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Pierre Berto, Axel Pointet, Cédric Le Coz, Stéphane Grelier, Frédéric Peruch. Recyclable Telechelic Cross-Linked Polybutadiene Based on Reversible Diels–Alder Chemistry. *Macromolecules*, 2018, 51 (3), pp.651-659. 10.1021/acs.macromol.7b02220 . hal-01717789

**HAL Id: hal-01717789**

**<https://hal.science/hal-01717789v1>**

Submitted on 24 Sep 2020

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# **Recyclable telechelic cross-linked polybutadiene based on reversible Diels-Alder chemistry.**

Pierre Berto, Axel Pointet, Cédric Le Coz, Stéphane Grelier, Frédéric Peruch

Univ. Bordeaux, CNRS, Bordeaux INP/ENSCBP

Laboratoire de Chimie des Polymères Organiques, UMR 5629, 16 avenue Pey-Berland, F-33607 Pessac Cedex, France

E-mail: peruch@enscbp.fr

## **Abstract:**

Chain-end modification of low molar mass polybutadienes allowed the formation of thermo-reversible networks based on the Diels-Alder chemistry. Furan telechelic polybutadienes with various chain length were first synthesized. Addition of a bis-maleimide (BM) compound to the liquid polymer led to the formation of elastomeric networks. Properties of this material were highly affected by the chain length of the polymer precursor and the cross-linking density, monitored by changing the quantity of the BM compound. Finally, the capacity of recycling of the rubber was shown by remolding the used material over 5 cycles without mechanical properties loss.

## INTRODUCTION

In 2016, the total rubber production was over 26 millions of ton. Natural and synthetic rubbers (polyisoprene, polyethylene/propylene/diene (EPDM), polybutadiene (PB), etc) are widely used in many areas such as automotive, sport equipment, building materials or tires.<sup>1-3</sup> Their elasticity, strength, creep resistance, chemical resistance and stiffness are the main properties expected for these materials. To maintain these properties over time, the rubber has to be chemically cross-linked. Sulfur vulcanization and peroxide curing are currently the main methods used in industry. However, the produced networks are irreversibly cross-linked. Consequently, the material is difficult to recycle and a huge quantity of waste is produced.<sup>4-6</sup> Recently, new routes to synthesize recyclable materials through reversible cross-linking were investigated. Reversible covalent and non-covalent linkers like boronic esters, disulfide linkages, imine bond, H-bonding, metal coordination or ionic interactions were investigated.<sup>3,6-13</sup> The Diels-Alder (DA) reaction was the most studied to create reversible network for various polymers like polyurethane, polycaprolactones, polyepoxides or more recently polybutadiene.<sup>14-19</sup> The most investigated DA reaction uses furan/maleimide coupling, yielding an adduct that can dissociate under thermal treatment with no side reaction in pretty mild conditions.<sup>20</sup>

The thiol-ene reaction was generally employed to graft furan group along the polybutadiene backbone onto the 1,2 units.<sup>2,16</sup> Bismaleimide (BM) was then added to form a thermosensitive dynamic network. However, with thiol-ene chemistry, side reactions like cyclization or uncontrolled cross-linking can occur.<sup>21-28</sup> Moreover, the molar mass of the polybutadiene used in these studies was very high ( $M_w$  between 135 and 200 kg.mol<sup>-1</sup>), which thus increase the solubilization time and molding can be difficult due to high viscosity.

Recently, we developed a new route in order to by-pass these difficulties.<sup>29</sup> Low molar mass furan telechelic 1,4-cis polydienes (polybutadiene or polyisoprene) were first synthesized.

The addition of a BM compound to the liquid furan telechelic polydienes led to the formation of a reversible network based on the DA chemistry. Recyclability of the materials was shown over 2 cycles of remolding.

In this study, the effect of the chain length of PB precursors was studied by varying the molar mass from 5000 to 19000 g.mol<sup>-1</sup>. The influence of the cross-linking density was also investigated by changing the ratio furan/maleimide. Finally, the mechanical properties were evaluated after 5 cycles of remolding

## EXPERIMENTAL SECTION

### Materials

Cis-1,4-polybutadiene (**1**, *cis*-1,4-PB, 98% *cis*-1,4,  $M_n = 200$  kg.mol<sup>-1</sup>,  $\bar{D} = 2.8$ ) was purchased from Scientific Polymer Products, Inc. 3-Chloroperoxybenzoic acid (mCPBA, 70-75%, Acros), periodic acid (H<sub>5</sub>IO<sub>6</sub>, ≥ 99%, Aldrich), acetic acid (99%, Aldrich), sodium triacetoxymborohydride (NaBH(OAc)<sub>3</sub>, 97%, Aldrich), diethanolamine (DEA, 99%, Alfa Aesar), furfuryl isocyanate (Furan-NCO, 97%, Aldrich), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (Bismaleimide, 95%, Alfa Aesar), celite 545 (VWR), dibutyltin dilaurate (DBTDL, 95%, TCI) were used without further purification. Tetrahydrofuran (THF) and dichloromethane (DCM) were dried on alumina column. Chloroform (CHCl<sub>3</sub>), methanol and diethyl ether (reagent grade, Aldrich) were used as received.

### Polybutadiene chemical modifications

#### *Synthesis of aldehyde telechelic cis-1,4-polybutadiene (2, Ald-xk-PB-Ald)*

High molar mass *cis*-1,4-polybutadiene **1** was first epoxidized with a known molar ratio of mCPBA/butadiene (BD) units, followed by subsequent one-pot cleavage of oxirane units by adding periodic acid as described in the literature.<sup>30-32</sup> A typical reaction procedure is as follows. mCPBA (300 mg, 1.25 mmol) dissolved in 10 mL of THF was added dropwise to a

solution of cis-1,4-polybutadiene (3.22 g, 59.6 mmol of BD units) in 80 mL of THF at 0°C. After 2h of reaction at room temperature, periodic acid (1.05 eq. compared to mCPBA, 342 mg, 1.31 mmol) dissolved in 10 mL of THF were added dropwise and stirred during 2 h at room temperature. The solvent was then removed under reduced pressure and the crude product was dissolved in diethyl ether before filtration on celite to remove insoluble iodic acid. The filtrate was then concentrated before washing 2 times with saturated solution (30 mL of each) of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, NaHCO<sub>3</sub> and distilled water. Finally, the organic layer was dried with MgSO<sub>4</sub>, filtered on celite and the solvent was evaporated to dryness yielding a yellow liquid **2**.  $M_n$  NMR = 5 300 g.mol<sup>-1</sup>,  $M_n$  SEC = 5 750 g.mol<sup>-1</sup>,  $\bar{D}$  = 1.9, yield: 90 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): (δ, ppm) 9.77 (t, 2x1H, -CH<sub>2</sub>-H(C=O)), 5.38 (m, 194H, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-), 2.49 (t, 4H, -CH<sub>2</sub>-H-(C=O)), 2.38 (t, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-H-(C=O)), 2.09 (s, 388H, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-).

