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Synthesis of cyclic and multicyclic polyisoprenes

Jean-Marc Boutillier, Bénédicte Lepoittevin, Jean-Claude Favier†, Michèle Masure, Patrick Hémery *, Pierre Sigwalt

Laboratoire de Chimie des Polymères associé au CNRS, UMR 7610, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cédex 05, France

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Abstract

Cyclic polyisoprenes have been synthesized by reaction of α,ω-dilithiopolyisoprenes with dichlorodimethylsilane or 1,2-bis(isopropenyl-4-phenyl) ethane (BIPE). Using the dihalide compound, the effect of the solvent polarity on the coupling reaction is more pronounced in the case of α,ω-dilithiopolyisoprene than with monofunctional polyisoprenyllithium. The yield in cyclic compound falls from 88% in pure hexane down to 53% in the presence of 15 vol% of tetrahydrofurane (THF). Using the nonconjugated diene (BIPE) as linking agent the addition of THF is required but the formed cycle retains its living character and allows the synthesis of cycles having two arms (after addition of isoprene) and of a bicyclic structure after a second cyclization reaction. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Cyclic polymers have always been known by chemists because nature has provided numerous examples such as cyclodextrins or some viruses. Polymer physicists have a deep interest in the properties and characterization of ring polymers. The earlier studies on this subject are essentially theoretical [1–3]. For the last fifteen years numerous groups have synthesized ring polymers with the hope of obtaining products with new properties [4,5]. The first synthetic path is an application of the ring polymerization of heterocyclic monomers essentially cyclosiloxanes the polymerization of which yields a mixture of cycles and linear polymers due either to an equilibration or to a kinetically controlled process [6–8]. The second synthetic method to produce ring polymers uses living polymerization and coupling techniques. The advantage of this method is in particular the narrow molecular weight distribution of the cycles obtained. Cyclic polystyrenes [9–16], polydienes [17], poly (2-vinylpyridine) [18], poly(styrene-b-2-vinylpyridine) [19] and poly(styrene-b-butadiene) [20] have been prepared using several dihalogeno or diethylenic compounds as coupling agents.

The coupling can be achieved according to several procedures:

1. addition of a difunctional organic compound (i.e. dichlorosilane) to a bicarbanionic polymer leading to a neutral monocyclic polymer;
2. reaction of the same living polymer with a diethylenic compound which gives bicarbanionic macrocycles able to reinitiate the polymerization of the same or other monomers;
3. reaction of a monofunctional polymer on a diethylenic compound followed by 1 or 2.

Nevertheless these methods have their own limits. The difficulty lies in the fact that the intramolecular cyclization step is in competition with intermolecular reactions leading to linear polymer of higher molar masses. Cyclization is favored for low concentrations in polymer as shown by Stockmayer [3]. This explains the low concentrations of the polymer solutions used during this type of reaction and an important problem generally not examined in the literature is the yield of the cyclization reaction.

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* Corresponding author. Fax: +33-1-44-27-55-89.
E-mail address: hemery@ccr.jussieu.fr (P. Hémery).

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Moreover a perfect control of the reactions is needed in order to synthesize polymers with a well-defined structure.

It has been recently reported [21,22] that 1,2-bis(isopropenyl-4-phenyl)-ethane [$CH_2{=}C(CH_3){-}C_6H_4{-}CH_2{-}]_2$ (BIPE) is a highly efficient coupling agent for the cyclization of α,ω-dilithiopolyisoprene. If $SiCl_4$ is used instead of BIPE a fair yield in bicyclic polymer has been obtained.

This paper examines the influence of the solvent and of the concentration on the formation of cyclic polyisoprenes and on the model coupling reaction of monofunctional polyisoprenyllithium by addition of dichlorodimethylsilane and of tetrachlorosilane (procedure 1). It also describes an experimental study of the control of the cyclization reaction using BIPE as coupling agent (procedure 2) to optimize the coupling and the quantitative reinitiation by the resulting α-methylstyryl carbanions on the ring favoring the synthesis of bicyclic polymers with high yields.

2. Experimental

Experiments involving α,ω-dilithiopolyisoprene were carried out in all-glass apparatus using high vacuum techniques. Those concerning the synthesis and the coupling reaction of monofunctional polyisoprenyllithium were performed in a dry box. The solvents were distilled from calcium hydride and dried under vacuum on several sodium mirrors.

Isoprene was fractionated by distillation on a spinning band column, dried on barium oxide and several sodium mirrors. An ultimate purification was performed in the presence of *n*-butyllithium. Isoprene was then cryodistillated on a sodium mirror prior to each experiment in order to eliminate compounds which are formed even if the monomer is kept at low temperature [24]. Tert-Butyllithium was purified by sublimation and dissolved in pure hexane. *n*-Butyllithium was filtered on sintered-glass filters under vacuum.

