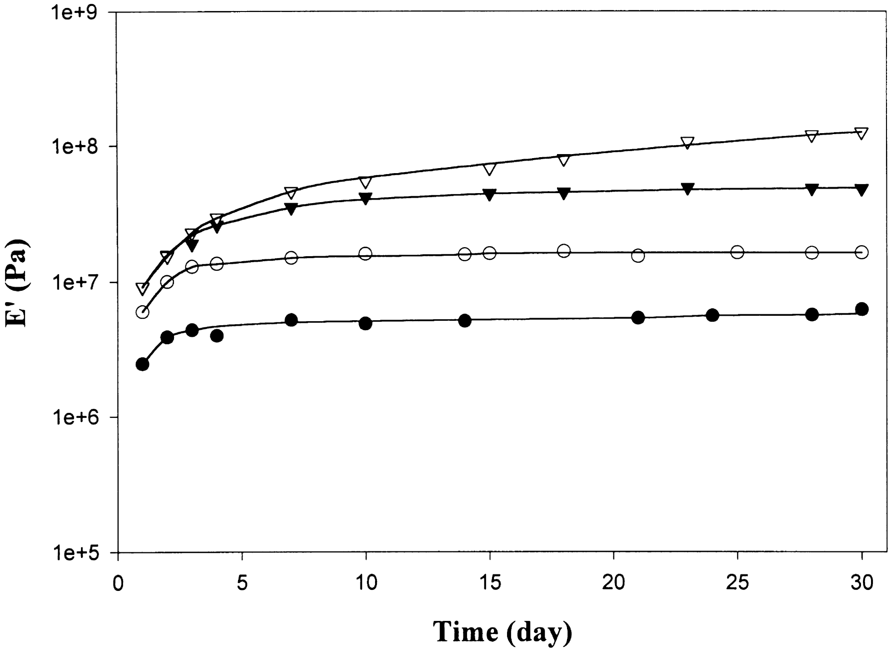


Fig. 7. Storage modulus at the rubbery plateau versus crosslinking time at 80°C/humidity with 10^3 [DBTL]/[Si] = 5, for different PBS,*n*Si: $n = 1.05$ (●); 2 (○); 4 (▼); 7.9 (▽).

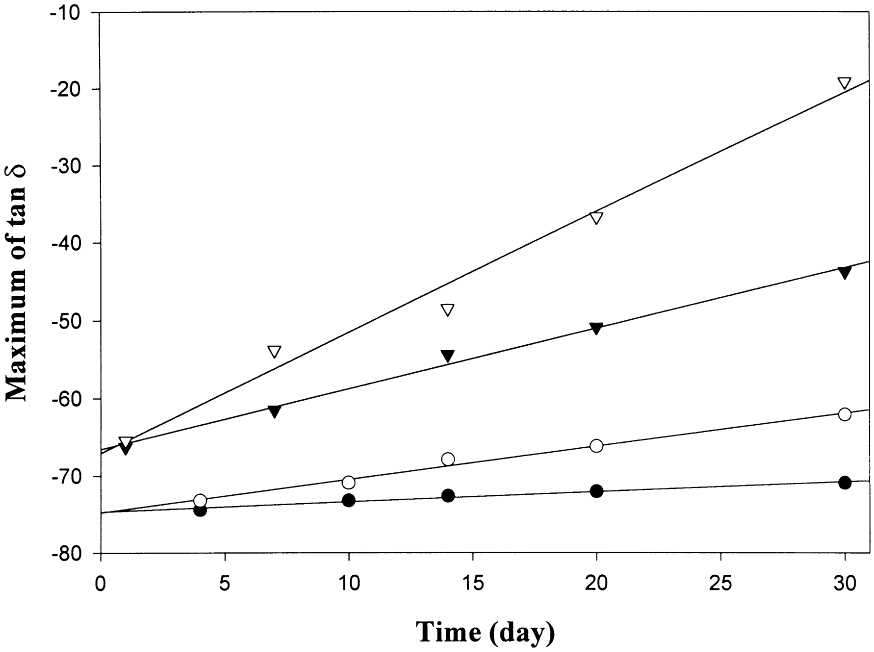


Fig. 8. Maximum of tan δ versus crosslinking time, with 10^3 [DBTL]/[Si] = 5, for different PBS,*n*Si: $n = 1.05$ (●); 2 (○); 4 (▼); 7.9 (▽).

Influence of temperature: This study was carried out with [DBTL]/[Si] = 5×10^{-3}. Swelling (Q) and modulus at the rubbery plateau (E') curves are reported in Figs. 4 and 5. An important increase of ethoxy silane hydrolysis and silanol condensation is observed from 20 to 80°C. For example, Q and E' after 30 d at 20°C are similar to those measured after 1 d at 80°C. As E', tan δ perfectly accounts for the progress of the reaction with a maximum which increases from −67 (for 20°C after 30 d) to −56°C (for 80°C). One can also notice a broadening of the peak when the temperature increases and a drop of damping efficiency. Moreover, whatever the temperature, the crosslinking is sufficiently gone forward so that the transition T_2 cannot be observed as expected. Finally, it is noteworthy that if the reaction rate is faster at the beginning at 80°C under humidity, E' and tan δ are slightly lower than at 80°C after 30 d. Our interpretation of these experimental observations is based on plasticization of the sample by water. As a matter of fact, this difference disappears after drying.

Influence of the number of silane groups per chain: Polymer bearing 1.05, 2, 4 and 7.9 silane groups per chain were used with DBTL as catalyst ([DBTL]/[Si] = 5×10^{-3}) at 80°C under humidity.

Swelling: Fig. 6 perfectly illustrates this influence with values of Q which reaches a plateau in about 8–10 d except for $n = 7.9$ where a decrease of Q is always noticeable after 30 d. When n increases, the crosslinked polymer changes from soft material to more and more rigid.

Storage modulus: These latest swelling results are strengthened by the variation of E' at the rubbery plateau (Fig. 7). The same behaviours are observed with a plateau up to $n = 4$ and a noticeable increase of E' even after 30 d for $n = 7.9$. If E' is similar in glassy region ($E' = 10^9$ Pa), an increase in T_α of about 50°C is observed with n owing to an increase of crosslinking density that is to say a decrease of $\overline{M_c}$, the average molar mass per crosslinked unit.

Evolution of tan δ: In all cases (Fig. 8), we observe an increase of the maximum of tan δ with time, a broadening of the peaks and a decrease of their intensity. The shift of T_α (connected to T_g) is all the more important as n increases. In the case of $n = 1.05$, one can notice the presence of the transition T_2 even after 30 d. This result is in agreement with a low perturbation of vinyl double bonds due to a low modification of the chain. Finally, this transition is still observable for $n = 2$ after 4 d of reaction.

4. Conclusion

The modification of low molar mass polybutadiene by silane moities introduced via addition of thiol to double bond allows to largely increase the rate of crosslinkable functions (up to 7.9 per chain in this work) with regard to urethane linkage (2.4 to the maximum). By using DBTL as catalyst at 80°C under moisture, the crosslinking is relatively fast and leads to material with variable properties. Thus, the modification within the polymer chain induces a decrease of the molar mass per crosslinked unit and the consequences are the disappearance of the second mechanical transition, assigned to vinyl sequences, the increase of the glass transition temperature and storage modulus at the rubbery plateau (T_g in the range −70 to −20°C and E' in the range 6.5–130 MPa).

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