*Synthesis of tetrahydroxyl telechelic cis-1,4-polybutadiene (3, (OH)<sub>2</sub>-xk-PB-(OH)<sub>2</sub>)*

Ald-xk-PB-Ald **2** (1.71 g, 0.68 mmol aldehyde) dissolved in 8.5 mL of dry THF and 3 eq of DEA (21.5 mg, 2.04 mmol) were mixed and stirred at 40°C during 2h under inert atmosphere. 3 eq of NaBH(OAc)<sub>3</sub> (433 mg, 2.04 mmol) and 1.2 eq of acetic acid (47 μL, 0.82 mmol) were added to the solution and stirred at 40°C overnight under inert atmosphere. After concentration, the product was purified by precipitation/dissolution in methanol/DCM several times and dried under vacuum to obtain a colorless liquid **3**. Yield = 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): (δ, ppm) 5.38 (m, 194H, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-), 3.72 (t, 8.0H, -CH<sub>2</sub>-CH<sub>2</sub>-OH), 2.81 (t, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-OH), 2.70 (t, 4H, -CH<sub>2</sub>-N(-CH<sub>2</sub>)<sub>2</sub>-), 2.09 (s, 388H, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-).

*Synthesis of tetra furan telechelic cis-1,4-polybutadiene (4, Fur<sub>2</sub>-xk-PB-Fur<sub>2</sub>)*

(OH)<sub>2</sub>-xk-PB-(OH)<sub>2</sub> **3** (1.37 g, 1.09 mmol hydroxyl groups) was dissolved in 6.5 mL of dry DCM. 1.5 eq of furan-NCO (176 μL, 1.64 mmol) and 5% mol of DBTDL (32 μL, 55 μmol)

were added to the solution and stirred at 40°C during 6h under inert atmosphere. After concentration, the product was purified by precipitation/dissolution in methanol/DCM several times and dried under vacuum to obtain a brown liquid **4**. Yield = 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): (δ, ppm) 7.34 (m, 4H, -CH=CH-O- furan), 6.29 (m, 4H, -CH=CH-O- furan), 6.21 (m, 4H, C=CH-CH=CH-O- furan), 5.38 (m, 194H, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-), 4.32 (d, 8H, furan-CH<sub>2</sub>-NH-), 4.14 (s, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.76 (s, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-O-), 2.54 (s, 4H, -CH<sub>2</sub>-N(-CH<sub>2</sub>)<sub>2</sub>-), 2.09 (s, 388H, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-).

### **Preparation of Polybutadiene network (Net<sub>RMF-xk-PB-n</sub>)**

The notation for the synthesized networks is Net<sub>RMF-xk-PB-n</sub> with R<sub>MF</sub> the molar ratio Maleimide/Furan, xk the molar mass of the PB precursor and n the cycle of molding. For example, Net<sub>1-5k-PB-1</sub> was obtained with 1 g of Fur<sub>2</sub>-5k-PB-Fur<sub>2</sub> (1g, DP=93, 0.80 mmol of furan) dissolved in 1 mL of CHCl<sub>3</sub> and mixed with 1 eq of maleimide groups (0.5 eq of bis-maleimide, 150 mg, 0.40 mmol) dissolved in 0.5 mL of CHCl<sub>3</sub>. The mixture was heated 10 min at 60°C in a closed glassware and deposited in a Teflon mold. The solvent was let evaporated for 24h at room temperature and the sample was completely dried under vacuum for an extra 24h to obtain a transparent film without air bubble.

### **Swelling and soluble fraction of the network**

Dried networks (initial mass,  $m_i$ , approximately 40 mg) were put into chloroform at room temperature for 24h. Chloroform was changed and samples were immersed again for 48h at room temperature. Swollen sample were weighted (swollen mass,  $m_s$ ) and dried under vacuum until constant mass (dry mass,  $m_d$ ). Each sample was analyzed in triplicate. Swelling degree and soluble fraction were determined by Eqs. 1 and 2 respectively.

$$\text{Swelling degree} = (m_s - m_d)/m_d \times 100 (\%) \quad (\text{eqs. 1})$$

$$\text{Soluble fraction} = (m_i - m_d)/m_d \times 100 (\%) \quad (\text{eqs. 2})$$

### **Remolding of the films**

All the strips used for DMA and tensile tests analyses were put into a closed glassware (1 g in 1.5 mL of  $\text{CHCl}_3$ ) and heated at  $120^\circ\text{C}$  for 10 minutes. After 5 minutes at room temperature, the liquid solution was put in a Teflon mold before waiting for 24h for solvent evaporation and was further dried under vacuum for 24h to obtain a transparent film without air bubble.

### **Characterization**

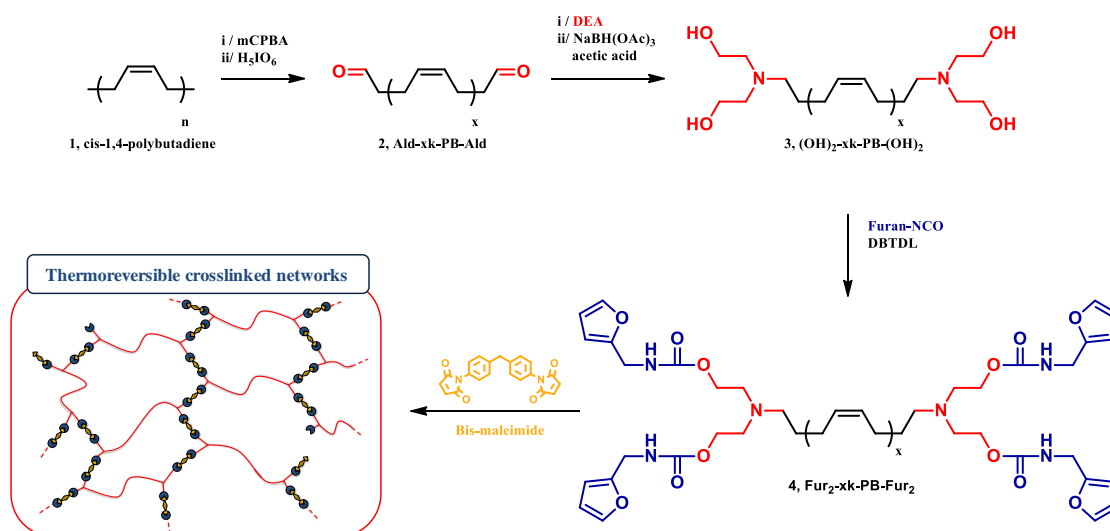
Liquid-state  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz and 100 MHz respectively in appropriate deuterated solvents. Polymer molar masses were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the eluent (THF with 250 ppm of Butylated hydroxytoluene as inhibitor, Aldrich). Measurements were performed on a Waters pump equipped with Waters RI detector and Wyatt Light Scattering detector. The separation is achieved on three Tosoh TSK gel columns ( $300 \times 7.8$  mm) G5000 HXL, G6000 HXL and a Multipore HXL with an exclusion limits from 500 to 40 000 000  $\text{g}\cdot\text{mol}^{-1}$ , at a flow rate of 1 mL/min. The injected volume was  $100\mu\text{L}$ . Columns' temperature was  $40^\circ\text{C}$ . Molar masses were evaluated with polyisoprene standards calibration. Data were processed with Astra software from Wyatt. Thermo-gravimetric measurements (TGA) of polybutadiene samples ( $\approx 12$  mg) were performed on a TA Instruments Q500 under nitrogen atmosphere with platinum pans from room temperature to  $600^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . Differential scanning calorimetry (DSC) measurements of polybutadiene samples ( $\approx 10$  mg) were performed using a DSC Q100  $\text{LN}_2$  apparatus from TA Instruments with a heating and cooling ramp of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . The samples were first heated from  $25^\circ\text{C}$  to  $80^\circ\text{C}$  and held at  $80^\circ\text{C}$  for 10 min in order to eliminate the residual solvent, then cooled to  $-150^\circ\text{C}$  and finally heated to  $200^\circ\text{C}$ . The analyses were carried out in a helium atmosphere with aluminum pans. Tensile tests were performed on a MTS Qtest 25 Elite controller (France). The initial grip separation was set at 20 mm and the crosshead speed at 50 mm/min. The results were obtained from at least 4