The precursor, BIPE, and α,ω-dilithiopolyisoprene were prepared according to the procedures previously described [25–27]. $(CH_3)_2SiCl_2$ was distilled twice under anhydrous argon atmosphere on magnesium turnings and collected in capillary tubes equipped with break-seals. The concentration of active centers and of BIPE were measured using UV spectrometry [26].

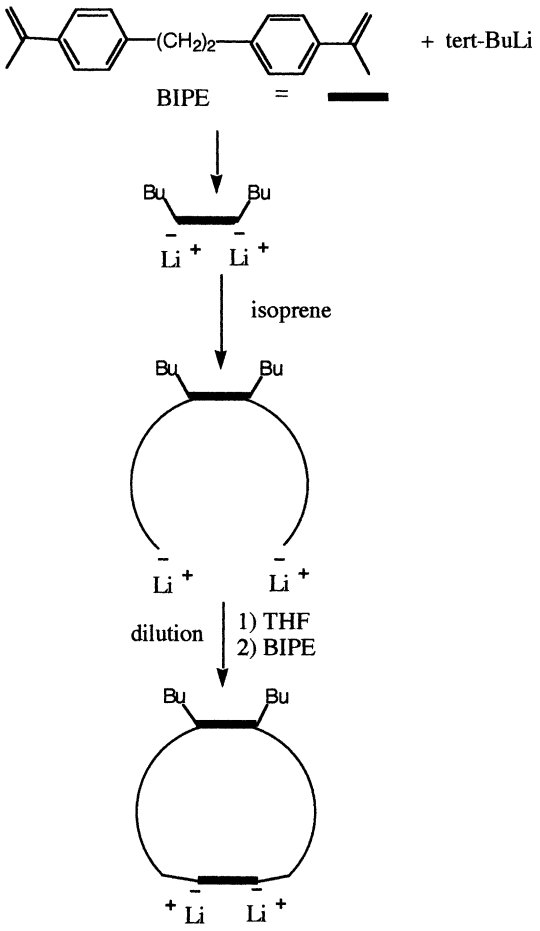
Coupling and cyclization reactions were made by addition of BIPE to hexane solutions of α,ω-dilithiopolyisoprene at room temperature; the mixture was then cooled at -45 ± 5°C and refrigerated THF was added, leading to cyclization. When using $(CH_3)_2SiCl_2$ as coupling agent, the chlorosilane was directly distilled under vacuum into the stirred solution containing or not THF at −50°C.

All the polymer samples were recovered by solvent evaporation and analyzed using size exclusion chromatography (SEC) with a 10^6, 10^5, 10^4, 10^3, 500 and 100 Å set of μ-styragel columns. THF was used as eluent (flow-rate 1 ml min^{-1}). The molar mass calibration curve was obtained using polyisoprene or polystyrene standards.

3. Results and discussion

3.1. Cyclization of α,ω-dilithiopolyisoprene with BIPE

It was previously shown [21,22] that cyclization of α,ω-dilithiopolyisoprenes via the use of a diethylenic compound, BIPE (Scheme 1), requires the addition of THF (15 vol%). The reaction leads to a quantitative formation of cyclic polyisoprene for DP up to 200, and for DP = 500 the fraction of higher molar mass polymer



Scheme 1. Reaction pathway for synthesis of cyclic polyisoprenes.

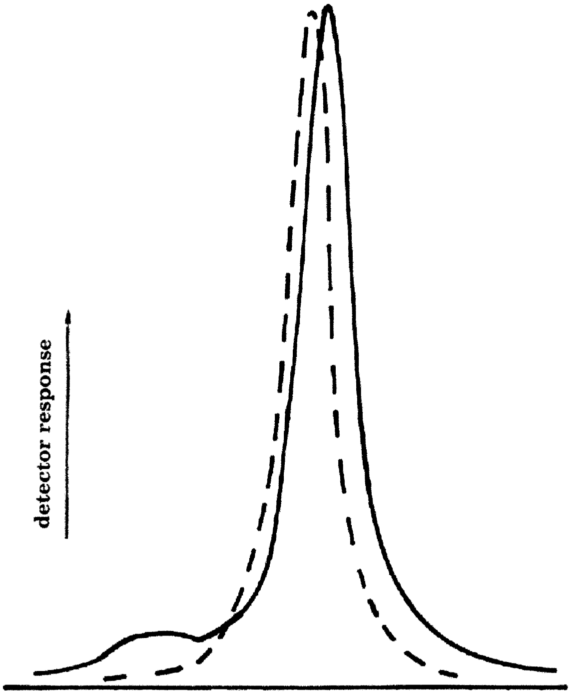


Fig. 1. Size exclusion chromatogram of cyclic polyisoprene prepared with BIPE ($DP_n = 500$) compared with that of the initial linear polymer (dotted line).

