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Low molar mass polybutadiene made crosslinkable by the introduction of methacrylate moieties via urethane linkage. 5. Synthesis and crosslinking study

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Abstract

Hydroxy telechelic low molar mass polybutadiene was modified by using methacryloyl isocyanate (MAI). Immobilization of methacrylate functions was carried out at 40°C with or without dibutyl tin dilaurate (DBTL) as a catalyst. The reaction was fast and nearly instantaneous with DBTL. Methacrylate moieties were introduced quantitatively at the rate of 1.2, 2 and 2.4 per polymer chain. The photoinitiated radical kinetic of crosslinking shows that conversion increases with temperature and light intensity. A preliminary thermal polymerization alters the experimental results at temperatures above 80°C. Catalyzed thermal crosslinking was carried out with three initiators: dibenzoyl peroxide (POB), dicumyl peroxide (DCUP) and *t*-butyl perbenzoate (TBPB). The effects of the nature of the initiator, of the temperature, of the concentration of initiator and of the number of methacrylate moieties per polymer chain were investigated by measuring swelling and mechanical properties (storage modulus E' and maximum of tan δ). The participation of polybutadiene double bonds to the crosslinking is clearly shown. Depending on the experimental conditions, ranging from a few minutes to a few hours, various crosslinked materials can be obtained with controlled mechanical properties. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polybutadiene; Methacrylate; Kinetic

1. Introduction

Hydroxy telechelic polybutadiene (HTPB) is a polyol, which is commonly used with di- or poly-isocyanates for the synthesis of polyurethane networks. Isocyanates in general are toxic chemicals and great care must be exercised in handling them since their inhalation presents a hazard for the people who work with them. Moreover, it is imperative, for human health and environmental considerations, to remove the remaining free isocyanates, which could be present within imperfectly crosslinked material. For these reasons, our aim was to find less hazardous alternative curing systems for the users other than isocyanate–alcohol. This is why we have recently reported the synthesis of modified HTPBs by silane moieties and their crosslinking under moisture [1–4]. In those cases, three-dimensional networks were obtained with good mechanical properties. Another way to avoid the isocyanate–alcohol crosslinking reaction is a radical crosslinking via (meth)acrylate functions immobilized onto HTPB. Several papers and patents dealt with this type of HTPB modification either by esterification with (meth)acrylic acid, anhydride or esters [5], for example, or via urethane linkage. This linkage can be performed either in two steps, by using first a diisocyanate and secondly hydroxyethyl (meth)acrylate [6–12], or else in one step with isocyanato ethyl methacrylate [13–15] or methacryloyl isocyanate (MAI) [15]. In all those cases, only the synthesis is really described, and modified HTPBs are always crosslinked with reactive diluents. No results about the crosslinking kinetics and the properties of modified HTPBs were mentioned.

In this paper, we have also focused our attention on the hydroxy-isocyanate reaction leading to urethane linkage by using MAI as a modification reactant. Nevertheless, the present work is not only devoted to synthesis and crosslinking kinetic in relation to different parameters (nature and concentration of the initiators, temperature, number of methacrylate functions onto HTPB), but it is also concerned with crosslinking conditions (thermal or photoinitiated) and to the evolution of swelling and of mechanical properties (E', tan δ) during crosslinking.

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2. Experimental

2.1. Materials

Polybutadiene (Poly Bd R45 HT®) was kindly supplied by Atofina. MAI was used as received and obtained from Nippon Paint. Dibutyl tin dilaurate (DBTL) (Aldrich), dibenzoyl peroxide (POB) (Aldrich), dicumyl peroxide (DCUP) (Aldrich), *t*-butyl perbenzoate (TBPB) (Aldrich) and 2,2-dimethyl-2-hydroxyacetophenon (Darocur 1173) (Ciba-Geigy) were used without further purification.