replicates for each sample. A TA Instrument RSA3 was used to study dynamic mechanical properties of polybutadiene samples. The samples were analyzed under nitrogen atmosphere from - 105 °C to 200 °C at a heating rate of 4 °C.min<sup>-1</sup>. The measurements were performed in tensile mode at a frequency of 1 Hz, an initial static force of 0.1 N, and strain sweep of 0.3 %. Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 instrument (4 cm<sup>-1</sup> resolution, 32 scans, DLaTGS MIR) equipped with a Pike GladiATR plate (diamond crystal) for attenuated total reflectance (ATR) at room temperature.

## RESULTS AND DISCUSSION

### Preparation of furan-functionalized telechelic polybutadiene

In order to synthesize furan-functionalized telechelic polymers (Scheme 1) with different chain lengths, aldehyde telechelic polybutadiene **2** (Ald-xk-PB-Ald) were first prepared by the controlled degradation of high molar mass *cis*-1,4-PB **1** by varying the epoxidation rate with mCPBA followed by the oxidative scission of epoxides with periodic acid.<sup>30–32</sup>



*Scheme 1 : General synthetic route for the preparation of furan-telechelic polybutadienes.*

Results are summarized in Table 1. Polybutadienes with molar masses ranging from 5 000 to 19 000 g.mol<sup>-1</sup> were targeted. The aldehyde functions can be easily observed on <sup>1</sup>H NMR



spectra with a signal at  $\delta = 9.77$  ppm allowing to evaluate the molar masses (Figure 1, spectrum a).

Table 1. Synthesis of polybutadienes with various molar masses

Epoxidation rate (%)	$M_{n,NMR}^a)$ (g.mol <sup>-1</sup> )	$DP_{NMR}^b)$	$M_{n,SEC}^c)$ (g.mol <sup>-1</sup> )	$\bar{D}^d)$	f (-OH) <sup>e)</sup>	f (-furan) <sup>f)</sup>
2.10	5 300	97	5 750	1.9	3.9	4.0
1.20	8 800	160	12 000	1.6	4.0	4.0
0.91	13 300	246	15 800	1.6	4.0	3.9
0.63	16 000	296	20 000	1.8	4.0	3.9
0.53	19 000	352	23 000	1.7	3.9	4.0

<sup>a)</sup> Molar mass of Ald-xk-PB-Ald calculated by <sup>1</sup>H NMR using following formula :  $M_{n,NMR} = [54 \times I(5.38) / I(9.77)] + 100$  ; <sup>b)</sup> Degree of polymerization (DP) calculated by using the following fomula  $DP_{NMR} = I(5.38) / I(9.77) = (M_{n,NMR} - 100) / 54$  ; <sup>c)</sup> molar masses of Ald-xk-PB-Ald measured by SEC calibrated with polyisoprene standards; <sup>d)</sup> dispersity measured by SEC; <sup>e)</sup> hydroxyl group functionality calculated by <sup>1</sup>H NMR using the following formula: f (-OH) =  $I(3.72)$  when  $I(5.38) = DP_{NMR}$  ; <sup>f)</sup> furan group functionality calculated by <sup>1</sup>H NMR using the following formula: f (-furan) =  $I(4.12)$  when  $I(5.38) = DP_{NMR}$ .

Hydroxyl telechelic polybutadienes **3** ((OH)<sub>2</sub>-xk-PB-(OH)<sub>2</sub>) were prepared by reductive amination of aldehyde groups of **2** with an excess of diethanolamine (DEA) in the presence of NaBH(OAc)<sub>3</sub> to end up with an hydroxyl functionality of 4.<sup>33,34</sup> The <sup>1</sup>H NMR analysis of the product showed indeed the complete disappearance of the aldehyde signal ( $\delta = 9.77$  ppm) and the appearance of a new signal corresponding to the N-CH<sub>2</sub>- at 2.7 ppm indicating a total conversion into amine (Figure 1, spectrum b).

Furan-functionalized telechelic polybutadienes **4** (Fur<sub>2</sub>-xk-PB-Fur<sub>2</sub>) were obtained from (OH)<sub>2</sub>-xk-PB-(OH)<sub>2</sub> by reacting this latter with furan-NCO in the presence of dibutyltin dilaurate at 40 °C. The <sup>1</sup>H NMR of the product showed all the expected signals corresponding to Fur<sub>2</sub>-xk-PB-Fur<sub>2</sub>. The shift of the HO-CH<sub>2</sub>- signal from 3.72 ppm to 4.12 ppm (Figure 1, spectrum c) and the appearance of the furan signal -CH<sub>2</sub>-NCO at 4.31 ppm allowed confirming the full conversion of hydroxyl groups into urethane functions. The calculated furan group functionality is very close to 4 as shown in Table 1.