(linear or cyclic) obtained by condensation remains lower than 10% (Fig. 1).

It is well known that the hydrodynamic volume of a cyclic polymer is lower than that of a linear one having the same molar mass. The ration ⟨G⟩ of the apparent molar mass of cyclic product to that of linear is equal to 0.77 for linear products of DP equal to 80 and 500. Several explanations can be given for the very high yield in cyclic product observed. It was already observed during the formation of the dilithium initiator that the rate of addition of tert-BuLi in toluene on the second double bond was ten times higher than for the first one [27]. It was postulated that this effect might be due to the formation of cross-associated species favoring the reaction between the organolithium compound with the second double bond. Moreover, it is known that aggregates of poly(isoprenyllithium) subsist at low temperature for low ratio of THF [23] which correspond to the experimental conditions of this work.

The advantage of cyclization using a diethylenic compound is that the formed cycle possesses two active centers able to initiate further polymerization leading to a cyclic polymer with two arms then to a bicyclic one after a second cyclization reaction. In order to control the successive steps by analyzing samples after each reaction, it was necessary to determine the stability of active centers in hexane/THF mixtures at room temperature. Working under high vacuum in sealed apparatus, such a temperature is required to wash the walls of the vessels by cryodistillation before sealing off the samples. As a model of monocyclic polyisoprene possessing two α-methylstyryl carbanions, a solution of dilithium initiator (product of addition of BIPE with BuLi) was chosen. In the presence of THF the concentration of α-methylstyrylcarbanions decreases rapidly as shown in Fig. 2, curve A. The maximum at 350 nm decreases and moves slowly down to 340 nm and a new maximum appears at 590 nm. It was known that α-methylstyryl carbanions are not stable in THF at room temperature [29] and Obriot et al. [27] have shown that the dilithium initiator has an half-life of about 20 min at 20°C in pure THF. In the presence of 15 vol% of THF, 20% of the active centers are deactivated in 10 min at room temperature (half-life of about 1 h). Keeping in mind the use of the vacuum techniques with break-seals, this shows that the stability of the active centers is not sufficient to take samples of the solution in order to study the result of the cyclization.

In order to confirm the progressive deactivation of the carbanions a large amount of isoprene was added after 200 min of reaction. The polymerization was carried out during 10 h at 0°C and then for 48 h at room temperature. The solution became progressively discolored. The polymer was analyzed by SEC and the chromatogram shows the presence of a high molar mass

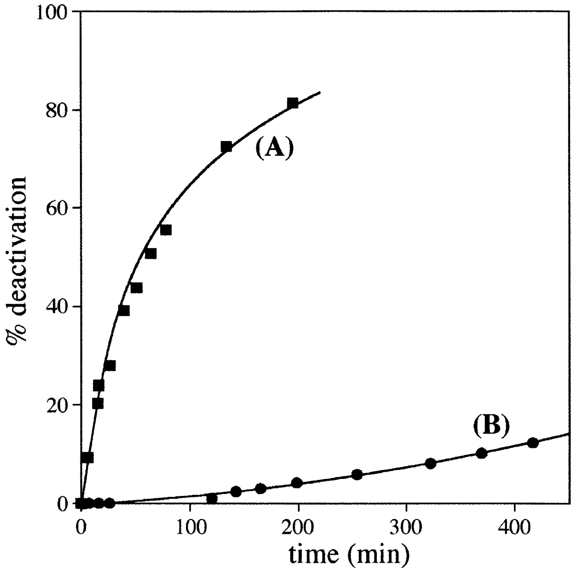


Fig. 2. Evolution of the active centers concentration with time in hexane/THF (85/15 vol%) mixture at room temperature. (A) Product of addition of BIPE with BuLi (initiator) (λ_{max} = 350 nm) and (B) cyclic polyisoprenyllithium with two arms (λ_{max} = 330 nm).

polyisoprene ($M_n = 75\,000$ g mol^{-1}) with broad molecular weight distribution ($M_w/M_n = 1.75$) which could result from the progressive deactivation of the poly(isoprenyllithium) (spreading towards lower molar masses). Besides this high polymer one can observe the signals due to the deactivated initiator (rightmost peak) and of slightly higher molar masses resulting from side reactions.

3.1.1. Stability of a monocyclic living polyisoprene having two arms in the presence of 15 vol% THF

Gourdenne and Sigwalt [30] have studied by UV the evolution at room temperature of a solution of poly(isoprenyllithium) in a mixture of hexane and THF (82 vol%). They observed that the intensity of the λ_{max} (287 nm) remains stable during 70 min and decreases thereafter, followed by a bathochromic shift with the appearance of a maximum at 330 nm the intensity of which decreases with time. These results were in good agreement with those of Bywater et al. [31] who explained this behavior by an isomerization reaction giving a more symmetric allylic carbanion.