2.2. Synthesis

0.01 mol (28 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 graduated vacuum up to 10^{-1}–10^{-2} mmHg at 60°C. Then, the reactor was placed at 40°C under nitrogen. When a catalyst was used (DBTL), the latter was added (1.2×10^{-3} mol kg^{-1}) and the mixture was stirred for 5 min; 0.012, 0.02 or 0.024 mol of MAI (respectively, 1.33, 2.22 or 2.66 g) was introduced with care as rapidly as possible. The reaction was allowed to proceed until complete disappearance of isocyanate functions.

2.3. Photocrosslinking conditions

The photocrosslinking reactions were carried out in a differential scanning calorimeter (DSC 7 Perkin Elmer), which included an irradiation unit. Heat flow versus time was recorded in isothermal mode under a nitrogen atmosphere. The optical part of the calorimeter, the treatment of the thermogram and the computation of the conversion and the reaction rate are described elsewhere [16]. The UV radiation intensity was measured at the sample level by a radiometer at 365 nm and was 2.7 mW cm^{-2}.

The photoinitiator, 2,2-dimethyl-2-hydroxyacetophenon (Darocur 1173), was dissolved in the oligomer while being stirred at room temperature for 3 h at 1% (w/w). About 2 mg of mixture was laid down over a polyethylene film (0.1 mm) covering the bottom of an aluminum DSC pan in order to cause a maximum spreading out of the monomer as a thin and plane layer. Indeed, if a PE film is not used, a hemispherical drop is obtained and optical disturbance can disturb the experimental data. It should be noted that the presence of the PE film does not change our measurements when the experimental temperature is above PE melting point. This is due to a further thermal stabilization during 5 min, which occurs before irradiation under nitrogen ($\leq$0.5 ppm O_2) and which removes residual oxygen and allows temperature to stabilize.

2.4. Thermal crosslinking conditions

POB and DCUP, which are solids, were previously dissolved in the minimum amount of methyl ethyl ketone (MEK). Subsequently, a variable amount of thermal initiator (see text) was dissolved in the oligomer while being stirred at room temperature for 10 min. Then MEK was removed by vacuum at ambient temperature. The mixture was cast in PTFE or steel moulds (2 mm deep) and placed into a vacuum oven at different temperatures. After degassing until entire disappearance of bubbles, the vacuum was cut off and the oven was placed under a nitrogen atmosphere. Crosslinking was allowed to proceed for 9 h.

2.5. Measurements

Synthesis and crosslinking were observed by using different methods.

2.5.1. Volumetric titration

Free isocyanate functions were classically treated by an excess of dicyclohexylamine and back-titrated with an HCl standard solution by using a self-acting apparatus (Titroline Schott).

2.5.2. FTIR spectroscopy

IR spectroscopies were carried out with a Nicolet 510 M IR/FT. Samples were set apart from the reactive mixture during reaction time and spread out on IRTRAN window. The variable thickness of the films implied the use of a reference band in the spectrum to calculate the reaction conversion (*C*) according to Beer–Lambert law. This reference band at 960 cm^{-1}, which undergoes no modification during the reaction, corresponds to CH vibration of HTPB 1,4 *trans* double bond. Thus, the disappearance of isocyanate band at 2270 cm^{-1} allows us to determine conversion versus time:

$$C = 1 - \frac{(A_{2270\ \mathrm{cm}^{-1}}/A_{960\ \mathrm{cm}^{-1}})_t}{(A_{2270\ \mathrm{cm}^{-1}}/A_{960\ \mathrm{cm}^{-1}})_0}$$

where *A* is the absorbance and subscript 0 corresponds to initial time.

2.5.3. Swelling measurement

Samples ($8 \times 8 \times 2$ mm^3) were cut off during the crosslinking process and swollen in toluene for 24 h. Afterwards, samples were first weighed (m_s), then dried under vacuum for 24 h at room temperature, until constant mass, and weighed again (m_d). Swelling (*Q*) is calculated as

