Synthesis and Characterization of Poly-(isoprene-b-carbonate)s Derived from Hydroxytelechelic Polyisoprenes

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ABSTRACT: The purpose was to develop a procedure to synthesize copolymer incorporating flexible polyisoprene blocks and rigid polycarbonate blocks, to obtain thermoplastic elastomer characteristics. The choice was directed towards poly(isoprene-b-carbonate) structures by using a condensation mechanism consisting to create carbonate functions by reaction between an organic dihalide and a diol carried out in presence of potassium carbonate, and by using hydroxytelechelic polyisoprenes as reagents. Polycarbonates of various structures were synthesized, followed by that of the required poly(isoprene-b-carbonate)s. The synthetic procedure thus developed has the advantage to allow a control of the structure and the composition of the copolymer according to the nature and the proportions of the reagents involved. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2843–2858, 2007

Key words: rubber; block copolymers; polycarbonates; polycondensation; thermal properties

INTRODUCTION

Contrary to thermoplastics, elastomers are soft and elastic materials that are used for dynamic applications in a broad range of temperature (from -50 to $150°C$, according to the polymer nature). Their elastic properties result owing to the fact that they are composed of long macromolecular chains, sufficiently flexible, and mobile to adopt a high number of conformations.[1,2] Under stretch, they are forced to line up in the direction in which the rubber is being pulled, and after release, they recover their original size, but on condition to create some chemical bonds between the rubber chains by using a vulcanization procedure. The main disadvantage of vulcanization is to make difficult the recycling of the material.

A new elastomer type was introduced during the last fifties namely thermoplastic elastomers. They are composed of two noncompatible phases at the service temperature: a rigid phase which ensures the reinforcement of the material (thermoplastic), and a soft phase that gives the elastic character to the material (elastomer). Each phase has its own glass temperature T_g, which determines the limit of use temperature: T_g higher than the service temperature for the rigid phase, and lower for the soft phase.

Consequently, they show the characteristics of a vulcanized rubber at the service temperature, i.e., elasticity, and they behave like thermoplastics at the processing temperature, i.e., a softening is observed with the heating above their T_g, which facilitates the processing. Thanks to this ease of processing, to the possibility of recycling, as well as to some specific properties depending on the nature of the two phases, the thermoplastic elastomers not only enter in competition with vulcanized rubbers (particularly in the industry of shoes) and with thermoplastics, but also, with some nonpolymeric materials as metals or inorganic glasses.[3]

Thermoplastic elastomers can be distributed in three families:

- The copolymers composed of soft and rigid blocks,[3,4] in particular the triblock copolymers including polystyrene blocks (SBS, SIS, and SEBS), which roughly represent about 50% of the totality of thermoplastic elastomers.[4] From the structural point of view, the thermoplastic blocks gather to form physical network knots within the polydiene phase (possibly hydrogenated), which prevents the uncontrolled chain flow or slippage.

- The ionic thermoplastic elastomers whose network knots are thermolabile ionic microdomains formed by associations between ionic groups present on nonpolar polymer chains.

- The thermoplastic elastomers that are prepared by physical blending of an elastomer with a

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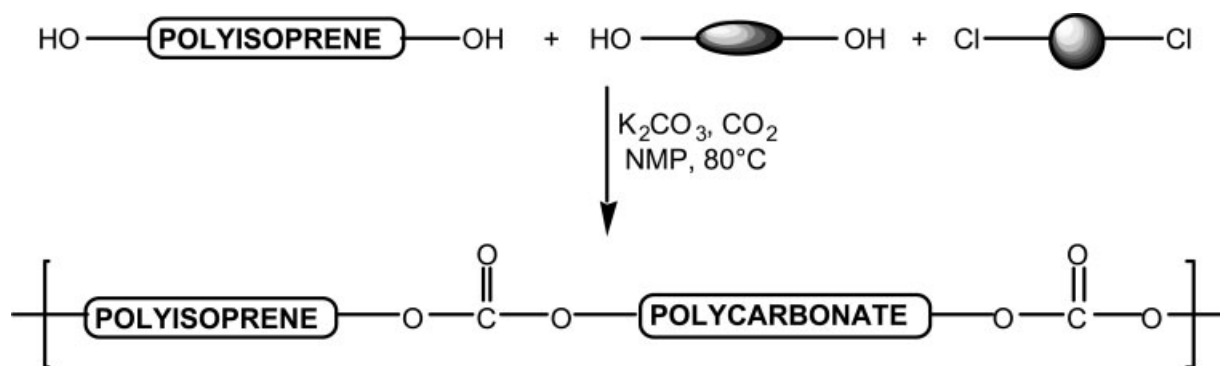
Scheme 1 Diagram of the synthesis of poly(isoprene-*b*-carbonate)s.

thermoplastic are referred to as thermoplastic polyolefin elastomers. In these materials, the soft phase is sometimes slightly crosslinked.

On the basis of these considerations, our purpose was to develop a synthesis methodology to prepare new copolymers incorporating soft polyisoprene blocks and rigid polycarbonate blocks, likely to have the characteristics of thermoplastic elastomers. The choice was made on rigid polycarbonate blocks because these thermoplastics, in particular the aromatic polycarbonates, show high glass temperatures [$T_g > 150°C$ for the commercial poly(bisphenol A carbonate)]. For that, a condensation mechanism leading to the formation of carbonate structures by reaction between an organic halide and an alcohol carried out in presence of potassium carbonate under CO_2 atmosphere was considered,[5,6] and adapted to hydroxytelechelic polyisoprenes as reagents (Scheme 1).

Initially, a modeling of the condensation was performed to define the optimal conditions for the formation of carbonate structures.[7] Thereafter, these optimized conditions were generalized and adapted to the synthesis of polycarbonates of varied structures, then to that of the required poly(isoprene-*b*-carbonate)s.

The purpose of the paper is to relate the various studies that were carried out to allow the achieving of the set objective, i.e., the development of a general procedure to conveniently prepare well defined poly-(isoprene-*b*-carbonate)s.

EXPERIMENTAL

Materials

Hydroxytelechelic polyisoprene HTPI (Atochem) was purified by re-precipitation from dichloromethane into methanol [after purification: $\overline{M_n} = 5200$, polydispersity index (PDI) = 1.8, hydroxyl functionality = 2–2.5}]. 1,10-decanediol and 1,4-bis(chloromethyl)benzene (BCMB) were recristallized in

dichloromethane and benzene respectively, and then dried under vacuum at 40°C. 1,4-bis(hydroxymethyl)benzene (97%, Fluka), 1,4-bis(hydroxyethoxy)-benzene (99%, Acros), 4,8-bis(hydroxymethyl)tricy-clo[5.2.1.0^{2,6}]decane (96%, Aldrich) and Bisphenol A propoxide (BPAP) (Aldrich) were dried under vacuum at 40°C, then stocked over P_2O_5. K_2CO_3 (PA, Janssen) was dried at 400°C under vacuum during 2 h, then 1 h during the cooling in vacuum, and kept over P_2O_5. DMF and NMP were dried over calcium hydride, and then distilled under reduced pressure before use. THF (for HPLC, Acros) was used as received. Dichloromethane and methanol were purified according to classical methods.

Polycondensation

Reactions were carried out in a three-necked round-bottom flask equipped with a condenser and a gas entrance. After introduction of reagents, air was replaced by CO_2. Carbon dioxide atmosphere was maintained at atmospheric pressure using a pressostate-control valve system. The mixture was stirred at 80°C.

During reaction, samples for analysis were taken out from the reaction mixture with a syringe and dissolved in THF. Residual K_2CO_3 was removed by filtration. The filtrate was evaporated at 40°C under vacuum, and then analyzed by SEC (in solution in THF) and NMR (in CDCl$_3$) respectively.

At the end of the reaction, the obtained mixture was diluted with CH_2Cl_2 (or THF), and then K_2CO_3 was filtered off. The filtrate was concentrated using a rotary evaporator, and the formed polymer was precipitated in methanol. Finally, it was retrieved, and dried at 40°C under vacuum until constant weight.

The procedure used to retrieve the polymer coming from polycondensation of BCMB and HTPI, and copolycondensations of BCMB, BPAP, and HTPI, was slightly different from the general one described

above. It was carried out as follows. After reaction, the mixture was diluted with THF, and placed in a freezer to improve the precipitation of inorganic compounds in the bottom of the flask. After settling and decanting, the polymer contained in the liquid phase was precipitated in methanol. It was retrieved, purified by re-precipitation from dichloromethane into methanol, and finally dried at 40°C under vacuum to constant weight.

Remark: In the case of two-step reaction, BPAP solution in NMP was placed under CO_2 atmosphere separately before being transferred in the reaction mixture.

Product characterization

Polycondensation of BCMB and BPAP

^{13}C-NMR (CDCl$_3$) δ 154.46 ppm (C$_{carbonate}$), δ 128.4 ppm (CH$_{Ar-BCMB}$), δ 135.4 ppm (C$_{1,4 \ Ar-BCMB}$), δ 69–69.7 ppm (Ar—CH$_2$—OC(O)O—), and signals from BPAP moiety: δ 72.8 ppm (—CH(CH$_3$)—CH$_2$—OC(O)O—), δ 73 ppm (—CH(CH$_3$)—OC(O)O—), δ 113.4–127.6 ppm (CH$_{Ar-BPAP}$), δ 143.5–156.2 ppm (C$_{1,4 \ Ar-BPAP}$), δ 30.2 ppm (Ar—C(CH$_3$)$_2$—), δ 41.6 ppm (Ar—C(CH$_3$)$_2$—), δ 71.3 ppm (—Ar—O—CH(CH$_3$)—CH$_2$—), δ 69.6 ppm (—Ar—O—CH$_2$—CH(CH$_3$) —). ^{1}H-NMR (CDCl$_3$) δ 7.36 ppm (H$_{Ar-BCMB}$), δ 6.78–7.11 ppm (H$_{Ar-BPAP}$), δ 5.15 ppm (Ar—CH$_2$—OC(O)O—), δ 5.12 ppm (—CH(CH$_3$)—CH$_2$—OC(O)O— and —CH$_2$—CH(CH$_3$)—OC(O)O—), δ 4.57 ppm (Ar—O—CH(CH$_3$)—CH$_2$—OC(O)O—), δ 4–4.9 ppm (Ar—O—CH$_2$—CH(CH$_3$)—OC(O)O—), δ 1.33 ppm (—Ar—O—CH(CH$_3$)—CH$_2$—), δ 1.4 ppm (—OC(O)O—CH(CH$_3$)—CH$_2$—), δ 1.61 ppm (Ar—C(CH$_3$)$_2$—).