The results of the two groups allows us to suppose that the stability of poly(isoprenyllithium) at room temperature decreases with an increase of the THF percentage. The isomerization reaction gives a new carbanion able to initiate polymerizations. The deactivation of carbanions is highly reduced when the temperature decreases but the percentage of added THF has an opposite effect.

The stability of the α-methylstyryllithium in solution in a mixture of hexane and THF (15 vol%) being poor, and considering the results of Sigwalt and Bywater it was of interest to add a small amount of isoprene immediately after the cyclization reaction with BIPE at −50°C and to study the stability of the resulting cyclic compound with two poly(isoprenyllithium) arms.

At room temperature it was observed (in agreement with the literature) a change of the initial species ($\lambda =$ 290 nm) to a new species absorbing at 330 nm. The intensity at this last wavelength remained stable during 2 h and then decreased slowly with time. The absorption at 290 nm decreased very rapidly during the two first hours and diminished thereafter at the same speed as the maximum at 330 nm. This result suggests that the isomerization reaction is complete after 2 h of reaction.

Due to the simultaneity of the reactions of isomerization and of deactivation of the active centers it is difficult to determine with accuracy the percentage of terminated carbanions from the variation of the optical densities at 290 or 330 nm. Nevertheless it can be observed that poly(isoprenyllithium) in solution in a mixture of hexane and THF (85/15 vol%) is fairly stable at room temperature (Fig. 2, curve B) which allows to take off a sample, process which requires at maximum 20 min. In such a case less than 5% of active centers are deactivated. In a first time, coupling of α,ω-dilithiopolyisoprene and monofunctional polyisoprenyllithium with (di)chlorosilane was studied.

3.2. Cyclization of α,ω-dilithiopolyisoprene with chlorosilanes

In a previous paper [21] it was shown that a coupling experiment of α,ω-dilithiopolyisoprene ($M_n = 5000$ g mol^{-1}) with $SiCl_4$ (10 mol% of Li in excess with respect to Cl in order to limit cross-linking) in the presence of 15 vol% of THF at −40°C leads to the formation of three main products. The most important fraction (70%) was assigned to the presence of a bicyclic "eight-shaped" structure and the higher molar masses were attributed, owing to experimental conditions, to "necklace" type structures resulting of intermolecular condensation reactions.

3.2.1. Cyclization in the presence of tetrahydrofurane

In order to suppress the formation of multiple structures which can take place during the reaction of the bifunctional living polymer with $SiCl_4$, it was of interest to cyclize α,ω-dilithiopolyisoprenes with dichlorodimethylsilane. Such an experiment was carried out in the presence of 15 vol% of THF at −50°C, the active center concentration was 4×10^{-4} mol l^{-1} and the DP of the living polymer equal to 200. As shown on the SEC chromatogram (Fig. 3) the fraction of material having a

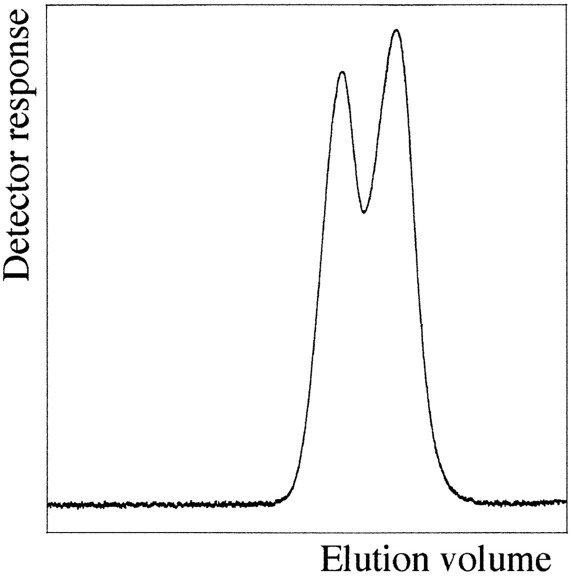


Fig. 3. Size exclusion chromatogram of a monocyclic polyisoprene prepared with $(CH_3)_2SiCl_2$ in the presence of 15 vol% of THF.

molecular weight larger than that of the monocycle is high (~47%) and the value of the elution volume shows that this compound is mainly the dimer of the cyclic product.

3.2.2. Cyclization in nonpolar solvent

Coupling reactions with chlorosilanes are generally carried out in the presence of THF to enhance the reactivity, but this additive is unnecessary, due to the high reactivity of the Si–Cl bond. Experiments were carried out in pure hexane, solvent of the α,ω-dilithiopolyisoprene.