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

2.5.4. Mechanical properties

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

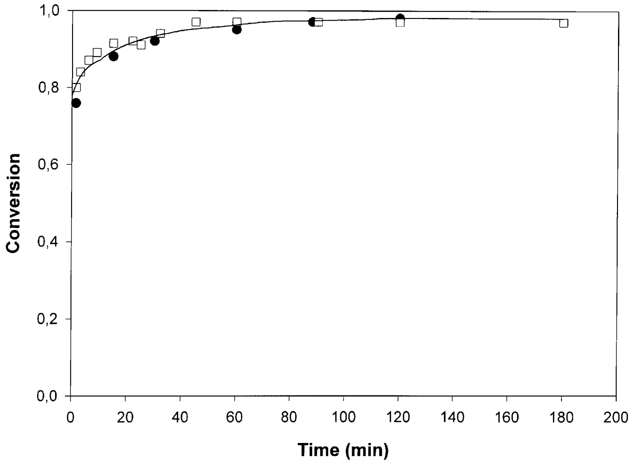


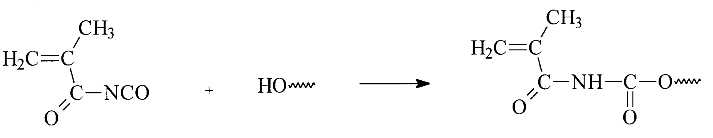
Fig. 1. FTIR (□) and titration (●) conversion curves for HTPB/MAI reaction at 40°C without catalyst.

3. Results and discussion

3.1. Synthesis

The low molar mass polybutadiene used in this work is synthesized by radical polymerization. Its main characteristics are an average molar mass $\bar{M}_n = 2800$ and an average hydroxy functionality $\bar{f}_{OH} = 2.4$. Microstructure studies indicate 22% of 1,2 units (vinyl units) and 78% of 1,4 units [17–19].

Hydroxy functions of HTPB can react with monoisocyanate compounds to lead to newly functionalized polymers. In order to obtain radical crosslinking, we have chosen to introduce methacrylate functions onto HTPB via urethane linkage, with MAI as a reactant, according to the following scheme:



MAI HTPB ($\overline{f_{OH}} = 2.4$) PBMAn ($n = 1.2$; 2 ; 2.4)

where n is the number of methacrylate functions per chain.

The reactions were carried out, with a catalyst (DBTL) or not, at 40°C to prevent secondary reactions and polymerization. Without any catalyst, MAI already shows great reactivity; the reaction is fast and quantitative after 1 h for PBMA2. We can follow the concomitant disappearance of the NCO band at 2270 cm^{-1} and the appearance of the NHCO band at 1760 cm^{-1}. The two conversion curves obtained by titration or by IR analyses are in good agreement (Fig. 1).

In the presence of a catalyst (DBTL), the reaction is nearly instantaneous and no kinetic measurement is possible.

The resulting samples of modified polybutadiene (PBMAn) are transparent. An increase in viscosity with the modification rate is observed. This phenomenon is probably due to an increase in intermolecular hydrogen bonds between NH and C=O favored by the acylurethane group. This assumption is confirmed by IR spectroscopy where two different bands are observed for carbonyl (bonded at 1710 cm^{-1} and free at 1760 cm^{-1}) and a band at 3310 cm^{-1} for NH, which is characteristic of hydrogen bonding. PBMAn are not thermally stable. To avoid any polymerization, it is necessary to preserve them in the dark in the presence of an inhibitor like hydroquinone.

3.2. Photocrosslinking

3.2.1. Influence of the temperature

The influence of the temperature on crosslinking was studied on PMBA2 with Darocur 1173 as a photoinitiator at a concentration of 1% (w/w). The light intensity of the UV radiation at 365 nm was 2.7 mW cm^{-2}. Reaction enthalpy ($-\Delta H$) was measured for temperatures in the 40–160°C range (Fig. 2). This plot shows a maximum at around 110°C. Enthalpy vs. time was plotted in Fig. 3 for temperatures below 110°C. At the beginning of the reaction, the initial slopes increase very slightly with temperature. This phenomenon, which corresponds to a very low value of apparent activation energy, has already been observed for other methacrylate compounds [16,20].