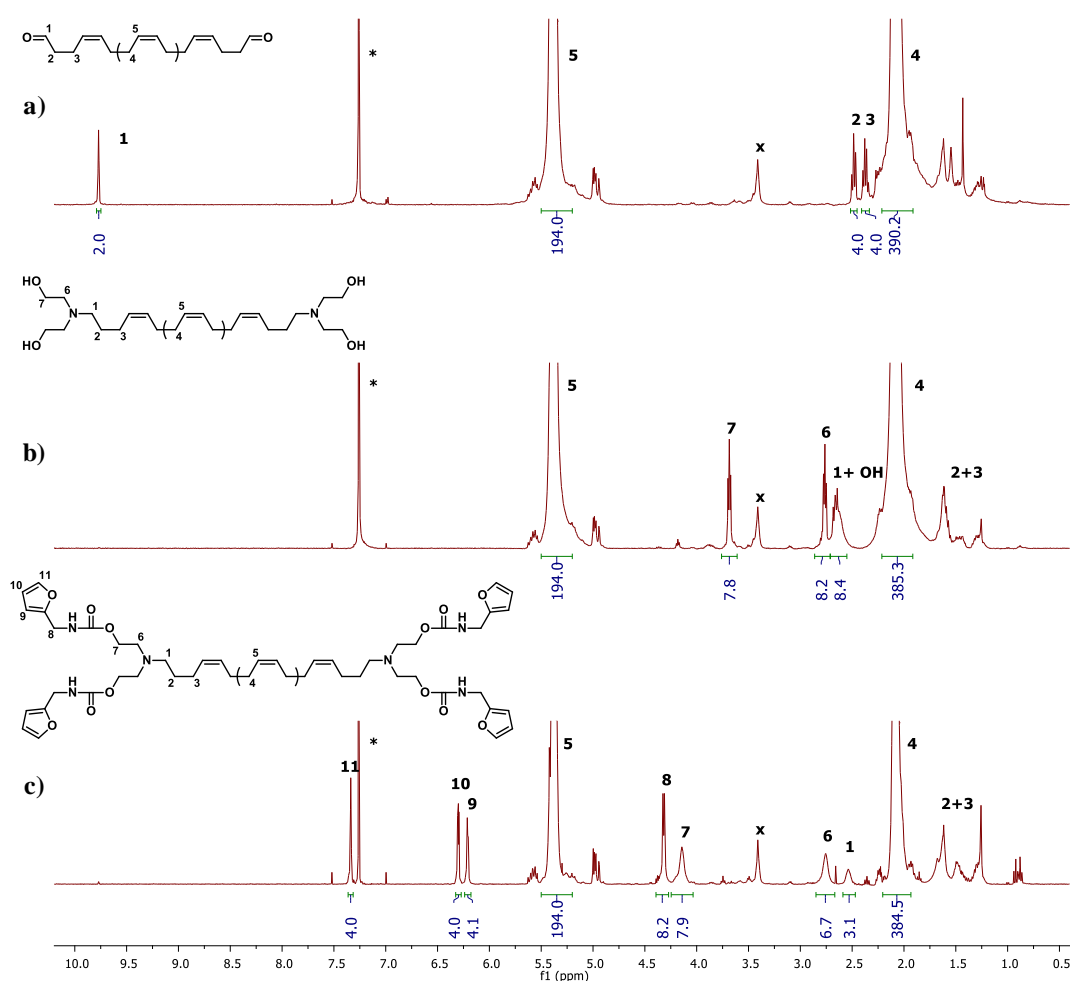


Figure 1. <sup>1</sup>H NMR spectra for the 5 000 g.mol<sup>-1</sup> series in CDCl<sub>3</sub> (\*) (A) aldehyde telechelic polybutadiene, (B) hydroxyl telechelic polybutadiene, (C) furan telechelic polybutadiene.

SEC analysis of all the samples confirmed the molar masses calculated by NMR. Besides, comparison of the different chemical intermediates for each molar mass series confirm that no side reactions occurred during the chain-end modification steps as all chromatograms are perfectly superimposed (see for example, elution profiles of the 9 000 g.mol<sup>-1</sup> intermediates series on Figure S1).

### Formation of polybutadiene networks and recycling

Films were prepared by mixing Fur<sub>2</sub>-xk-PB-Fur<sub>2</sub> samples dissolved in CHCl<sub>3</sub> with a stoichiometric quantity of bismaleimide. After evaporation of the solvent and drying under vacuum, transparent film without air bubble were obtained (Figure 2). Strips (5 mm width, 25 mm length and 0.4-0.7 mm thick) were prepared from the film for the different mechanical and thermo mechanical analysis. Reversibility of the networks was then investigated. Figure 2 shows the efficient redissolution of used strips when heated in chloroform at 120°C in a closed glassware and the formation of a new film after drying.

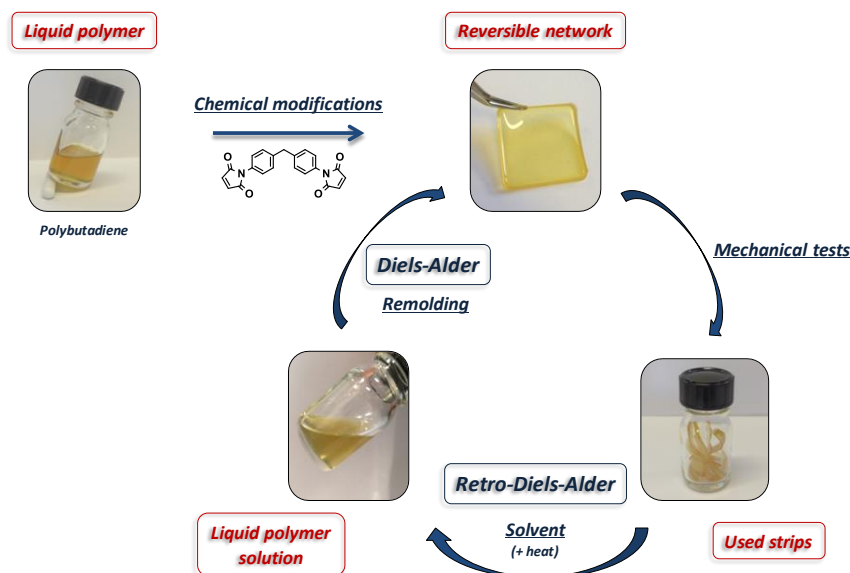


Figure 2. Formation and remolding process for the polybutadiene film preparation.

The networks were further characterized by measuring their swelling degree and soluble fraction. The networks constituted by the smallest chain (5 kg.mol<sup>-1</sup>, Net<sub>1</sub>-5k-PB) exhibit a

very low soluble fraction of 3 % associated with a swelling degree of 470 % (Figure 3). The swelling degree and the soluble fraction both increase with the chain length of the precursor and goes up to 1300 % and 9 % respectively for Net<sub>1</sub>-19k-PB. Increasing the chain length between the cross-linkers allows a higher mobility of the chain and therefore a better swelling. Surprisingly, a similar swelling degree was observed for the network obtained from precursors with molar masses of 19 kg.mol<sup>-1</sup> and 16 kg.mol<sup>-1</sup>. This could be attributed to the entanglement of the polymeric chains. Indeed, when the network is formed with precursors of 5 kg.mol<sup>-1</sup>, entanglement is negligible compared to the cross-linking density. However, when  $M_n$  of the precursor is over 16 kg.mol<sup>-1</sup>, entanglement could limit the swelling of the network. Finally, in all cases, the soluble fraction remains relatively low and confirms the good efficiency of the cross-linking.