Polycondensation of 4,8-bis(hydroxymethyl)-tricyclo[5.2.1.0^{2,6}]decane and BCMB

^{13}C-NMR (CDCl$_3$) δ 155 ppm (C$_{carbonate}$), δ 128.3 ppm (CH$_{Ar-BCMB}$), δ 135.5 ppm (C$_{1,4 \ Ar-BCMB}$), δ 68.8 ppm (Ar—CH$_2$—OC(O)O—), δ 71–72.3 ppm (—tricycle—CH$_2$—OC(O)O—), δ 24.3–48.8 ppm (carbons from tricycle structure). ^{1}H-NMR (CDCl$_3$) δ 7.38 ppm (H$_{Ar-BCMB}$), δ 5.14 ppm (Ar—CH$_2$—OC(O)O—), δ 3.84–4.03 ppm (—tricycle—CH$_2$—OC(O)O—), δ 2.28–2.53 ppm (protons from tricycle structure).

Polycondensation of BCMB and 1,4-bis(hydroxyethoxy)benzene

The obtained polymer being insoluble in usual solvents was washed with water and methanol respectively. FTIR (KBr): 1270 cm^{-1} (ν_{C-O}), 1735 cm^{-1} ($\nu_{C=O}$), 3400 cm^{-1} (ν_{O-H}). ^{13}C-NMR (CP/MAS, 8 kHz) δ 156.1 ppm (C$_{carbonate}$), δ 112.8–118.4 ppm (CH$_{Ar}$), δ 152.6 ppm (C$_{1,4 \ Ar}$), δ 131.8–134.2 ppm (C$_{Ar \ BCMB}$). ^{1}H-NMR (CP/MAS, 10 kHz) δ 6.9 ppm (H$_{Ar}$), δ 4.1 ppm (Ar—O—CH$_2$—CH$_2$—OC(O)O—), δ 5.0 ppm (Ar—CH$_2$—OC(O)O).

Polycondensation of BCMB and 1,4-bis(hydroxymethyl)benzene

The obtained polymer being insoluble in usual solvents was washed with water and methanol respectively. FTIR (KBr): 1269 cm^{-1} (ν_{C-O}), 1742 cm^{-1} ($\nu_{C=O}$), 3354 cm^{-1} (ν_{O-H}). ^{13}C-NMR (CP/MAS, 8 kHz) δ 155.8 ppm (C$_{carbonate}$), δ 130.2 ppm (CH$_{Ar}$), δ 136.8 ppm (C$_{1,4 \ Ar}$), δ 69.7 ppm (Ar—CH$_2$—OC(O)O—). ^{1}H-NMR (CP/MAS, 10 kHz) δ 6.9 ppm (H$_{Ar}$), δ 5.1 ppm (Ar—CH$_2$—OC(O)O—) δ 4.2 ppm (Ar—CH$_2$OH).

Polycondensation of BCMB and hexadecamethyleneglycol

^{13}C-NMR (CDCl$_3$) δ 155.13 ppm (C$_{carbonate}$), δ 128.4 ppm (CH$_{Ar}$), δ 135.6 ppm (C$_{1,4 \ Ar}$), δ 68.9 ppm (Ar—CH$_2$—OC(O)O—), δ 68.3 ppm (—OC(O)O—CH$_2$—(CH$_2$)$_{14}$—), δ 25.6–30.8 ppm (—OC(O)O—CH$_2$—(CH$_2$)$_{14}$—). ^{1}H-NMR (CDCl$_3$) δ 7.38 ppm (H$_{Ar}$), δ 5.14 ppm (Ar—CH$_2$—OC(O)O—) δ 4.13 ppm (—OC(O)O—CH$_2$—(CH$_2$)$_{14}$—), δ 1.66 ppm (—OC(O)O—CH$_2$—CH$_2$—(CH$_2$)$_{12}$—), δ 1.20–1.40 ppm (—OC(O)O—CH$_2$—CH$_2$—(CH$_2$)$_{12}$—).

Measurements

Liquid NMR spectra were recorded on a Bruker AC 400 Fourier-transform spectrometer, at 400.13 MHz for ^{1}H and at 100.61 MHz for ^{13}C. Samples were analyzed in solution in deuterated chloroform-D (99.8% purity; Spectrometrie Spin et Techniques). In ^{1}H and ^{13}C-NMR, the chemical shifts were expressed in ppm in the δ scale, compared to the singlet of tetramethylsilane (TMS), as internal standard. Solid-state ^{1}H and ^{13}C CP/MAS NMR spectra were recorded on a Bruker MSL300 spectrometer at 7.05 T with samples in double air bearing 4-mm rotors of ZrO$_2$.

IR spectra were recorded on a Fourier transform Bruker IFC 66 spectrometer in the 4000–500 cm^{-1} range (liquid samples were analyzed between two KBr or NaCl cells, and solid ones as KBr pellets).

SEC measurements were performed on a Spectra System equipment from Thermo Finigan composed of a P 1000 pump, an AS1000 injector, a double detection system [UV absorption (UV 2000 spectrophotometer with variable wavelength set at λ = 254 nm) and differential refractometry (RI 150 refractometer)], in addition to a computer equipped with Chrom Quest 4.0 acquisition and PL Cirrus processing softwares. SEC analyses were carried out in THF at 35°C, with a
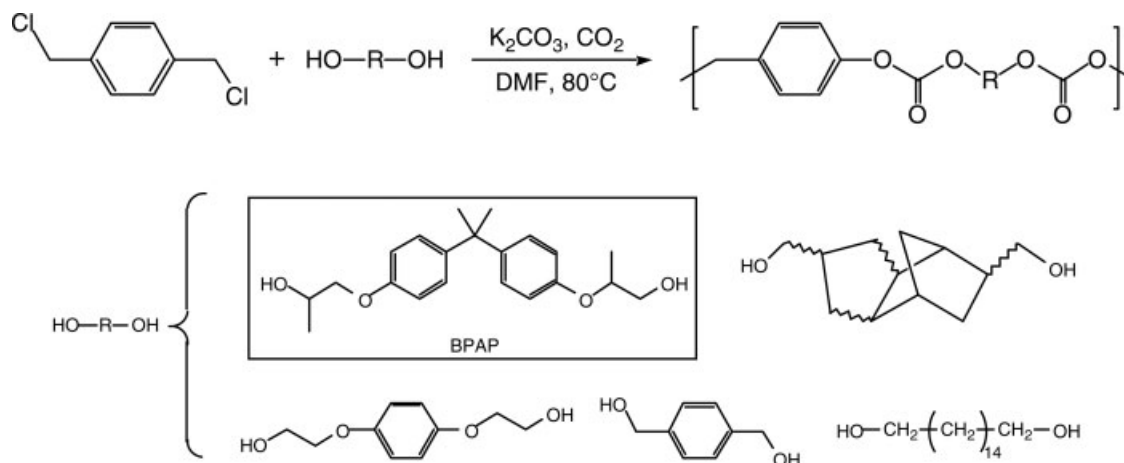
Scheme 2 Polycondensation of BCMB and various diols.

1.0 mL min^{-1} flow-rate, through a column set built up with a precolumn PL Gel 5 μm Guard (5 cm × 7.5 mm) and two columns PL Gel 5 μm Mixed D (30 cm × 7.5 mm) in series. Toluene was used as marker (t_R = 20.38 min) and calibration was accomplished with polystyrene standards. All samples (5 mg ml^{-1} of toluene/THF mixture 1/1000 v/v) were filtered through 0.45 μm microfilter prior to analysis.

Thermoanalyses were performed on Perkin–Elmer apparatus (DSC 7 and TGA 7) equipped with a Thermal Analysis Controller (TAC 7/DX). Acquisition and data processing were performed using Pyris software. For DSC analyses, samples were sealed in pierced capsules, and an empty capsule was used as reference. After a one-minute isothermal at −70°C, a first acquisition was carried out from −70 to 200°C with a heating rate of 10°C min^{-1}. The temperature was then brought back to −70°C with a cooling rate of 10°C min^{-1}. The last acquisition was carried out in the same conditions as the first one. TGA analyses were performed in air between 50 and 650°C with a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

The reaction chosen for the synthesis of poly(iso-prene-b-carbonate)s,[5,6] was previously tested and optimized on monofunctional molecules selected as models of difunctional comonomers for the present study. Details of this study will be the object of a forthcoming publication.[7] Thanks to this preliminary study, it was shown that, contrary to that of CO$_2$, the presence of K$_2$CO$_3$ is necessary for the formation of the carbonate function. In absence of CO$_2$ the reaction occurs, but the yields are lower. Optimal condensation yield was obtained for a reaction carried out in DMF, under CO$_2$ atmosphere, at 80°C, and with a double molar quantity of K$_2$CO$_3$ in comparison to the reactive functions.

The advantage of the modelization study was also to help us to characterize two side reactions:

The first one was a transesterification between the formed carbonate compound and the starting alcohol. It occurs always whatever the initial conditions used, and is particularly efficient when the condensation is performed in absence of CO$_2$ and/or in unsuitable solvents.

The second one was a direct condensation between K$_2$CO$_3$ and chlorinated functions. This last reaction is accelerated in the absence of alcohol. Otherwise, the considered reaction can be accelerated in presence of a phase transfer catalyst, such as a crownether or an ammonium salt.

Following the modelization study, the polycondensation study was started by taking into account the informations so obtained. For that, 1,4-bis(chloromethyl)benzene (BCMB) was selected as an α,ω-dichloro monomer, and at first, its polycondensation with various diols of complex structure was considered to compare its reactivity towards the chosen diols, as well as the thermal characteristics of the polycarbonates formed. Apart from the solvent, the optimized conditions defined at the end of the modelization study[7] were systematically extended to the various polycondensations described in this paper.