Moreover, the theoretical heat evolved, which was calculated for complete conversion of only dimethacrylate functions of PBMA2, is $-\Delta H_0^{\text{theor}} = 36.5$ J g^{-1} from $-\Delta H_{\text{theor}} = 13.1$ kcal mol^{-1} for a methacrylate double

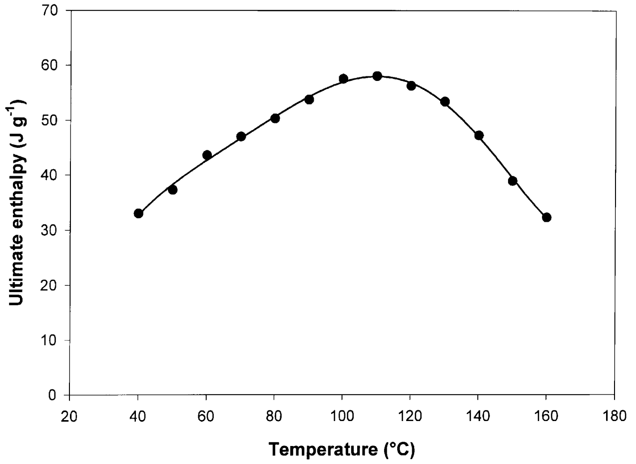


Fig. 2. Ultimate enthalpy vs. temperature for PMBA2 with 1% (w/w) of Darocur 1173.

bond [21]. It was observed that the reaction enthalpies rise largely above this theoretical value ($-\Delta H_0^{\text{theor}}$) when the temperature increases. This fact necessarily implies the involvement of polybutadiene double bonds in crosslinking, at least above 50°C. Therefore, depending on temperature, one can obtain more or less crosslinked material in about 500 s. Enthalpy vs. time for temperatures above 110°C is plotted in Fig. 4. We notice that the initial reaction rate and overall enthalpy decrease as the temperature increases. Our interpretation is directly related to our experimental conditions. In our case, before irradiation, the sample remained at the reaction temperature for 5 min so that thermal polymerization occurred, which used up the monomer, when the temperature is high enough. To confirm this assumption, ultimate enthalpy was followed with increasing time, at reaction temperature, before irradiation (Fig. 5). The higher the temperature and time, the more preliminary thermal polymerization occurs, the more the remaining enthalpy decreases.

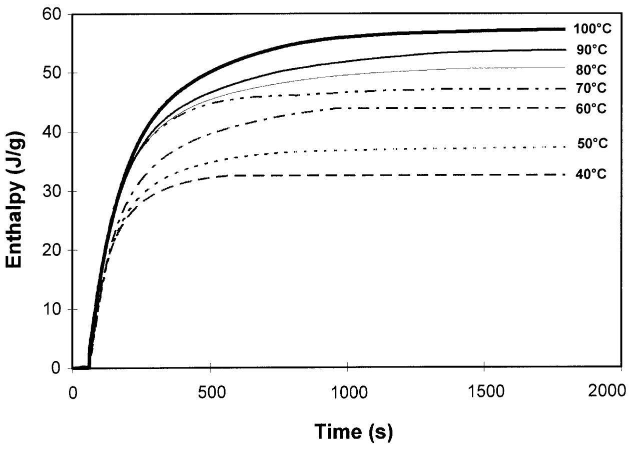


Fig. 3. Enthalpy vs. time for PMBA2 with 1% (w/w) of Darocur 1173 at different temperatures (below 110°C).

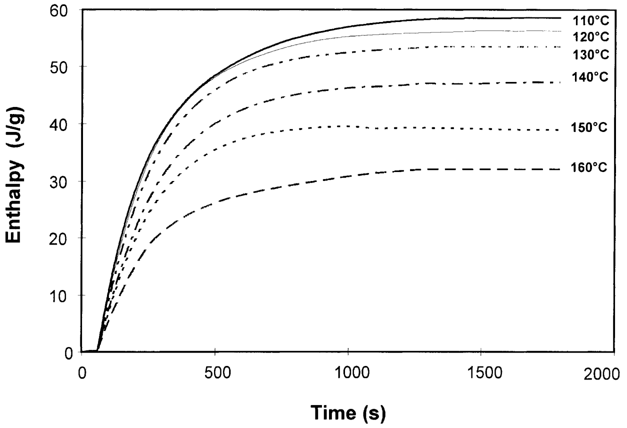


Fig. 4. Enthalpy vs. time for PMBA2 with 1% (w/w) of Darocur 1173 at different temperatures (above 110°C).