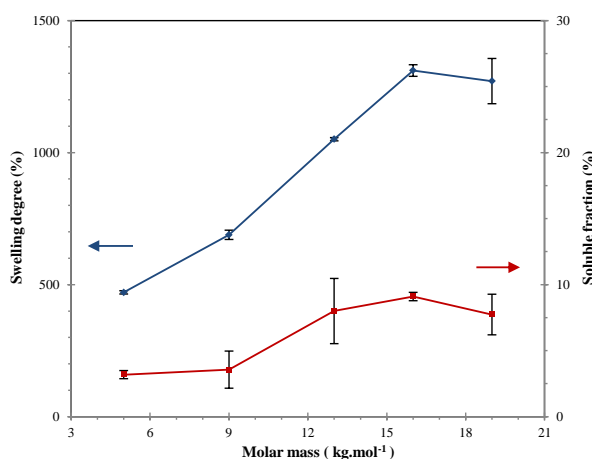


Figure 3 : Chain length effect on the swelling degree and soluble fraction of the PB networks.

### Thermo-mechanical analyses of the networks

DSC analyses revealed a similar  $T_g$  value around -103 °C for each sample regardless the chain length and the chain-end modification of the polybutadiene (Figure 4a and b). The different DSC curves for the Net<sub>1</sub>-xk-PB networks were shown on Figure 4a. In all cases, two endothermic peaks corresponding to the *retro*-Diels-Alder (*rDA*) at 110 and 140 °C can be observed due to the formation of the endo- and the exo-adducts during DA reaction.<sup>15</sup> The

exo-adduct is thermally more stable than the endo and its reversibility occurs at higher temperature, which explains these two peaks. Comparison of the  $9\,000\text{ g.mol}^{-1}$  intermediates series confirm that these peaks are associated to the *rDA*, indeed they appear only when the polybutadiene is cross-linked (Net<sub>1</sub>-9k-PB, Figure 4b).

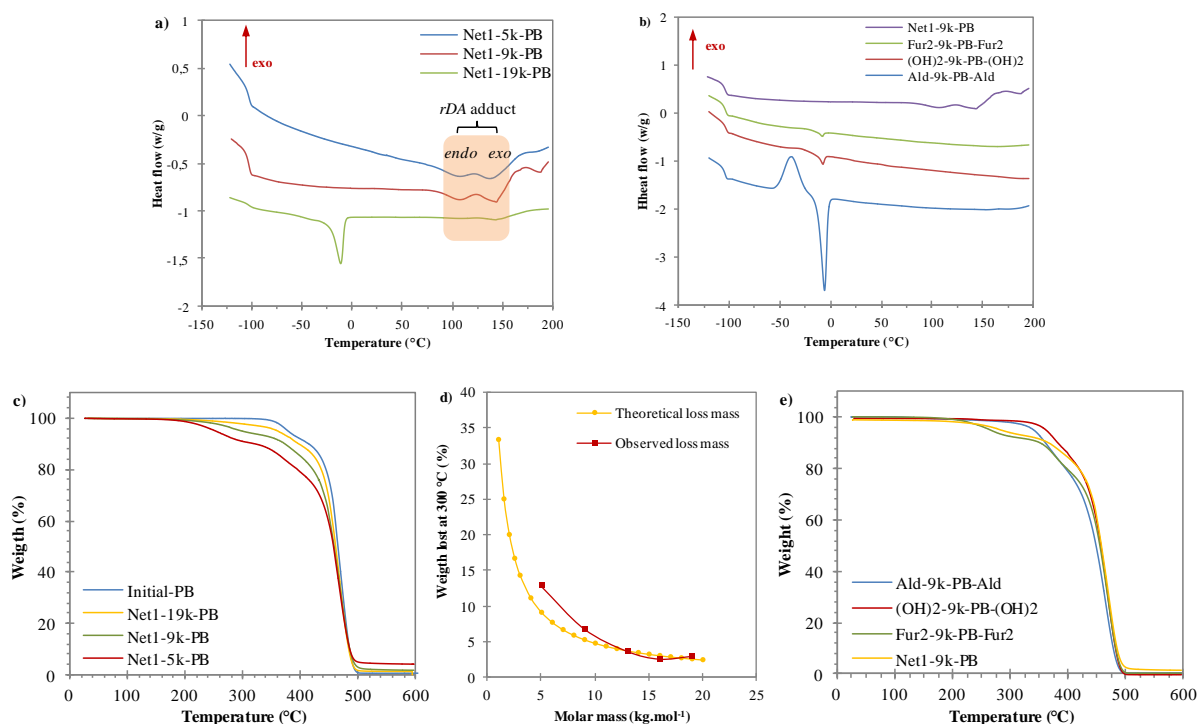


Figure 4. a) Normalized DSC curves of cross-linked PB. b) Normalized DSC curves of the  $9\,000\text{ g.mol}^{-1}$  modification. c) TGA curves comparison of the Net<sub>1</sub>-*xk*-PB series. d) Theoretical weight loss vs observed weight loss of the polymer at 300°C. e) TGA curves comparison of the  $9\,000\text{ g.mol}^{-1}$  modification series.

Crystallization and fusion of the *cis*-1,4-polybutadiene are known to occur in the range  $-40\text{ }^{\circ}\text{C}$  /  $-10\text{ }^{\circ}\text{C}$ .<sup>35,36</sup> In this study, it can be observed that the aldehyde telechelic polybutadiene with a chain length of  $9\,000\text{ g.mol}^{-1}$  was able to crystallize like the hydroxyl and furan homologues (Figure 4b). However, the intensity of the crystallization and melting peaks located at  $-40$  and  $-8\text{ }^{\circ}\text{C}$  respectively decreases significantly at each step of the PB modifications until a complete disappearance for the network. An increase of the steric

hindrance of the chain-end could prevent the polymer to crystallize leading to a decrease of the melting peak intensity. As shown on Figure 4a, only the crosslinked elastomer with a PB precursor of 19 000 g.mol<sup>-1</sup> was able to crystallize. This phenomenon could be attributed to the incapacity for the shorter chain to crystallize due to the lack of mobility induced by the cross-linking.

All the networks were further analyzed by TGA. A higher weight loss is observed at 300 °C for lower chain length. The initial-PB exhibited a weight loss of 0.5 % whereas for the Net<sub>1</sub>-19k, 9k and 5k-PB, the weight loss is equal to 3.5, 6.8 and 12.9 % respectively (Figure 4c). This could be attributed to the degradation of the furan rings. Indeed, the shortest chains have a butadiene units/furan ratio lower than the highest ones. Consequently, a higher weight loss was observed in agreement with a higher furan mass fraction. Comparison of the theoretical weight loss with experimental of the furan loss at 300 °C in function of the chain length is in good agreement with this hypothesis (Figure 4d, equation S1). To further confirm the furan moieties degradation, curves of 9 000 g.mol<sup>-1</sup> intermediate series were compared and the weight loss only appeared for Fur<sub>2</sub>-9k-PB-Fur<sub>2</sub> and Net<sub>1</sub>-9k-PB with an equivalent weight loss (Figure 4e).<sup>37-39</sup>