Synthesis of polycarbonates by polycondensation

Aromatic and polycyclic diols were selected as diol comonomers, with the aim to obtain rigid polycarbonate structures with high T_g values (Scheme 2). Every synthesis was performed in DMF for 48 h, by using equimolar quantities of comonomers. The polycarbonates formed were purified before analysis.
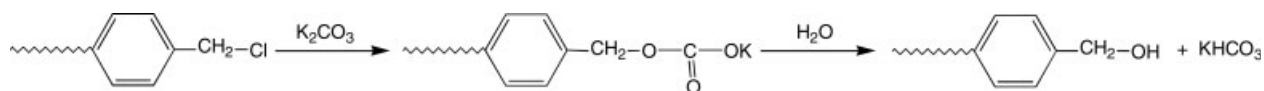
Scheme 3 Possible mechanism of formation of 4-(hydroxymethyl)benzyl chain ends after purification of polycarbonates.

In all cases, the formation of polycarbonate was characterized in FTIR (KBr) by the absorption bands of carbonate functions at 1270 cm^{-1} (ν_{C-O}) and 1740 cm^{-1} ($\nu_{C=O}$) (stretching vibrations).

Every synthesized polycarbonate showed the common p-xylylene groups coming from BCMB. This structure was characterized in ^{1}H-NMR by signals at δ = 5.15 ppm (methylene protons) and δ = 7.36 ppm (aromatic protons). In ^{13}C-NMR, the different carbons of the p-xylylene structure were identified at δ = 68 ppm (methylene carbons), δ = 135.41 ppm (quaternary aromatic carbons), and δ = 128.35 ppm (tertiary aromatic carbons).

On the other hand, after purification of the various polycarbonates (to see in experimental part), an additional ^{1}H-NMR signal was systematically noted on the polycarbonate spectrum at δ = 4.67 ppm. This signal that was absent before polycarbonate purification was attributed to methylene protons of an a-hydroxy-p-xylenyl chain ends. This

attribution agreed with results obtained from two-dimensional ^{13}C-^{1}H correlation. Hydrolysis of carbonate potassium chain ends formed by a side reaction between 4-(chloromethyl)benzyl functions and K$_2$CO$_3$ can be suggested to explain its formation (Scheme 3).

A detailed NMR characterization of each synthesized polymer is given in experimental part.

Synthesized polycarbonates were then characterized by Differential Scanning Calorimetry (DSC). Depending on the initial diol structure, their properties were amorphous to semicrystalline (Table I).

Polycarbonates coming from BPAP and 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane were shown amorphous with a quite low glass transition temperature (T_g = 36–37°C). This was unexpected as both diols contain rigid bisphenol A or polycyclic structures respectively. The low molecular weight of the polymers and/or the formation of isomeric structures could explain this characteristic.

TABLE I
Thermal Characteristics of the Synthesized Polycarbonates

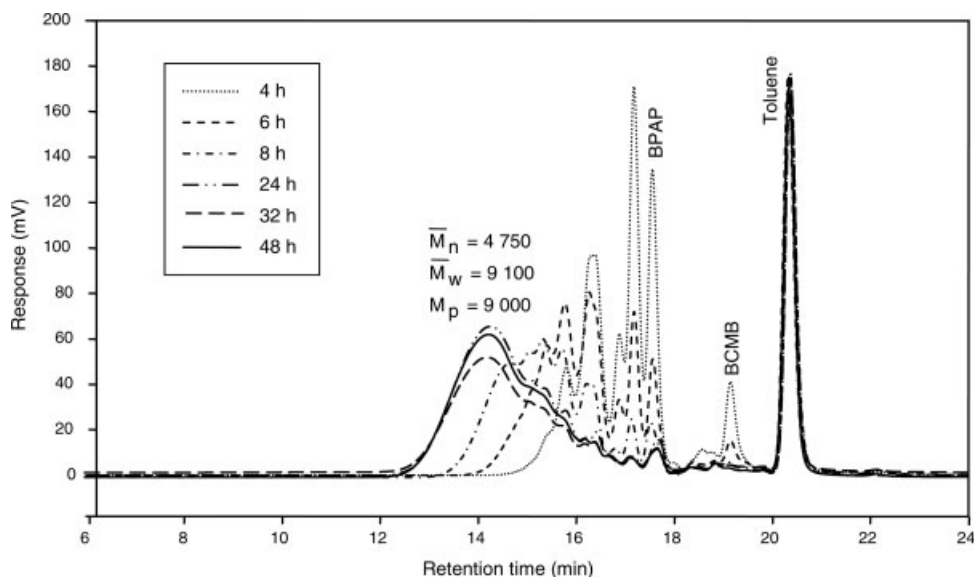| Polycarbonate structure	T_g (°C)	T_f (°C)	T_c (°C)
	37	–	–
	36	–	–
	–	89	58
	7	140	–
	–	193	171

Figure 1 Polycondensation of BPAP and BCMB: SEC chromatograms (UV detection) of the growing polycarbonate at various times. Reaction performed at 80°C, in DMF, under CO_2 atmosphere, and in presence of K_2CO_3. [BPAP] = [BCMB] = 0.5 mol L^{-1}, [K_2CO_3] = 4 [BCMB].

The other synthesized polycarbonates showed semicrystalline properties. It was noted that the intensity of the melting peak was generally large and bimodal, which is significant that crystalline phase is not homogeneous. Polycarbonates coming from rigid aromatic diols (polymers 4 and 5) showed quite high melting temperatures (140 and 198°C respectively). This can be explained by the high proportion of aromatic rings present in the polycarbonate chains. However, these two polymers are insoluble in usual organic solvents. Because of the very flexible structure of 1,10-decanediol used to prepare polymer 3, one can deduce that the crystallinity of polymer 3 is provided by the p-xylylene groups.

Kinetic of polycondensation of BPAP and BCMB:

BPAP was chosen for this study, as well as for the continuation of the research with HTPI, because of the solubility of corresponding polycarbonates in usual solvents, as chloroform and THF. The polycondensation of BPAP and BCMB was performed in DMF. SEC and ^{1}H-NMR were simultaneously used to follow reaction progress.

The analysis by SEC showed that the average molecular weights of the formed polycarbonate don't increase after 24 h (Fig. 1), and approach at this time $\overline{M_n} = 4750$ and $\overline{M_w} = 9100$ (PDI = 1.9) respectively. At the same time, one can note that, contrary to BPAP, BCMB is totally consumed.

These results were confirmed by ^{1}H-NMR analysis (Fig. 2). During the first 10 min, the conversions of the two monomers occur at same rate and are very fast. After 24 h, they reach a plateau: 90% conversion for BPAP and 95% for BCMB. This difference in the conversion rates indicated that, at the

end of the reaction, the majority of polycarbonate chain ends was of the hydroxypropoxy type. The incomplete transformation of BPAP at the end of the reaction can be in part explained by the possible formation of carbonate functions by reaction between BCMB chloride functions and potassium carbonate as shown during the modelization study.[7]

Feasibility of the synthesis of poly-(isoprene-b-carbonate)s

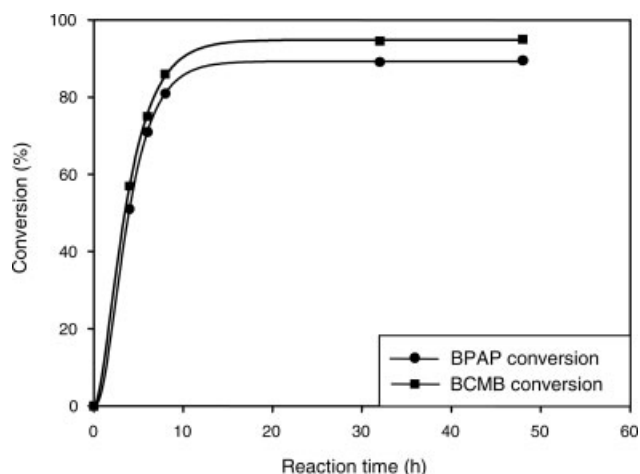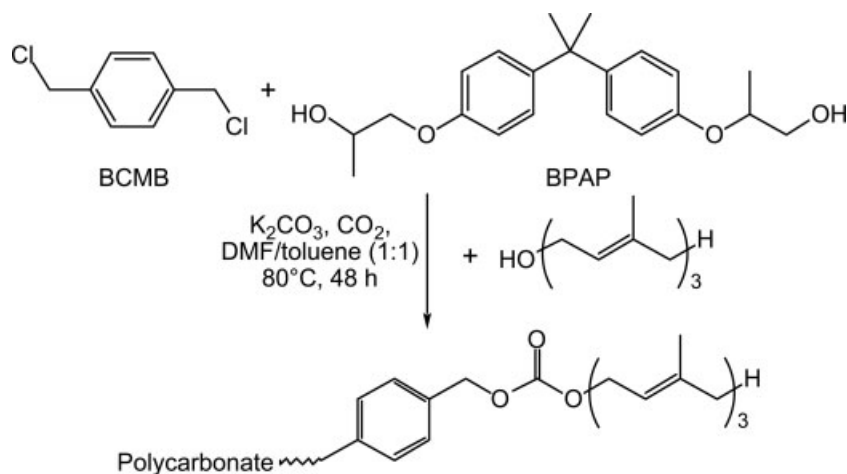Before considering the synthesis of poly(isoprene-b-carbonate)s by copolycondensation of BCMB, HTPI,

Figure 2 Polycondensation of BPAP and BCMB: monomer conversions calculated from ^{1}H-NMR spectra of reaction mixture samples taken at different times.

Scheme 4 Polycondensation of BPAP and BCMB, performed in presence of farnesol.

and BPAP, it was advisable to check the feasibility of the considered reaction by making sure that the reactivity of the HTPI hydroxy-terminal groups was comparable with that of BPAP hydroxyls, and that nonpolar and flexible aliphatic blocks could be inserted within rigid polycarbonate chains during the reaction of BCMB and BPAP.