3.2.2. Influence of light intensity

The influence of light intensity was studied on PBMA2 with a photoinitiator concentration of 1% (w/w). The study was carried out at 40°C with light intensity at 365 nm in the range 0.19–2.7 mW cm^{-2}. We observed that ultimate enthalpy increased with light intensity and very rapidly reached to 0.5 mW cm^{-2} (Fig. 6). Enthalpy vs. time plots (Fig. 7) show clearly that polymerization rates and conversions increase with light intensity. In agreement with standard kinetic equations, the initial slopes of the curves (dH/dt) are proportional to $I_0^{1/2}$ (Fig. 8). Moreover, in the case of photoinitiated polymerization, the initiation rate is very high. Thus, crosslinking systems cannot be in volumic equilibrium because the volume shrinkage rate is much lower than the chemical reaction rate. This difference generates a temporary excess of free volume, which increases the mobility of residual double bonds and allows us to reach higher conversion than for systems in volumic equilibrium. Therefore, the higher the light intensity, the higher the polymerization rate and the bigger the free volume excess is, which leads to higher conversions.

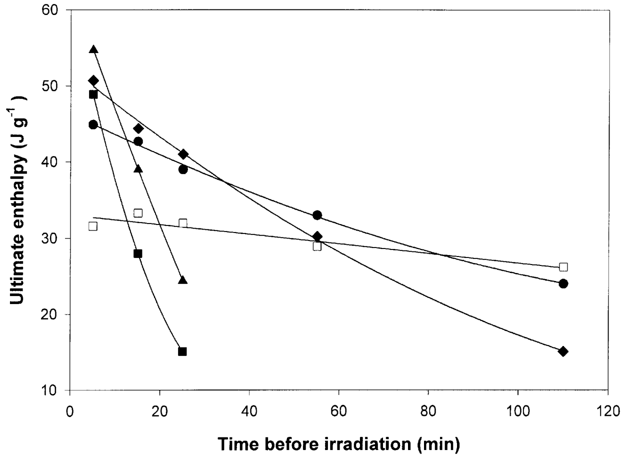


Fig. 5. Ultimate enthalpy vs. time before irradiation at different polymerization temperature: (□) 40°C; (●) 60°C; (◆) 80°C; (▲) 110°C; (■) 130°C.

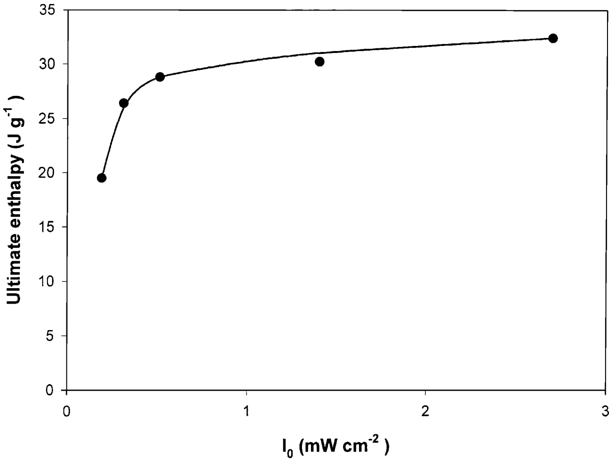


Fig. 6. Ultimate enthalpy vs. light intensity for PMBA2 with 1% (w/w) of Darocur 1173 at 40°C.