DMA analysis was further performed in tensile mode in order to evaluate the properties of the Net<sub>1</sub>-xk-PB (Figure 5a and b). Solid lines represent the first molding of the polymer whereas the dotted lines correspond to the recycled ones. Moduli of the samples were measured during the heating ramp (4 °C/min) between -105 to 100 °C after a controlled cooling ramp (4 °C/min) from room temperature to -105 °C. Values of the storage modulus (*E'*) clearly show that shorter is the chain length of the precursor, higher is the value of the rubbery plateau (Figure 5a). For instance, the modulus at 25 °C increased from 1.4 MPa to 11.4 MPa for Net<sub>1</sub>-

19k-PB and Net<sub>1</sub>-5k-PB respectively. This can be attributed to the higher cross-linking density of the network formed by the shortest chains. However, the rubbery plateau for the Net<sub>1</sub>-5k-PB reaches its value directly after the T<sub>g</sub> (-93 °C) whereas for all of the other networks, the rubbery plateau is reached at -20 °C (Figure 5a). A secondary plateau near 400 MPa is observed until -20 °C for the networks with molar masses higher than 9 000 g.mol<sup>-1</sup>. This could be associated to the crystallization and fusion of the chains. Indeed, the PB can crystallize as shown previously by DSC (Figure 4a and b). At higher temperature, all curves indicate a loss of the elastic properties of the network at 70-80 °C. This is again due to the rDA reaction. Indeed, even if in the literature it is reported that rDA started to occur at 90-110 °C depending on the system, the loss of these properties at 70-80°C in DMA analysis is due to the tensile mode which adds an additional strength promoting the rDA at lower temperature as already shown for other polymeric materials.<sup>2,14,16,40</sup>

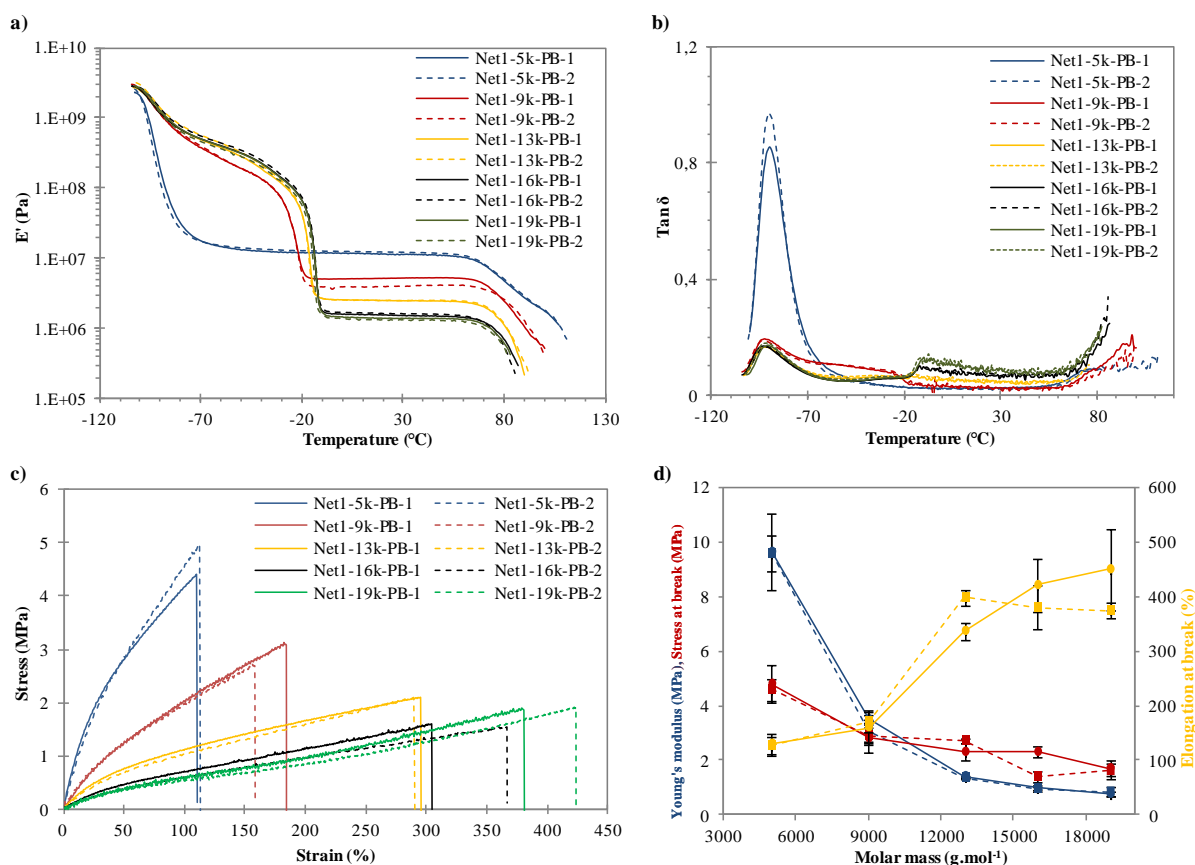


Figure 5. DMA analyses of the cross-linked PB. a) Effect of the chain length on the rubbery plateau ( $E'$ ). b) Effect of the chain length on the loss factor ( $\delta$ ). c) Tensile test curves of the  $Net_1-xk-PB_x$  (first molding in solid lines, second molding in dotted lines). d) Young's modulus (blue), stress at break (red) and elongation at break (yellow) of the network obtained by tensile analysis vs the chain length (first molding in solid lines, second molding in dotted lines).

Comparison of the loss factor ( $\tan \delta$ ) curves of the networks allows to distinguish three peaks regardless the chain length (Figure 5b). The first one at -90 °C is associated to the  $T_g$  of the polybutadiene chains, close to the one observed in DSC. A secondary peak, associated to the fusion of the polymer chain around -15°C is observed for network with chain length over 9 kg.mol<sup>-1</sup> (Figure 5b). This is also in good agreement with the DSC analysis (melting of the PB



at -8 °C). The last peak near 80 °C can be attributed to the flowing of the chains due to the *r*DA reaction.

A first set of recyclability experiments were performed. As explained previously, the used strips were re-dissolved to make a new molding. DMA results were reported in dotted line on Figure 5a and b. The second molding did not affect the mechanical properties of the cross-linked materials. Indeed, curves from the first and second molding overlap perfectly showing an excellent recyclability of the elastomer, whatever the chain length of the PB precursor.

Tensile tests were then performed to further study the chain length effect on the mechanical properties. Tensile curves recorded at ambient temperature are represented on Figure 5c (first molding with solid lines and second one with dotted lines). The tensile strength, the Young's modulus and the elongation at break were determined on an average of at least four samples. Results are summarized in Table S1. Mechanical properties were affected by the chain length of the precursor. For example, the Young's modulus went from 9.6 MPa to 0.8 MPa for Net<sub>1</sub>-5k-PB and Net<sub>1</sub>-19k-PB respectively. The stress at break was close to 5 MPa for Net<sub>1</sub>-5k-PB but decreased gradually till 1.7 MPa for Net<sub>1</sub>-19-PB. Finally, elongation went from 120 % for the shortest chains to 450 % for the highest ones. This is in good agreement with DMA analysis. In Figure 5d, it appears that the characteristics of the network do not change much for the highest molar masses as a plateau seem to be reached. Recyclability of the polymer was again tested in tensile analyses (dotted lines) and a very good reproducibility was observed as for DMA.