In the first one, a stoichiometric amount of dimethyldichlorosilane was added to a low concentration in Li active centers (3.5×10^{-4} mol l^{-1}) and the reaction was followed by monitoring the decrease of the concentration of active centers by UV spectrometry at 290 nm. The optical density decreased progressively over 5 h and remained stable afterward. The mixture was kept 24 h and a new small amount of dichlorosilane was added. No change in the spectrum was observed and, as a result, it was concluded that the coupling reaction was really achieved after 5 h reaction.

As shown on Fig. 4, curve A the yield in monocyclic polyisoprene is equal to 88%, and the molar mass of the remaining material is close to that of the bicyclic compound.

So the absence of THF in the medium favored greatly the synthesis of monocyclic species at low Li concentration. Keeping in mind this result, a second experiment involving an higher concentration in active centers (i.e. 2.65×10^{-3} mol l^{-1}) was made. The SEC chromatogram (Fig. 4, curve B) shows that the increase of the concentration in active centers by a factor 7 has only a little effect on the yield in monocyclic polyisoprene which remains high (82%).

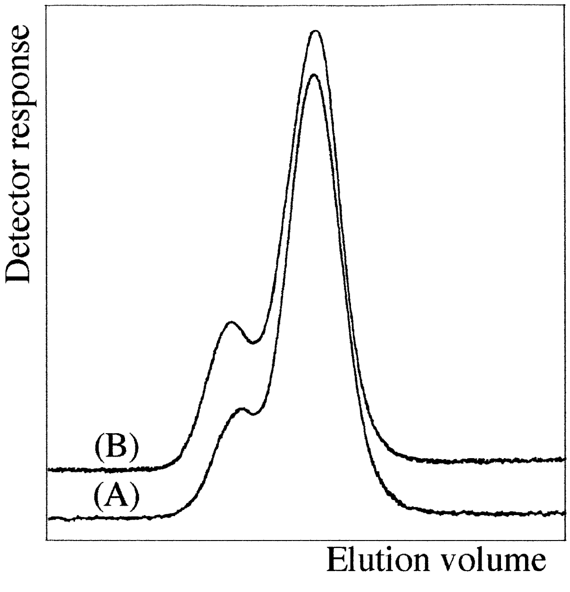


Fig. 4. Size exclusion chromatogram of a monocyclic polyisoprene prepared with $(CH_3)_2SiCl_2$ in pure hexane. (A) [Li] = 3.5×10^{-4} mol l^{-1}; (B) [Li] = 2.65×10^{-3} mol l^{-1}.

In order to follow the formation of high molar mass material (by polycondensation reaction) during the reaction of cyclization, experiments involving successive additions of dichlorodimethylsilane on a α,ω-dilithiopolyisoprene ([Li] = 5×10^{-4} mol l^{-1}) solution were carried out.

A first amount of chlorosilane ([Si–Cl]/[Li] ~ 0.3) was added to the solution and the reaction was monitored by UV spectrometry. The optical density at 290 nm decreased first and did not change after several hours. After hours of reaction 28% of the active centers were deactivated. A sample (A) was then taken off and a second amount of dichlorosilane ([Si–Cl]/[Li] ~ 0.7) was added leading to the deactivation of 42% of the living active centers. As a consequence only 30% of active chains remained in the medium. At this stage of the reaction a second sample (B) was taken off and isoprene was added in order to obtain information on the mixture. After polymerization, the solution was deactivated by addition of methanol (C).

The SEC analysis of the samples (A), (B) and (C) (Fig. 5) shows the progressive increase in cyclic dimer formed during the reaction: 5% after the first addition (Fig. 5, curve A) and about 10% (Fig. 5, curve B) after the second.

The polymerization of isoprene on the remaining active centers yielded a high molar mass polyisoprene ($M_n = 3.2 \times 10^5$ g mol^{-1}), in good agreement with the theoretical value ($M_n = 2.9 \times 10^5$ g mol^{-1}), calculated from the amount of added isoprene and the expected remaining active centers concentration after the addition of dichlorodimethylsilane, and showing a polydispersity index $M_w/M_n = 1.5$ (Fig. 5, curve C). The presence of nonreacted dichlorosilane being practically inconceivable, the relatively broad distribution of this material could be due to the presence of LiCl formed during the cyclization reaction. It could be assumed that this salt is involved in mixed aggregates with α,ω-dilithiopolyisoprene, even if a previous study by ^{7}Li NMR did not allow to detect them [28]. Such species could have an influence on the kinetics of the polymerization of isoprene. As the rate of polymerization of isoprene is low in these conditions, this observation could also be attributed to the presence of monofunctional polyisoprenyl-lithium resulting of a transfer reaction of the remaining Li active centers on the monomer units linked to the silicon atom of a cyclic or linear polymer leading to branched living polyisoprene.