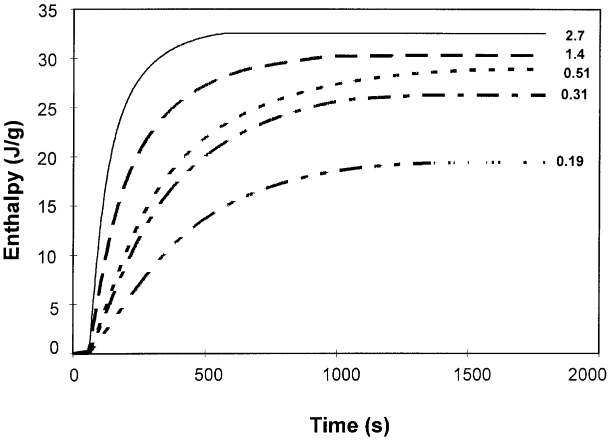


Fig. 7. Enthalpy vs. time at different light intensity for PMBA2 with 1% (w/w) of Darocur 1173 at 40°C.

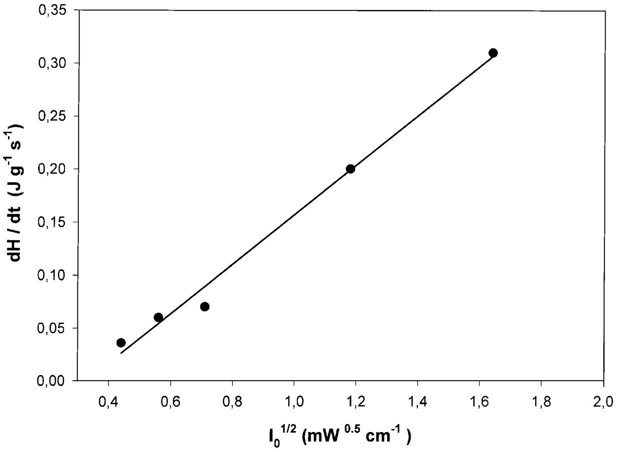


Fig. 8. Initial reaction rate vs. $I_0^{1/2}$ according to classical kinetic equation for PMBA2 with 1% (w/w) of Darocur 1173 at 40°C.

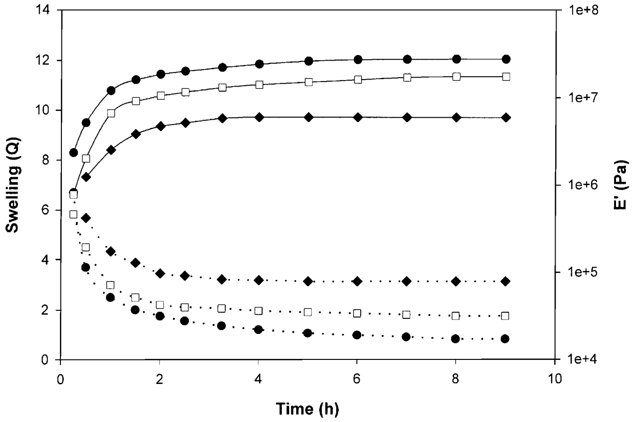


Fig. 9. Swelling (···) and storage modulus E' (—) vs. time for PMBA2 with POB (◆) at 91°C; TBPB (□) at 126°C; DCUP (●) at 136°C.

3.3. Thermal catalyzed crosslinking

Whatever the experimental conditions, the reaction was allowed to proceed for 9 h. Nevertheless, crosslinking materials, insoluble in HTPB solvents, were obtained in less than 30 min, which enabled the measurements of swelling and mechanical properties.

3.3.1. Nature of the thermal initiator

Three thermal initiators were used, POB, TBPB and DCUP, which have different half-life temperatures, respectively, 91, 126 and 136°C. Thermal crosslinking was carried out with PBMA2 in the presence of 0.13 mol kg^{-1} of initiator. The first experiments were carried out at the initiator half-life temperature in order to have the same initial radical concentrations. Indeed, these temperatures correspond to the same value of the dissociation constant k_d and, therefore, to the same initiation rate. In these conditions, one can consider that we observe only the influence of temperature on propagation (k_p), transfer (k_{tr}) and termination (k_t) constants. The reaction was followed by the measurement of the swelling (Q) and storage modulus (E') vs. time