### **Recyclability investigation**

It was shown that the networks recover their thermo-mechanical properties after 2 cycles of use/remolding. To investigate further the recyclability of the networks, the mechanical properties of the Net<sub>1</sub>-13k-PB were studied over 5 cycles of reprocessing. DMA analyses clearly demonstrated that the value of the elastic plateau  $E'$ , the  $T_g$  and the temperature of

rDA were not affected by the remolding of the material over 5 reprocessing (Figure 6a and b). Tensile tests analyses further confirmed the results obtained by DMA. Whatever the cycle of remolding, the Young's modulus, stress and strain at break were always similar (Figure 6c). All the values are given in Table S2. All of these results showed the excellent reprocessing ability of the polybutadiene networks.

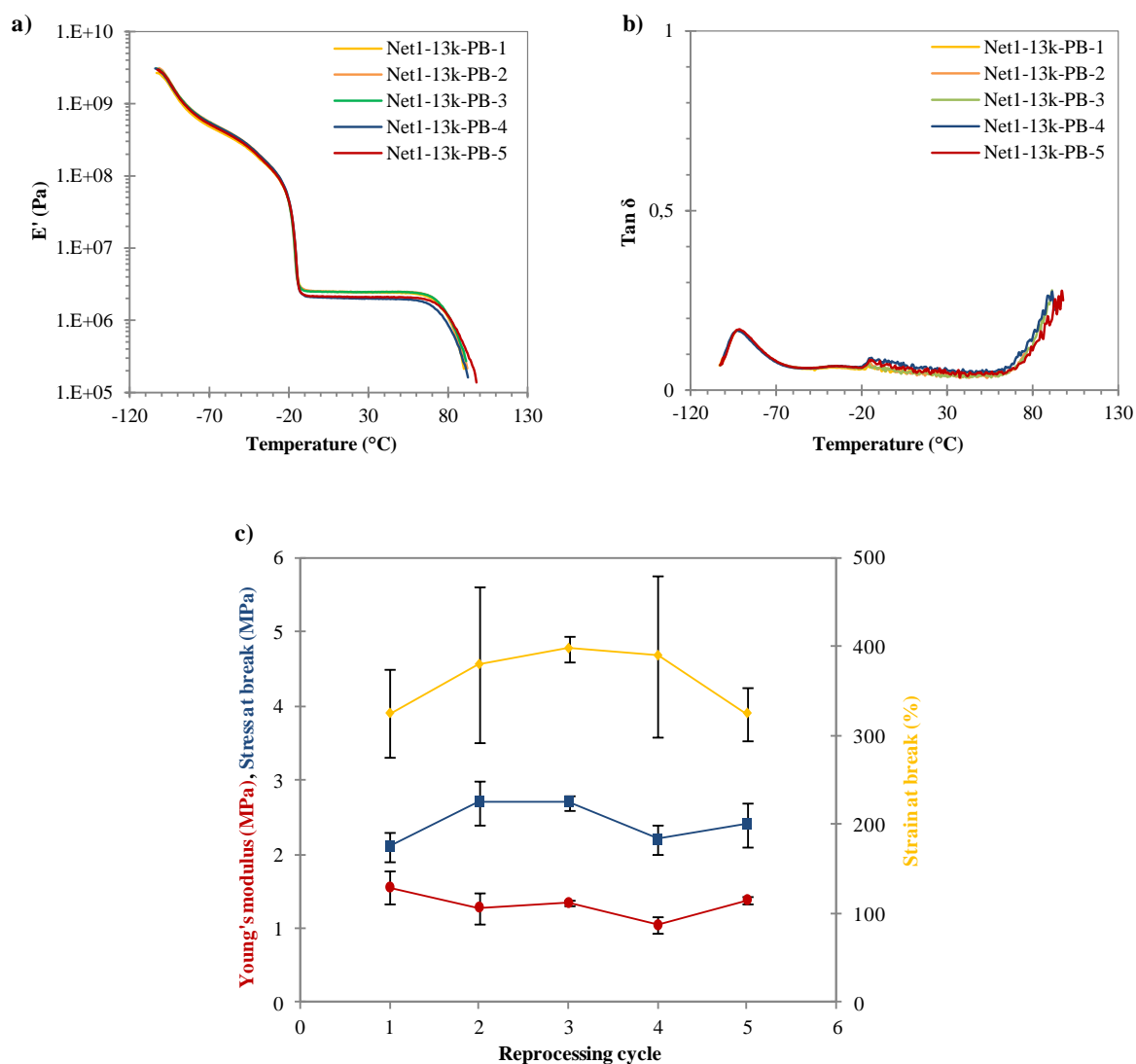


Figure 6. Storage modulus a) and  $\tan \delta$  b) obtained by DMA after 5 reprocessing cycles of the reversible crosslinked Net<sub>1</sub>-13k-PB. c) Effect on the tensile test analysis after 5 reprocessing of Net<sub>1</sub>-13k-PB-n.

### Effect of the cross-linking density on the polybutadiene properties

In the previously synthesized rubbers, the molar ratio between the maleimide and the furan end-groups ( $R_{MF}$ ) was always equal to 1:1. This ratio was then varied ( $R_{MF} = 1.0, 0.75$  and  $0.50$ ). Swelling properties of the  $9\ 000\ \text{g}\cdot\text{mol}^{-1}$  series were first analyzed (Figure 7). It can be seen that by decreasing the  $R_{MF}$  from 1 to 0.50, the swelling degree increase from 690 to 1 800 %. This was accompanied by a significant increase of the soluble fraction from 4 % to 28 % when  $R_{MF}$  is equal to 0.50. This phenomenon can be easily explained by the decrease in the cross-linking density: at 0.5 equivalent of BM, the network is statically not cross-linked explaining the high values of swelling and soluble fraction. For comparison, the swelling degree and soluble fraction reached 3 600 % and 55 % for the  $\text{Net}_{0.5}\text{-16k-PB}$ . The higher chain length reduces the chain ends encounter probability, explaining the high value of soluble fraction.