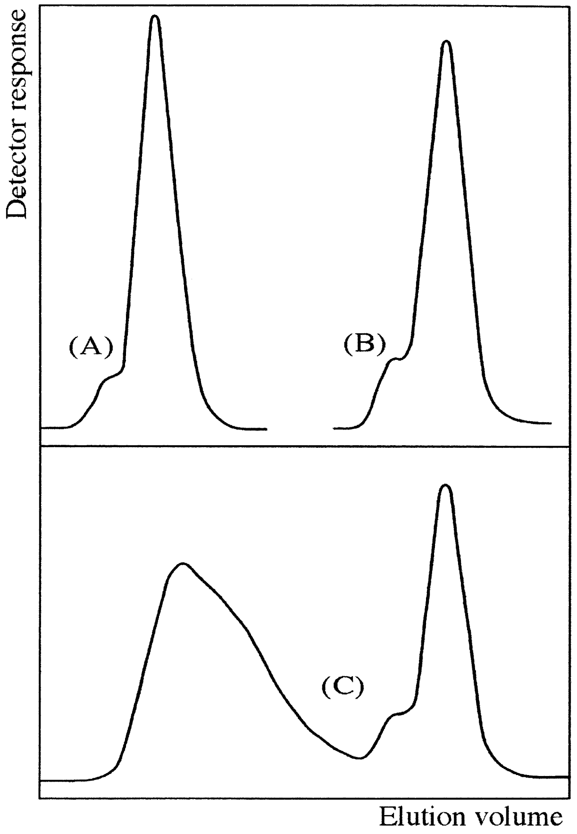


Fig. 5. Size exclusion chromatogram of cyclization reaction involving various concentrations in $(CH_3)_2SiCl_2$ in pure hexane. (A) Addition of 30% of dichlorosilane with respect to Li, (B) addition of 70% of dichlorosilane with respect to Li and (C) addition of isoprene onto (B).

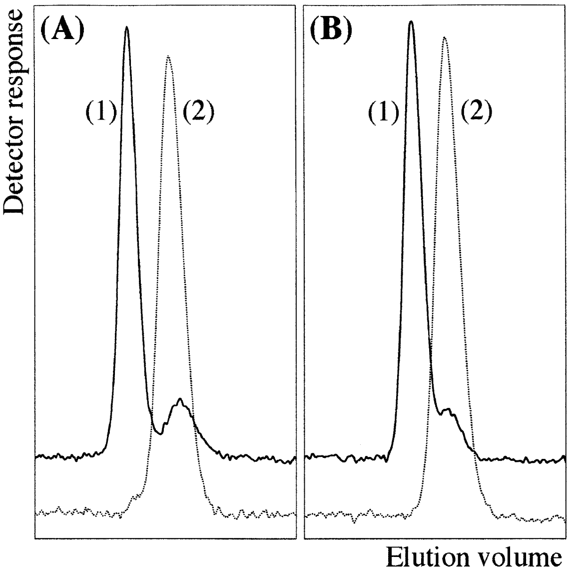


Fig. 6. Size exclusion chromatograms of coupling reaction of monofunctional polyisoprenyllithium with $(CH_3)_2SiCl_2$ in hexane. ([Si–Cl]/[Li] ~ 1.0). (A) In the presence of 15 vol% of THF, $T = -50°C$, $[Li] = 1.6 \times 10^{-2}$ mol l^{-1} and (B) in pure hexane, at r. t., $[Li] = 2 \times 10^{-2}$ mol l^{-1}. 1: After coupling reaction; 2: parent monofunctional polymer.

3.3. Coupling of monofunctional polyisoprenyllithium with chlorosilanes

In order to understand the origin of that behavior, the coupling reaction of monofunctional polyisoprenyllithium with dichlorodimethylsilane was studied as a model reaction in similar experimental conditions.

In the presence of 15 vol% of THF at −50°C, at a Li concentration equal to 1.6×10^{-2} mol l^{-1}, the coupling efficiency of a monofunctional living polymer having a DP equal to 35 was found (after 1 h reaction) higher than 80%, as shown in Fig. 6, curve A.