Polycondensation performed in presence of farnesol

To make sure of the reactivity of HTPI hydroxy-terminal groups towards BCMB chloromethyls and to compare it with that of BPAP hydroxyls, a polycondensation of BPAP and BCMB was carried out in presence of farnesol, a molecule whose structure is similar to that of HTPI chain ends (Scheme 4). The reaction was carried out in 1:1 (v/v) DMF/toluene, during 48 h. Farnesol was introduced in default compared to BPAP hydroxyls ([BPAP]/[farnesol] = 5 mol mol^{-1}). The quantity of BCMB was calculated to have an equivalence between the chloromethyls and the totality of the hydroxyls involved (BPAP plus farnesol).

The formation of polycarbonates with farnesyl chain ends was confirmed in ^{13}C-NMR by the peaks characteristic of the carbons of farnesyl substituents (carbons of mehylenes in α position to the carbonate functions at δ = 64.5 and 64.8 ppm, carbons of the other methylenes at δ = 20–30 ppm, unsaturated carbons at δ = 118–125 ppm), in addition with the signals characteristic of polycarbonate sequences formed by polycondensation of BPAP and BCMB (aromatic carbons of BPAP structures at δ = 156.2, 143.49, 127.67, and 113.89 ppm; aromatic carbons of *p*-xylylene groups at δ = 135.45 and 128.38 ppm).

In ^{1}H-NMR, the farnesyl chain ends in the obtained polycarbonate was confirmed by the presence of two signals: at δ = 4.62–4.7 ppm attributed to the protons of farnesyl methylene in α position to

the carbonate functions (protons d in Fig. 3), and at δ = 1.95–2.14 ppm corresponding to the protons of the other farnesyl methylenes (protons c in Fig. 3). However, the presence of signals at δ = 1.26 ppm (protons characteristic of methyls on carbons in β and γ position to BPAP hydroxyls) and at δ = 4.57 ppm (protons characteristic of the methylenes of 4-(chloromethyl)benzyl carbonate chain ends) showed that the polycarbonate chain ends were not totally of farnesyl type.

The weight average molecular weight of the polymer obtained ($\overline{M_n}$ = 3800 in polystyrene equivalents, PDI = 1.4) was lower than that of the corresponding polymer obtained in absence of farnesol. This result is obviously explained by the monofunctionality of farnesol that, after reaction, leads to a nonreactive chain end.

These results led to the conclusion that the synthesis of poly(isoprene-*b*-carbonate)s could be considered by a simple copolycondensation carried out in one-step.

Polycondensation performed in presence of hexadecamethyeneglycol

To check if the insertion of nonpolar aliphatic blocks within the polycarbonate chains could be obtained under the selected reaction conditions, a polycondensation of BCMB and BPAP was performed in presence of hexadecamethyleneglycol (M = 258) selected as a model of hydroxytelechelic polyisoprene oligomer (Scheme 5). The copolycondensation was performed in one-step in DMF/toluene (1:1 v/v), for 48 h. Hexadecamethyleneglycol was used in default compared to BPAP ([BPAP]/[hexadecamethylene-glycol] = 10 mol mol^{-1}), and BCMB in 5 mol % excess compared to the total molar quantity of the diols.

The statistical incorporation of hexadecamethylene groups within the polycarbonate chains formed
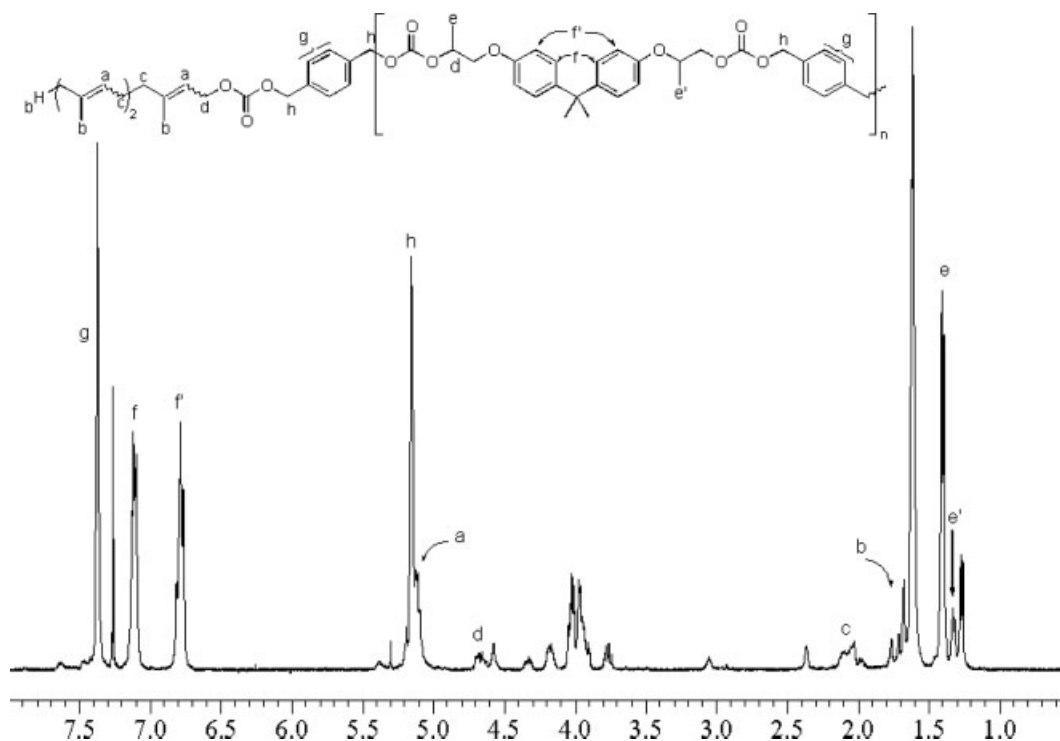
Figure 3 ^{1}H-NMR spectrum (CDCl$_3$) of the polycarbonate coming from copolycondensation of BPAP, BCMB, and farnesol. Reaction carried out at 80°C in 1:1 (v/v) DMF/toluene, under CO$_2$ atmosphere, and in presence of K$_2$CO$_3$. [BCMB] = [BPAP] + [farnesol]/2, [BPAP]/[farnesol] = 5 mol mol^{-1}, [K$_2$CO$_3$]/[BCMB] = 4 mol mol^{-1}.

between BPAP and BCMB was confirmed after ^{13}C-NMR analysis of the polymer obtained. The signals characteristic of the carbons of the hexadecamethylene sequences are noted at $\delta = 68.3$ ppm (carbons of the methylenes in α position to the carbonate functions) and at $\delta = 20$–30 ppm (carbons of the other methylenes) (Fig. 4).

In ^{1}H-NMR, the signals at $\delta = 1.15$–1.97 ppm characteristic of the methylene protons of the hexadecamethylene sequences are superposed on those of the methyl protons coming from the BPAP groups. It is

the same for the signals at $\delta = 5.1$–5.2 ppm that correspond to protons of methylenes in α position to carbonate functions, coming from the hexadecamethylene and BPAP structures.

The SEC chromatogram of the polymer obtained after 48 h showed a narrow distribution of the molecular weights, with the following average molecular weights: $\overline{M}_n = 5550$ and $\overline{M}_n = 4220$.

These results showed that polycarbonates with flexible blocks within their rigid structure could be prepared by direct copolycondensation of BCMB
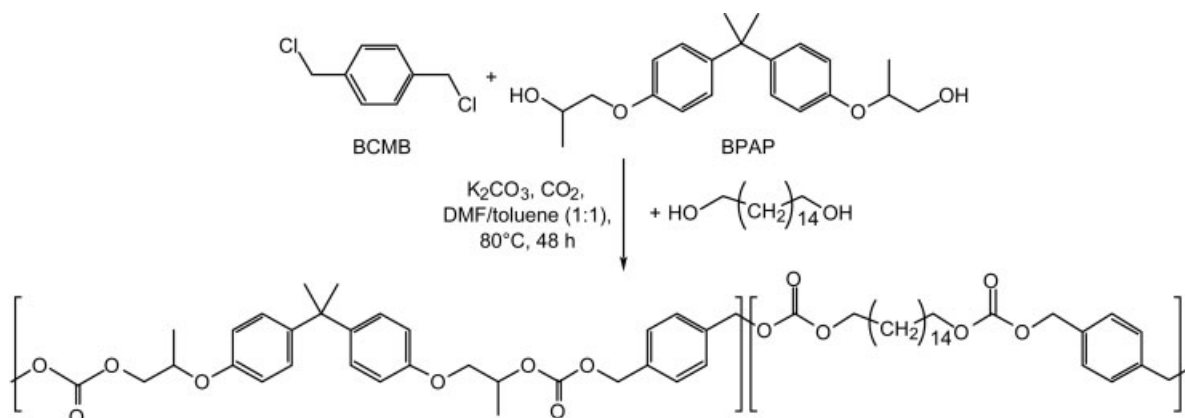
Scheme 5 Polycondensation of BPAP and BCMB, performed in presence of hexadecamethyleneglycol.
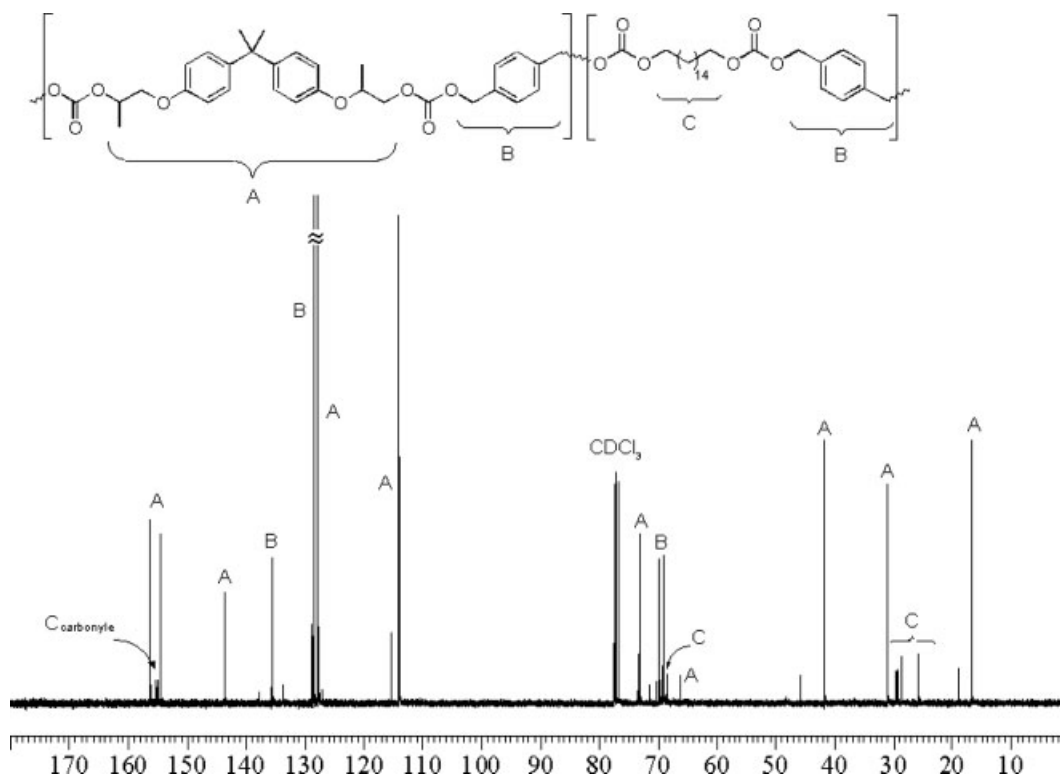
Figure 4 ^{13}C-NMR spectrum (CDCl$_3$) of the copolymer obtained after 48 h of reaction of hexadecamethyleneglycol, BPAP, and BCMB. Reaction carried out at 80°C in 1:1 (v/v) DMF/toluene, under CO$_2$ atmosphere, and in presence of K$_2$CO$_3$. [BCMB] = 1.05 × ([BPAP] + [hexadecamethyleneglycol]) = 0.5 mol L^{-1}, [BPAP]/[hexadecamethyleneglycol] = 10 mol mol^{-1}, [K$_2$CO$_3$]/[BCMB] = 4 mol mol^{-1}.