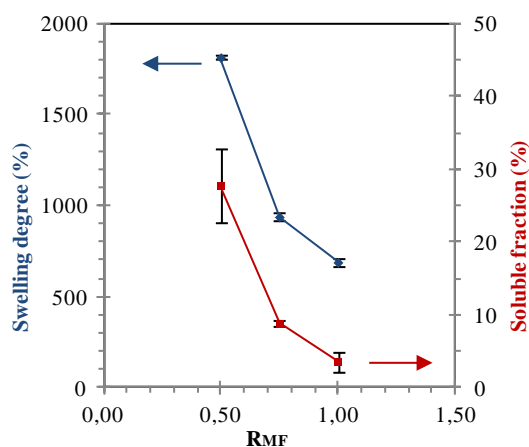
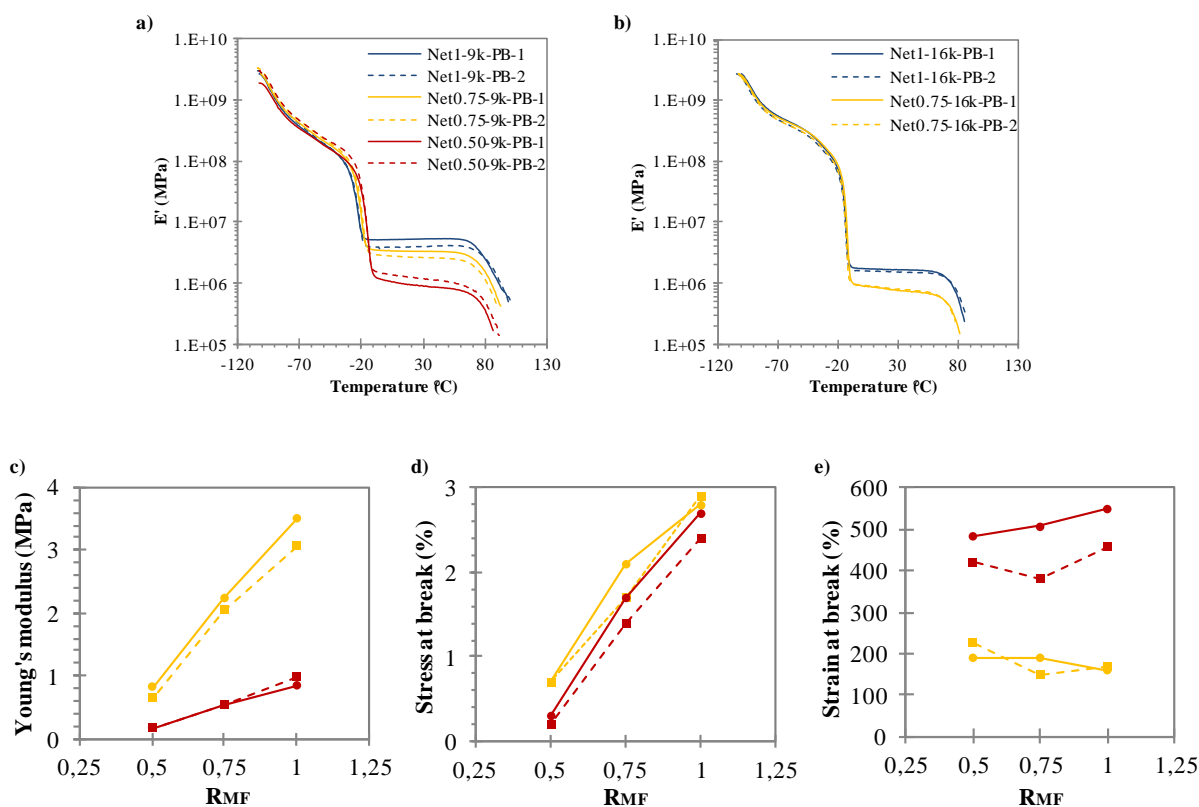


Figure 7 : Cross-linking effect on the swelling behavior and on the soluble fraction of the  $\text{Net}_{R_{MF}}\text{-9k-PB}$ .

DMA analysis was then performed. For the  $\text{Net}_{R_{MF}}\text{-9k-PB}$  series (Figure 8a), the elastic modulus decreased with the  $R_{MF}$  ratio. Indeed, when  $R_{MF}$  is equal to 1 ( $\text{Net}_1\text{-9k-PB}$ ), the elastic modulus is close to 5.2 MPa whereas for the  $\text{Net}_{0.50}\text{-9k-PB}$ ,  $E'$  is equal to 0.8 MPa. This phenomenon can be attributed to the cross-linking density of the network as the chain length stays the same while the maleimide content decreases. The network is not completely

cross-linked and some chain-ends are free. In this condition, the network is softer and the elastic modulus decreases. The same behavior can be observed on the Net<sub>RMF</sub>-16k-PB series (Figure 8b). It was even impossible to analyze the Net<sub>0.50</sub>-16k-PB by DMA. Indeed, the amount of BM was likely too low for the formation of a network, allowing a quick flow of the sample in our conditions.

Tensile tests were also carried out and revealed similar trends. Young's modulus for the Net<sub>RMF</sub>-9k-PB series decreased from 3.1 to 0.6 MPa like the maximum stress at break (2.9 to 0.7 MPa) by decreasing the RMF from 1 to 0.50. Similar results were obtained on the Net<sub>RMF</sub>-16k-PB series (Figure 8c and d). Surprisingly, strain at break was not affected by the cross-linking density and remained almost constant. As mentioned above, elongation at break seems to be only affected by the chain length (Figure 8e). Indeed, strain at break is around 180 % and 400 % for the series of 9 000 and 16 000 g.mol<sup>-1</sup> respectively. These results suggest that the network breaks along the PB backbone and not at the DA adduct level.



*Figure 8. Effect of  $R_{MF}$  and the chain length of the precursor on the network properties (yellow:  $Net_{RMF-9k-PB}$ , red:  $Net_{RMF-16k-PB}$ ). a) DMA analyses of the  $Net_{RMF-9k-PB}$  series; b) DMA analyses of the  $Net_{RMF-16k-PB}$  series. c) Young's modulus, d) Stress at break and e) Strain at break obtained by tensile test analyses.*

## CONCLUSION

Thermoreversible cross-linked polybutadiene networks were prepared from telechelic polybutadienes obtained via simple and efficient chemistry. Commercial high molar mass polybutadiene was first degraded into polymers of smaller molar masses to decrease significantly the viscosity of the rubber in order to facilitate its use. Furan telechelic polybutadienes with a functionality of 4 were then synthesized with various chain lengths. The addition of bismaleimide yielded cross-linked rubber through DA/rDA reaction. Reversibility of the cross-linking was shown by dissolution test in hot chloroform. DMA and tensile tests showed that the materials kept their properties after several remolding cycles, proving the recycling ability of the polybutadiene networks synthesized in this study. The networks can be used in a temperature range of  $-70^{\circ}\text{C}$  to  $80^{\circ}\text{C}$  without properties loss. Thermo-mechanical properties can be tuned by changing the molar mass of the telechelic PB. Higher chain length of the PB precursor reduces the Young and elastic moduli but increases the elongation at break, whereas shorter precursors reduce the elongation at break and increase the Young and elastic moduli. By changing the cross-linking density (the quantity of bis-maleimide), it was also possible to tune the mechanical properties of the polybutadiene network.

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## TOC

### Recyclable telechelic cross-linked polybutadiene based on reversible Diels-Alder chemistry.

Pierre Berto, Axel Pointet, Cédric Le Coz, Stéphane Grelier, Frédéric Peruch

Univ. Bordeaux, CNRS, Bordeaux INP/ENSCBP

Laboratoire de Chimie des Polymères Organiques, UMR 5629, 16 avenue Pey-Berland, F-33607 Pessac Cedex, France

E-mail: [peruch@enscbp.fr](mailto:peruch@enscbp.fr)