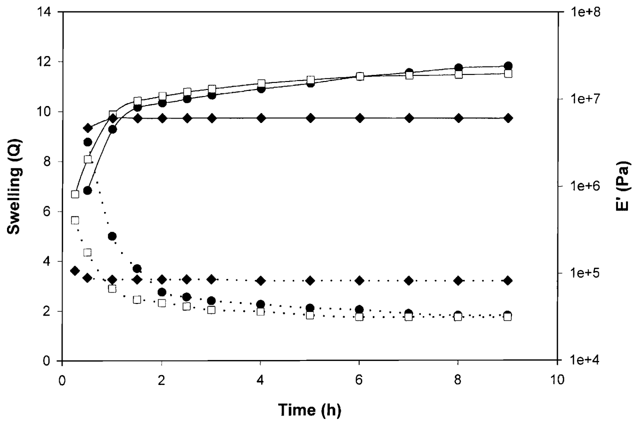


Fig. 10. Swelling (···) and storage modulus E' (—) vs. time for PMBA2 with POB (◆); TBPB (□); DCUP (●) at 126°C.

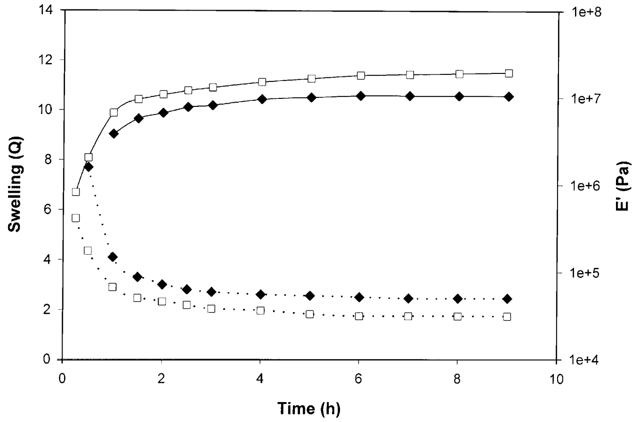


Fig. 11. Swelling (···) and storage modulus E' (—) vs. time for PMBA2 at 126°C with TBPB at different initiator concentration (w/w): (◆) 1%; (□) 3%.

(Fig. 9). The order for the rate and density of crosslinking is POB < TBPB < DCUP. It is well known that the temperature has little influence on k_t. Therefore, the rate increase can be attributed to an increase of k_p, and the increase in crosslinking density to an increase of transfer constant k_{tr} to the polybutadiene double bonds, which increases the number of branching units. This last result is in agreement with the evolution of photocrosslinking enthalpies with temperature as mentioned above.

Similarly, the shift of the maximum of tan δ (respectively, −72.5, −59 and −30°C for POB, TBPB and DCUP) perfectly accounts for the increase in crosslinking density with a broadening of the peak and a decrease of its intensity.

A second series of experiments was carried out at 126°C with the same initiators. In that case, the only difference is the initiation rate. Fig. 10 shows that similar results are obtained with TBPB and DCUP whereas, for POB (35°C above its half-life temperature), the reaction stops rapidly due to its entire disappearance in the first minutes of the reaction.

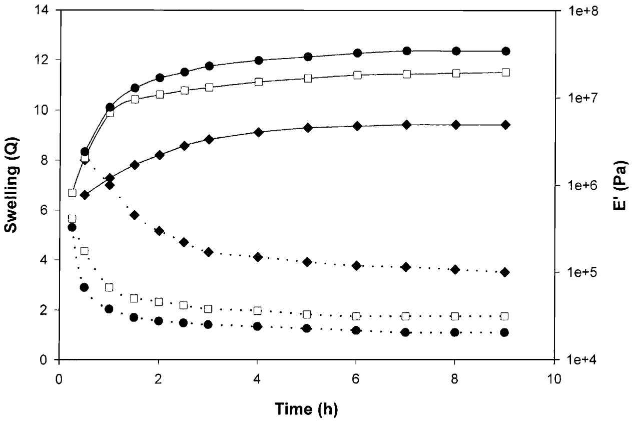


Fig. 12. Swelling (···) and storage modulus E' (—) vs. time for PMBAn with TBPB (3%, w/w) at 126°C and $n = 1.2$ (◆); 2 (□); 2.4 (●).