and diol mixtures composed of hydroxytelechelic hydrocarbon oligomers and aromatic diols.

Reaction of benzyl chloride and HTPI: Formation of benzylcarbonate telechelic polyisoprene

The purpose of the study was to make sure of the reactivity of HTPI hydroxy-terminal groups towards the benzyl chloride functions to form carbonate bonds, but also to get spectroscopic data useful for the characterization of the intended pol(isoprene-b-carbonate)s. The reaction of HTPI and BC (Scheme 6) was carried out with a large excess of BC compared to HTPI hydroxyls to optimize the transformation of HTPI hydroxy-terminal groups in benzylcarbonate ones. It was carried out in NMP, because of the solubility of HTPI in this medium at 80°C.

The presence of benzylcarbonate groups at the HTPI chain ends was characterized in FTIR by the absorption bands at 1745 cm^{-1} ($\nu_{C=O}$) and 1255 cm^{-1} (ν_{C-O}) of the carbonate functions (stretching vibrations). On the other hand, the absorption bands characteristic of polyisoprene carbon–carbon double bonds were noted at 1645 and 668 cm^{-1} ($\nu_{C=C}$), and that of the aromatic rings at 1600 and 1500 cm^{-1}. The total disappearance of the absorption band at about 3450 cm^{-1}, indicated a complete conversion of the hydroxyls in benzylcarbonates.

In ^{13}C-NMR, the transformation of HTPI hydroxy-terminal groups in benzylcarbonate functions was confirmed by a peak at δ = 155 ppm characteristic of carbonyl carbon of carbonate functions, and several peaks at δ = 128.27, 128.44, and 128.53 ppm corresponding to the aromatic carbons of benzyl groups. The peak characteristic of the methylene carbons in benzylcarbonate groups is noted at δ = 69.46 ppm. On the other hand, a peak noted at δ = 73.96 ppm was attributed to the HTPI methylene carbons situ-
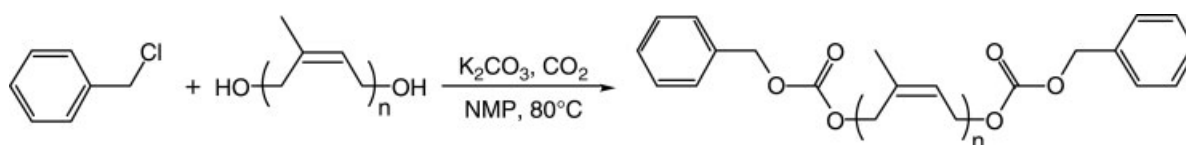
Scheme 6 Reaction of benzyl chloride with HTPI: formation of benzyl carbonate telechelic polyisoprene.

ated in α position to carbonate functions resulting from the transformation of hydroxyls coming from 1,4-*trans* HTPI chain ends.

In ^{1}H-NMR, in addition to the various chemical shifts characteristic of the different protons of polyisoprene backbone, aromatic protons from benzyl chain ends were characterized at 7.4 ppm. The total consumption of hydroxyls was confirmed by the disappearance of the signal at $\delta = 4$–4.2 ppm characteristic of the protons of the methylene in α position to the HTPI hydroxy-terminal groups. On the other hand, a singlet characteristic of the methylene protons of the benzyl groups bonded to carbonate functions appeared at 4.52 ppm.

The SEC analysis confirmed the success of the reaction. The UV absorption shown by the resulting polymer was significant of the bonding of benzyl groups at the polymer chain ends. Its number average molecular weight ($\overline{M_n} = 5200$, PDI $= 1.8$) same to that of the starting HTPI and the absence of very high molecular weight structures showed that, in the reaction conditions used (BC in large excess compared to HTPI hydroxyls), transesterification side reactions didn't occur.

This study allowed us to confirm that a total conversion of polyisoprene hydroxyls in carbonate functions can be performed without side reaction when the reaction is carried out according to the predefined conditions used in the present study.

Polycondensation of HTPI and BCMB

After having shown that the synthesis of poly(isoprene-*b*-carbonate)s could be performed according to the selected procedure, systems incorporating HTPI and BCMB as comonomers were then considered (Scheme 7). Polycondensations of HTPI and BCMB were studied in two homogeneous media (NMP and
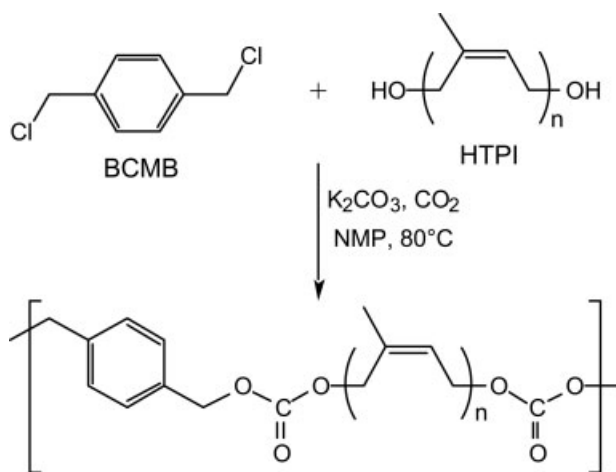
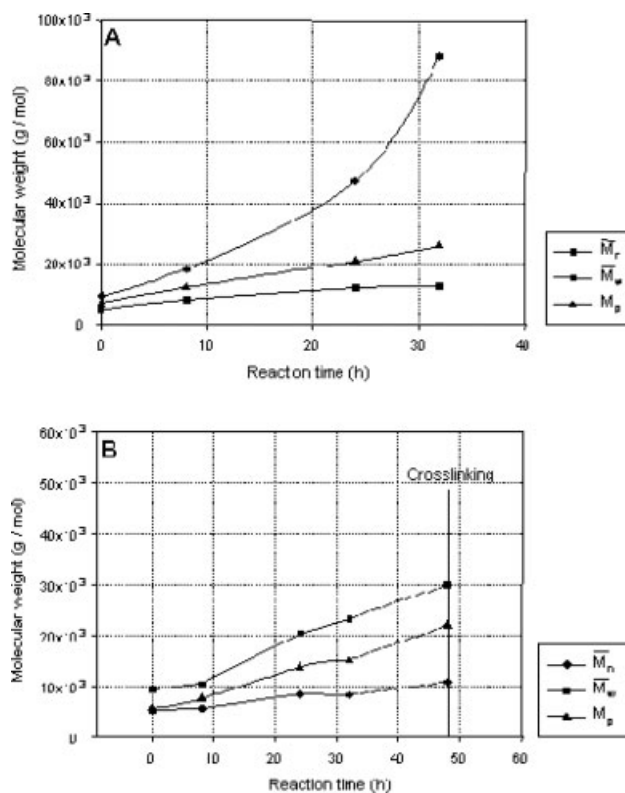**Scheme 7**   Polycondensation of HTPI and BCMB.

Figure 5   Progress of average molecular weights of the copolymer formed during polycondensation of HTPI and BCMB performed in NMP (A) and in 1:1 (v/v) DMF/toluene (B) respectively. Reactions carried out at 80°C, under CO_2 atmosphere, and in presence of K_2CO_3. [BCMB chloromethyls]/[HTPI hydroxyls] = 2.2 (in NMP) or 1.1 (in toluene) mol mol^{-1}, [K_2CO_3] = 2 mol L^{-1}, [HTPI] = 0.2 g mL^{-1}.

DMF/toluene). HTPI was used at concentration of 0.2 g/mL of solvent. Because the functionality of HTPI is higher than 2, a 10% excess of chloromethyls compared to the hydroxyls was used to prevent the crosslinking.