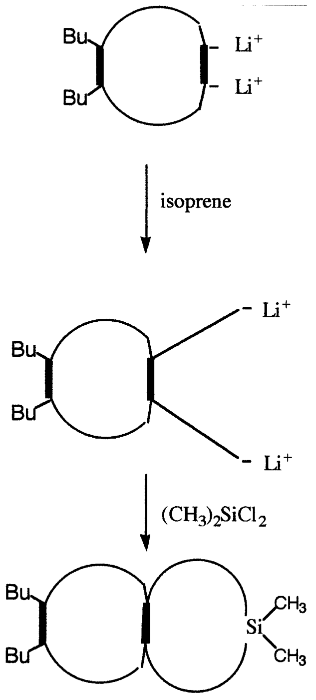
In pure hexane, the same reaction was carried out at room temperature (Li concentration $= 2 \times 10^{-2}$ mol l^{-1}, DP = 38) leading to a slightly higher efficiency (~90%), as previously observed in the case of the bifunctional living polymer (see Fig. 6, curve B). Nevertheless, for monofunctional polymer the effect is less pronounced due to the absence of polycondensation reaction leading to polymers having molar masses higher than the expected one by the coupling reaction.

Moreover, two samples of monofunctional polyisoprenyllithium having a DP equal respectively to 26 and 41 with an identical active center concentration ($[Li] = 2.4 \times 10^{-2}$ mol l^{-1}) were reacted during 24 h at room temperature with $SiCl_4$ ([Si–Cl]/[Li] ~ 1.0) in pure hexane. Both experiments led to a four branched polymer (DP = 112 and 165 respectively) with a transformation yield in the 83–85% range. This last result can be compared to that previously obtained by Sigwalt and coworkers [21] who observed an efficiency close to 70% for the reaction of α,ω-dilithiopolyisoprene with $SiCl_4$ in hexane in the presence of 15 vol% of THF at −45°C.

These observations confirm the difference between monofunctional and bifunctional polyisoprenyllithium and also stress the point that the substitution reaction at Si–Cl bond is preferably performed in the absence of a polar solvent such as THF even at low temperature (−50°C) in order to prevent the deactivation of the isoprenyl active centers.

3.4. Synthesis of an "eight-shaped" polymer

Sigwalt and coworkers [21] showed that an unexpected high yield (≈70%) of bicyclic compound was obtained through cyclization of α,ω-dilithiopolyisoprene with $SiCl_4$ in the presence of 15 vol% of THF. This type



Scheme 2. Reaction pathway for synthesis of bicyclic polyisoprenes.

of bicyclic compound may be obtained by cyclization of a monocycle having two living arms as shown in Scheme 2.

So starting from a bifunctional polyisoprenyllithium of DP = 200 at $[Li] = 4 \times 10^{-4}$ $mol\,l^{-1}$ a solution of BIPE (stoichiometric amount) was added at −50°C followed by the addition of 15 vol% of THF. After 3 h of reaction a small amount of isoprene (Isoprene)/[Li] ∼ 10) was distilled in the mixture and a sample was taken off for analysis after polymerization. The experimental DP was found equal to 220 which is very close to the theoretical value. The elution volume is slightly higher than that of the cyclic compound. Apparently, the two short arms seem to have an effect on the hydrodynamic volume, this effect being probably enhanced by the chemical structure of the two arms (1, 2/3, 4 vinyl units). A second addition of isoprene, leading to two branches of $DP_n = 35$ was made (SEC trace shown in Fig. 7 – curve A). A stoichiometric amount of dichlorodimethylsilane was then distilled into the medium. The resulting polymer was analyzed by SEC and the chromatogram (Fig. 7 – curve B) shows the presence of bicyclic polyisoprene ($DP_n = 260$) and of a polycondensate of higher molar mass ($DP_n = 550$).

The yield in bicyclic compound was about 60%, value which is similar to that obtained when the cyclization reaction was performed with $SiCl_4$ (70%) and to that of the synthesis of monocyclic polyisoprene carried out in the same experimental conditions with $(CH_3)_2SiCl_2$ as coupling agent (53%).

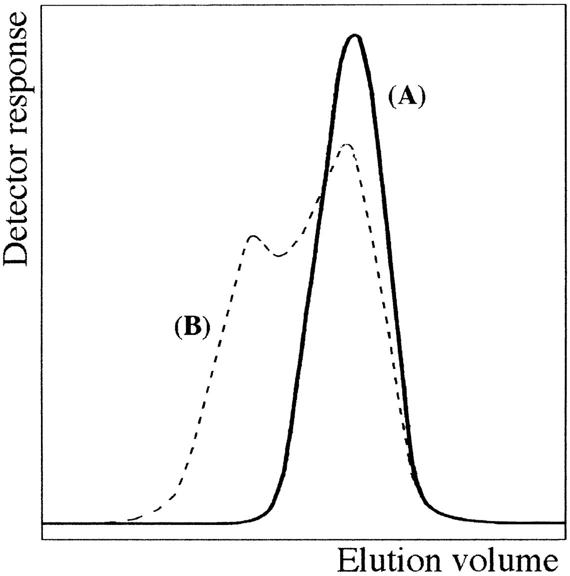


Fig. 7. Size exclusion chromatogram of the crude product (B) obtained during the synthesis of “figure of eight-shaped” polyisoprene ((A): starting material).