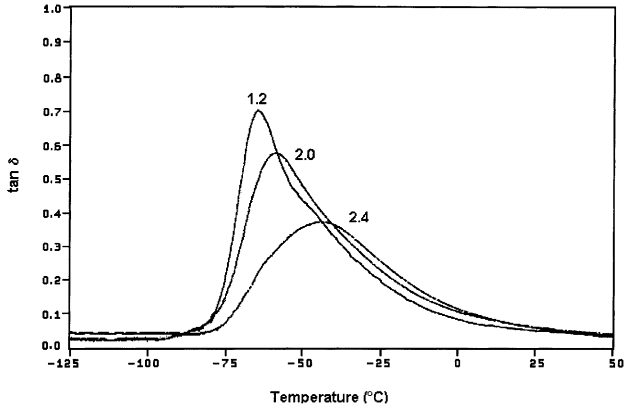


Fig. 13. Evolution of tan δ vs. temperature for PBMAn with $n = 1.2, 2, 2.4$.

3.3.2. *Influence of the initiator concentration*

This study was carried out at 126°C, with PBMA2 and TBPB at 1 and 3% (w/w) respectively, 0.043 and 0.13 mol kg^{-1}. Swelling and storage modulus curves are reported in Fig. 11. The curves are shifted but the shapes are similar. A higher crosslinking rate and density are obtained when the initiator concentration increases. We can also observe an increase of the maximum of tan δ: −64°C for 1% and −59°C for 3%.

3.3.3. *Influence of methacrylate functionality*

Three PBMAn were synthesized ($n = 1.2, 2, 2.4$). Crosslinking was carried out at 126°C with TBPB as an initiator (3%, w/w). The evolutions of Q and E' vs. time (Fig. 12) are similar to those in Fig. 11. The curves of tan δ vs. temperature are reported in Fig. 13. The maxima of tan δ for $n = 1.2$, 2, 2.4 are, respectively, −64, −59 and −43°C. It is noteworthy that we obtained exactly the same curves for $n = 1.2$ (3%) and $n = 2$ (1%). Thus, there is a direct relation between n and the initiator concentration. Moreover, there is a linear relation between n, log E' and Q (Fig. 14) at the end of the reaction (9 h). These results are very practical tools

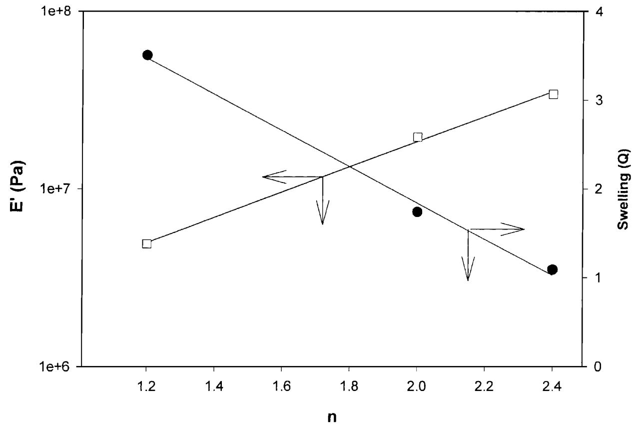


Fig. 14. Linear relationship between storage modulus E', swelling (Q) and the number of methacrylate functions per polymer chain n.

for the design of materials with a priori selected mechanical properties.

4. Conclusion

The introduction of methacrylate moieties onto low molar mass polybutadiene makes it possible to obtain photocrosslinked material in about 500 s. Crosslinking density depends on temperature and light intensity. By thermal catalysis, crosslinked material can be obtained with T_g (connected to tan δ) ranging from -72.5 to -30°C and E' at the rubbery plateau in the 5–40 MPa range depending on our experimental conditions (i.e. nature and concentration of initiator, temperature, number of methacrylate functions per polymer chain). Moreover, it is demonstrated that polybutadiene double bonds participate in the reaction. This study therefore shows that, by this type of modification, it is possible to modulate and adjust the mechanical properties of low molar mass polybutadiene networks by using various experimental conditions.

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