The increase of molecular weight of the poly-(polyisoprene-*p*-xylylene carbonate) formed was shown to be faster in NMP medium than in DMF/toluene (Fig. 5). In the two cases, the copolymer formed became partially soluble in THF after 32 h, then totally crosslinked after 48 h. However, the rate of network formation could be decreased by using a high excess of BCMB chloromethyls compared to HTPI hydroxyls, for instance a [chloromethyls]/[hydroxyls] ratio of only 2.2 mol mol^{-1}. Under these conditions, the transformation of HTPI hydroxy-terminal groups was total (complete disappearance of the IR absorption band at 3450 cm^{-1}), and the formation of a copolymer with essentially 4-(chloromethyl)benzyl chain ends was confirmed after analysis of the ^{1}H-NMR spectrum of the copolymer (only one singlet characteristic of the chain ends, at $\delta = 4.57$ ppm).
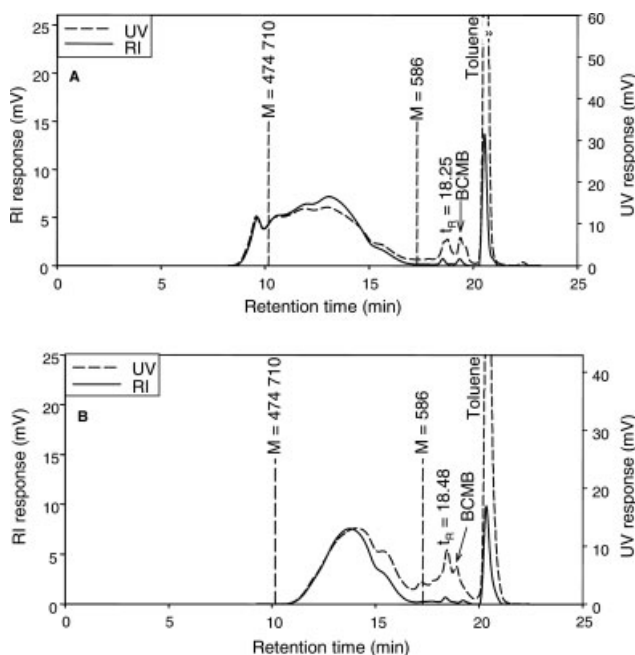
Figure 6 Polycondensation of HTPI and BCMB: SEC chromatograms (RI and UV detections) of the reaction mixture obtained after 24 h of reaction performed in NMP (A) and in 1:1 (v/v) DMF/toluene (B) respectively.

On the other hand, the difference between $\overline{M_n}$ and $\overline{M_n}$ values increases with reaction time (Fig. 5). This indicates that macromolecule growth is not regular during polycondensation progress. This is normal in a polycondensation process. However, in the present case, it can be also explained by the formation of grafted copolymers (even crosslinked) because of the HTPI functionality in hydroxyls is higher than two.

The good concordance between the chromatograms recorded using RI and UV detections (Fig. 6), indicates an homogeneous repartition of the p-xylylene groups within the copolymer, which could be significant of a good respect of the alternation of polyisoprene chains and p-xylylene groups.

The poly(polyisoprene-p-xylylene carbonate) obtained at the end of the reaction were purified, and then analyzed by FTIR, ^{1}H-NMR, and ^{13}C-NMR respectively.

In FTIR, the presence of carbonate functions was proved by the two absorption bands, at 1750 cm^{-1} ($\nu_{C=O}$) and 1265 cm^{-1} (ν_{C-O}) respectively, characteristic of the carbonate functions (stretching vibrations). On the other hand, the absorption band, at 3450 cm^{-1}, characteristic of HTPI hydroxy-terminal groups, was generally not totally disappeared, even when chloromethyl functions were introduced in excess compared to HTPI hydroxyls. To obtain its complete disappearance, it is necessary to use [chloromethyls]/[hydroxyls] ratios higher than 2 mol mol^{-1}.

In ^{1}H-NMR, the reaction of BCMB chloromethyls with HTPI hydroxy-terminal groups was confirmed by the presence of a singlet at $\delta = 4.52$ ppm characteristic of protons of methylenes coming from polyisoprene chain ends of 1,4-trans type and situated in α of carbonate functions, as shown at the end of the ^{1}H-NMR analysis of the polymer obtained from them. In addition, the p-xylylene groups and polyisoprene blocks were also characterized by signals at $\delta = 7.37$ ppm (aromatic protons of p-xylylene groups) and $\delta = 5.12$ ppm (protons of the polyisoprene carbon–carbon double bonds).

In ^{13}C-NMR, the internal carbonyl carbons were characterized by a peak at $\delta = 154$ ppm. The presence of p-xylylene groups within the copolymer chains was indicated by a peak at $\delta = 69.3$ ppm characteristic of the BCMB methylene carbons near the carbonate functions, and another one at $\delta = 128.45$ ppm characteristic of aromatic protons.

Because it was shown that the polycondensation rate is accelerated when a phase transfer catalyst is used (crown ethers, tetraalkylammonium halide salts),[7] a polycondensation of BCMB and HTPI was carried out in presence of a crown ether (10% of 18-crown-6 compared to HTPI hydroxy-terminal groups). The positive effect of the phase transfer catalyst on the polycondensation rate was shown (Fig. 7). The increase of $\overline{M_n}$ is faster when the reaction is performed in presence of the crown ether. In this case, the gel formation occurs after 24 h, against more than 60 h without the catalyst.
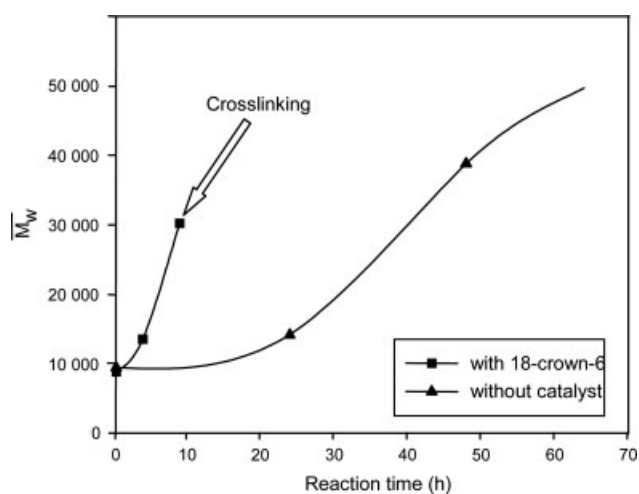

Figure 7 Progress of the weight average molecular weight of the copolymer formed during the polycondensation of HTPI and BCMB, carried out with and without 18-crown-6 as a catalyst. Reaction performed at 80°C in NMP, under CO_2 atmosphere, and in presence of K_2CO_3. [BCMB chloromethyls]/[HTPI hydroxyls] = 2.2 mol mol^{-1}, [K_2CO_3] = 2 mol L^{-1}, [18-crown-6]/[HTPI hydroxyls] = 0.1 mol mol^{-1}, [HTPI] = 0.5 g mL^{-1}.
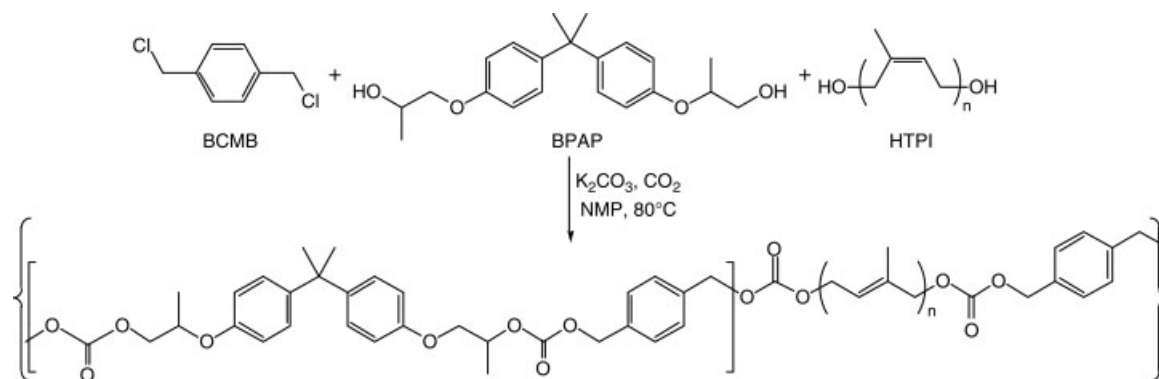
Scheme 8　Copolycondensation of HTPI, BPAP, and BCMB.

The obtaining of high molecular weight polymer by polycondensation of BCMB and HTPI according to the procedure developed here confirmed the reactivity of polyisoprene hydroxy-terminal groups towards BCMB chloromethyls, and therefore the opportunity to prepare poly(polyisoprene-*p*-xylylene carbonate) including alternated PI blocks and *p*-xylylene groups.

One-pot copolycondensation of HTPI, BCMB, and BPAP

Finally, the copolycondensation of HTPI, BPAP, and BCMB was considered (Scheme 8). It was carried out in NMP according to the conditions previously defined at the end of the study of the polycondensation of HTPI and BCMB. BCMB chloromethyls were used in 5% excess compared to the totality of hydroxyls (HTPI + BPAP). The BPAP quantity was calculated to theoretically prepare a copolymer containing 80% in weight of polycarbonate structures coming from BPAP.

SEC using UV detection was used to follow the polycondensation (Fig. 8). It was noted that it proceeds in two periods:

　　During the first 24 h, low molecular weight copolymers were formed. The absence of UV response in the part of the chromatogram corresponding to HTPI elution means that the reaction of BCMB with HTPI didn't occur during this first stage. The reaction begins by the formation of oligocarbonates between BPAP and BCMB.

　　Afterwards, a rapid increase of the average molecular weights is observed, corresponding to the reaction of HTPI with the oligocarbonates initially formed between BPAP and BCMB. A constancy of the values ($\overline{M_n} = 9000$; $\overline{M_n} = 20,000$) was noted after 72 h, while a total consumption of BPAP and BCMB was observed after 40 h

These observations denoted a higher reactivity of BPAP hydroxyls compared to that of polyisoprene ones. On the other hand, the fact that the polydispersity index of the copolymer formed is close to that of initial HTPI ($PDI_{HTPI} = 1.8$, $PDI_{copolymer} = 2.2$), is significant of a low action of transesterification side reactions.

The copolymers obtained were characterized by ^{1}H and ^{13}C-NMR spectroscopies.

In ^{1}H-NMR, a total consumption of BCMB chloromethyls was noted after 120 h of reaction, while in the same time, the conversion of BPAP hydroxyls was only 86% (Fig. 9). The polycarbonate blocks coming from reactions of BPAP with BCMB, were characterized by the aromatic protons of BPAP structures at $\delta = 6.78$ and $\delta = 7.1$ ppm, while the presence of soft polyisoprene blocks was identified by the methylene protons of 1,4-polyisoprene units at $\delta = 1.8–2.2$ ppm. However, the protons of the carbons in α position to carbonate functions could not be precisely characterized, because their signal is superimposed with that of the protons of polyisoprene carbon–carbon double bonds, at $\delta = 5.1–5.2$ ppm.

In ^{13}C-NMR, the chemical shifts characteristic of the polyisoprene blocks were noted at $\delta = 124–127$ ppm (peaks of unsaturated carbons), at $\delta = 20–40$ ppm (peaks of methylene carbons), and at $\delta = 15.99$ ppm (peak of methyl carbons). The presence of polycarbonate blocks coming from reaction of BCMB with BPAP was also confirmed by peaks at $\delta = 128.39, 127.68, 135.46$ ppm (aromatic carbons of *p*-xylylene groups) and $\delta = 113.9, 115.23, 143.52, 154.5, 156.23$ ppm (aromatic carbons of BPAP groups).

Furthermore, the proportion (in weight) of polycarbonate contained in the copolymer could be quantified by using ^{1}H-NMR. In ^{1}H-NMR, BPAP polycarbonate sequences were characterized by their aromatic protons at $\delta = 6.78$ ppm and at $\delta = 7.1$ ppm respectively. Polyisoprene blocks were identified by the 1,4-polyisoprene methylene protons at $\delta = 1.8–2.2$ ppm. By comparing the areas of these respective signals, it was thus possible to determine
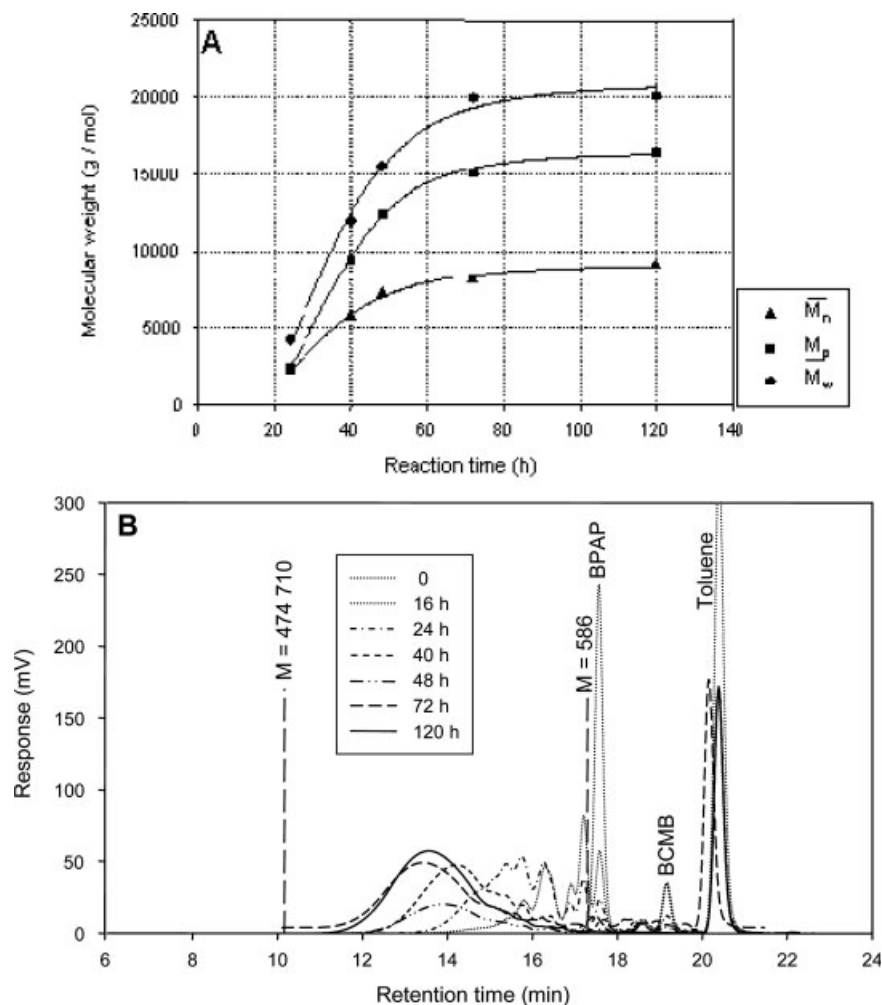
Figure 8 One-pot polycondensation of HTPI, BCMB, and BPAP: Progress of the reaction followed by SEC (UV detection). Reaction performed at 80°C in NMP, under CO_2 atmosphere, and in presence of K_2CO_3. [HTPI] = 0.1 g mL^{-1}, [BCMB chloromethyls]/[HTPI plus BPAP hydroxyls] = 1.05 mol mol^{-1}, [BPAP] calculated to obtain a copolymer containing 80% in weight of polycarbonate coming from BPAP, [K_2CO_3] = 4 [BCMB]. (A) Progress of the average molecular weights of the polymer formed, (B) SEC chromatograms of the growing polymer at various times (UV detection).

the weight % of polycarbonate stuctures in the co-polymer:

$$I_{PI} = \frac{I_{1.8-2.2}}{4} \quad I_{BCMB} = \frac{I_{7.4}}{4} \quad I_{BPAP} = \frac{I_{6.8} + I_{7.1}}{8}$$

% polycarbonate

$$= \frac{I_{BPAP} \times 534}{I_{BPAP} \times 534 + I_{PI} \times 68 + (I_{BCMB} - I_{BPAP}) \times 164} \times 100$$

% polyisoprene

$$= \frac{I_{PI} \times 68}{I_{BPAP} \times 534 + I_{PI} \times 68 + (I_{BCMB} - I_{BPAP}) \times 164} \times 100$$

I_x is the area of the signal at δx ppm, I_{PC} is the area relative to BPAP groups, I_{BCMB} is the area relative to p-xylylene groups (BCMB), and I_{PI} is the area relative to polyisoprene units.

By using these relations, it was deduced that the weight % of polycarbonate contained in the synthe-sized copolymer was 83%, which is not far from the 80% theoretical value. This result showed that, in spite of the relatively low average molecular weights obtained, the synthesis of poly(isoprene-b-polycar-bonate)s with preset compositions was possible by using the one-pot copolycondensation described here.

Two-step copolycondensation with postponed addition of BPAP

Because reactivity of BPAP hydroxyls towards BCMB was noted higher than that of HTPI hydroxy-terminal ones during the one-pot polycondensation of BPAP, HTPI, and BCMB, it was suggested that a postponed addition of BPAP would be able to
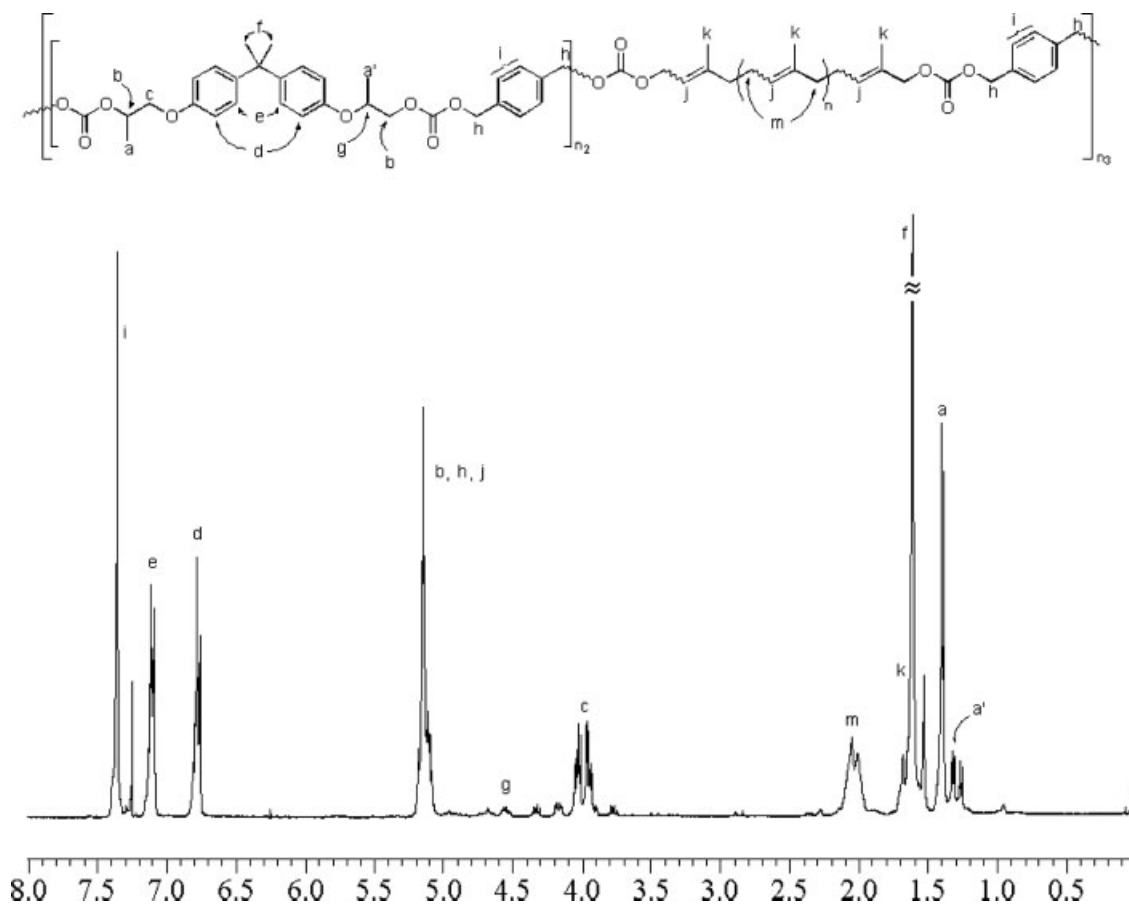
Figure 9 ^{1}H-NMR spectrum of the polymer obtained after 120 h of reaction of HTPI, BPAP, and BCMB.

facilitate the incorporation of polyisoprene blocks within the growing copolymer. To verify this hypothesis, a reaction was performed in the same conditions as one-pot copolycondensation, but BPAP was introduced to the reaction mixture after 8 h of reaction of HTPI with BCMB. However, it was noted that the average molecular weights of the poly(isoprene-b-carbonate) obtained after 72 h were almost similar to that observed at the same time during the one-pot polycondensation. On the other hand, as for the poly(isoprene-b-carbonate) obtained during the one-pot synthesis, a good concordance was noted between the polycarbonate content (in weight) in the synthesized copolymer (43%) and the preset value (45%).
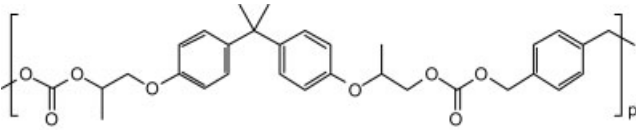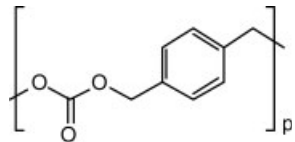
Thermoanalysis of poly(isoprene-b-carbonate)s

Thermoanalysis was performed on copolymers derived from BPAP and from 1,4-bis(hydroxy-methyl)benzene, which were synthesized using the one-pot method described in the present article.

At first, the two copolymers were analyzed by DSC (Table II). Generally, transitions characteristic of each type of block should be noted on DSC thermograms of block copolymers. For poly(isoprene-b-carbonate)s, a glass transition representing the polyisoprene phase (towards $-60°C$) and a glass transition (or a melting point) for the polycarbonate phase should be observed. In the case of the copolymer containing 83% of polycarbonate structures coming from BPAP, two glass transitions were noted at $-66°C$ (polyisoprene phase) and at $42°C$ (polycarbonate phase) respectively. The T_g noted for the polycarbonate phase ($T_g = 42°C$) is higher than that observed for the polycarbonate alone coming from the reaction of BCMB and BPAP ($T_g = 37°C$). This increase of T_g that indicates a reduction of the chain mobility in the polycarbonate phase, is surprising. The poly(isoprene-b-carbonate) prepared from 1,4-bis(hydroxymethyl) benzene and composed of 30% in weight of polycarbonate showed a glass transition at $-59°C$ (polyisoprene phase) and a melting at $T_f = 188°C$ (polycarbonate phase). During the cooling stage, a recrystallization peak was noted at $T_c = 163°C$. The melting point is lower than that noted for the polycarbonate coming from the polycondensation of BCMB with 1,4-bis(hydroxymethyl)-benzene ($T_g = 193°C$). This can be explained by insertions of polyisoprene in the polycarbonate

TABLE II
Comparison Between the Thermal Characteristics of the Synthesized
Poly(isoprene-*b*-carbonate)s with Those of the Corresponding Polycarbonates

Polycarbonate	Poly-(isoprene-*b*-carbonate)
$T_g = 37°C$	83% polycarbonate $T_g = -66°C$ $T_g = 42°C$
$T_f = 193°C$; $T_c = 171°C$	30% polycarbonate $T_g = -59°C$ $T_f = 188°C$ $T_c = 163°C$

phase, which would disturb the crystallization of this phase.

The two poly(isoprene-*b*-carbonate)s were also analyzed by thermogravimetry (Figs. 10 and 11, respectively). As HTPI and polycarbonates, poly(isoprene-*b*-carbonate)s are stable up to 200°C, and start degrading between 200 and 250°C. Their decomposition occurs in two stages [the surprisingly low first decomposition temperature (200°C) of the polycarbonate coming from 1,4-bis(hydroxymethyl)benzene and BCMB can be explained by the presence of small molecules not eliminated during the recovery of the polymer because of its insolubility in usual solvents]. At the beginning, the rates of decomposition of poly(isoprene-*b*-carbonate)s and polycarbonates are faster than that of HTPI, but at the end of this stage, the residual weight for HTPI is much lower than those observed for poly(isoprene-*b*-carbonate)s and polycarbonates. The effects are more marked, when the polycarbonate content in the copolymer is higher. Because carbonate linkages in polycarbonates are easily cleaved to form carbon dioxide and stable cyclic oligomers and phenols under heating,[8] it can be deduced that the weight loss observed at the beginning of the decomposition of poly(isoprene-*b*-carbonate)s and polycarbonates corresponds to a CO_2 release.
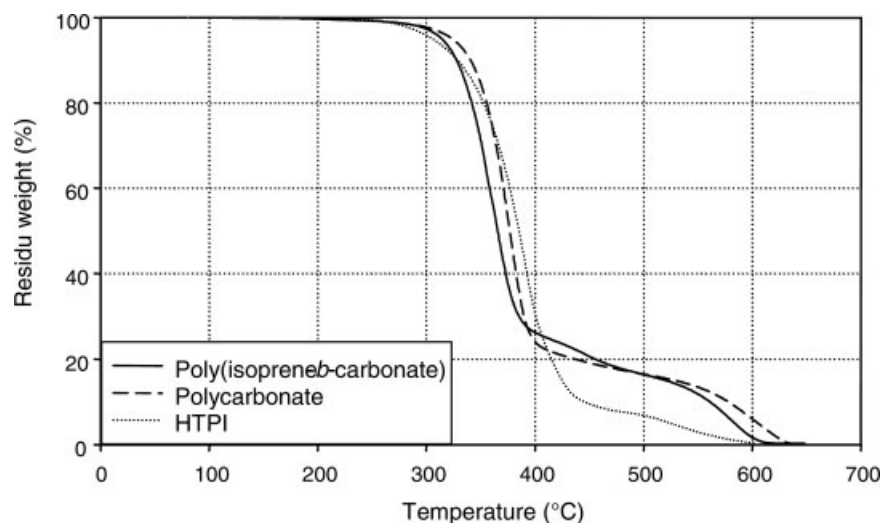

Figure 10 TGA analyses of the HTPI used as reagent, the polycarbonate obtained by reaction of BPAP with BCMB, and the corresponding poly(isoprene-*b*-carbonate) that contained 17% of polyisoprene structures.
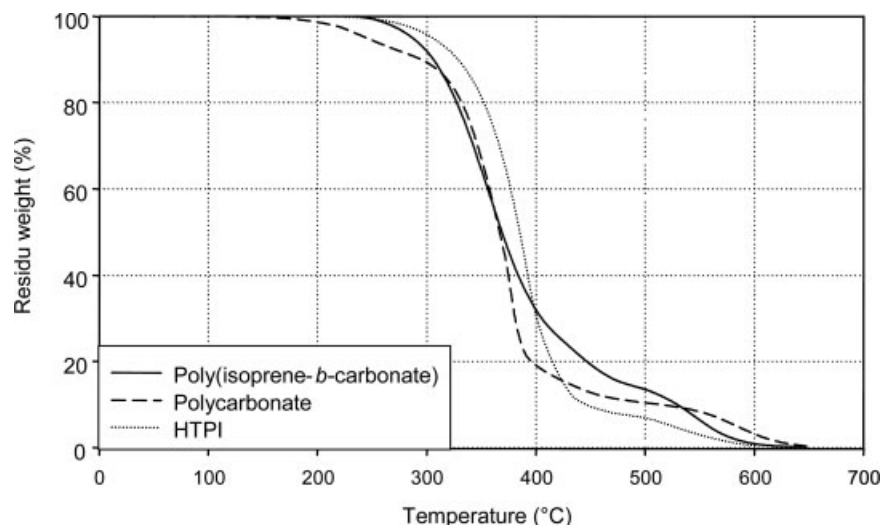
Figure 11 TGA analyses of the HTPI used as reagent, the polycarbonate obtained by reaction of 1,4-bis(hydroxymethyl)-benzene with BCMB, and the corresponding poly(isoprene-*b*-carbonate) that contained 70% of polyisoprene structures.

CONCLUSIONS

A general procedure was developed to conveniently prepare well defined poly(isoprene-*b*-carbonate)s composed of soft polyisoprene blocks and rigid polycarbonates ones, able to show the characteristics of thermoplastic elastomers. For that, a reaction between an organic halide and an alcohol carried out in presence of potassium carbonate under CO_2 atmosphere was considered,[5,6] and adapted to hydroxytelechelic polyisoprenes (HTPI) as reagents.

By taking into account the previous modelization of the synthesis performed to adapt and optimize the selected reaction to the objectives,[7] polycondensations were at first considered between 1,4-bis-(chloromethyl)benzene (BCMB) and various diols to prepare various polycarbonates with different properties and to choose a diol for further study. Because of the good solubility of the polycarbonate prepared from Bisphenol A propoxide (BPAP), this diol was selected.

To make sure of the feasibility of the synthesis of poly(isoprene-*b*-carbonate)s according to a polycondensation methodology involving three comonomers (BCMB, BPAP, and HTPI), a number of preliminary studies were performed. After having shown that the reactivity of HTPI hydroxy-terminal groups towards BCMB chloromethyls was similar to that of BPAP ones, and that nonpolar rubbery chains could be inserted within rigid polycarbonate structures, the final step of the study could be considered. A one-pot synthesis of poly(isoprene-*b*-carbonate)s by copolycondensation of HTPI, BPAP, and BCMB as comonomers was performed. Soluble poly(isoprene-*b*-carbonate)s were obtained with weight average molecular weights $\overline{M_n}$ from 20,000 to 30,000 (PDI ~2.2–3.6) and with compositions in agreement with the preset compositions.

The analyses performed by DSC with two poly-(isoprene-*b*-carbonate)s synthesized in this way with two different diols (BPAP and 1,4-bis(hydroxy-methyl)benzene), showed that these copolymers have two transitions characteristic of each type of phase. This is in agreement with the characteristics of thermoplastic elastomers.

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