4. Conclusion

The main purpose of this study was to synthesize a bicyclic polyisoprene according to the following mechanism: (i) cyclization of a α,ω-dilithiopolyisoprene with a diethylenic compound (BIPE), (ii) branching of two arms on the resulting cycle and (iii) cyclization of this compound by a second coupling reaction. As the cyclization reaction with BIPE requires the addition of 15 vol% of THF, the stability of various living solutions has been studied at room temperature.

The stability of the α-methylstyryllithium type carbanions formed during the first cyclization is not sufficient at room temperature. Nevertheless the addition of some isoprene units to the living monocycle at low temperature leads to a monocycle with two isoprenyllithium centers stable enough at room temperature for further transformations.

If the excellent efficiency (near 100% up to DP = 200) of the coupling with BIPE in the presence of 15 vol% THF was already known [21], this work shows that cyclization is much less efficient with dichlorodimethylsilane $(CH_3)_2SiCl_2$. The reaction seems to be greatly disfavored by the presence of 15 vol% of THF (only 53% of monocyclic polyisoprene are obtained for a concentration of $[Li] = 4 \times 10^{-4}$ $mol\,l^{-1}$). However, in a nonpolar solvent (pure hexane) and for same dilute solutions

($[\mathrm{Li}] = 3.5 \times 10^{-4}$ $\mathrm{mol\,l^{-1}}$) a high yield of monocyclic compound was obtained (88%). At higher concentration in pure hexane ($[\mathrm{Li}] = 2.65 \times 10^{-3}$ $\mathrm{mol\,l^{-1}}$) the yield in cyclic polymer remains approximately the same.

Cyclization of a two armed monocyclic polyisoprene leading to bicyclic compounds gives only 60% of pure material, confirming the harmful effect of THF on the cyclization reaction using chlorosilanes.

References

[1] Kramers HAJ. Chem Phys 1946;14:415.
[2] Zimm BH, Stockmayer WHJ. Chem Phys 1949;17:1301.
[3] Jacobson H, Stockmayer WHJ. Chem Phys 1950;18:1600.
[4] Semlyen JA. Large ring molecules. New York: Wiley; 1996.
[5] Ederle Y, Naraghi S, Lutz PJ. Synthesis of polymers: materials science and technology series. New York: Wiley; 1999. p. 622.
[6] Chojnowski J, Cypryk M. Cyclic siloxanes in polymeric material encyclopedia. 1995.
[7] Sigwalt P, Masure M, Moreau M, Bischoff R. Makromol Chem Macromol Symp 1993;73:147.
[8] Semlyen JA. Adv Polym Sci 1976;21:41.
[9] Hild G, Kohler A, Rempp P. Eur Polym J 1980;16:525.
[10] Geiser D, Höcker H. Macromolecules 1980;13:653.
[11] Vollmert B, Huang JX. Makromol Chem Rapid Commun 1980;1:333.
[12] Vollmert B, Huang JX. Makromol Chem Rapid Commun 1981;2:467.
[13] Roovers J, Toporowski PM. Macromolecules 1983;16:843.
[14] Antonietti M, Folsch KJ. Makromol Chem Rapid Commun 1988;9:423.
[15] Quirk RP, Ma JJ. Polym Prepr Am Chem Soc Div Polym Chem 1988;29(2):10.
[16] Behda MC, Gibson HW. Polym Prepr Am Chem Soc Div Polym Chem 1990;31(1):588.
[17] Roovers J, Toporowski PM. J Polym Sci Polym Phys Ed 1988;26:1251.
[18] Hogen-Esch TE, Sundarajan J, Toreki W. Makromol Chem Macromol Symp 1991;47:23.
[19] Gan YD, Zöller J, Yin R, Hogen-Esch TE. Makromol Chem Macromol Symp 1994;77:93.
[20] Ma JJ. Polym Prepr Am Chem Soc Div Polym Chem 1993;34(2):626.
[21] El Madani A, Favier JC, Hémery P, Sigwalt P. Polym Int 1992;27:353.
[22] Hémery P, Boutillier JM, El Madani A, Favier JC, Sigwalt P. Polym Prepr Am Chem Soc Div Polym Chem 1994; 35(2):478.
[23] Morton M, Fetters LJ. J Polym Sci Part A2 1964: 3311.
[24] Brody M, Ladacki M, Milkovitch R, Szwarc M. J Polym Sci 1957;XXV:221.
[25] Guyot P, Favier JC, Uytterhoeven H, Fontanille M, Sigwalt P. Polymer 1981;22:1724.
[26] Guyot P, Favier JC, Fontanille M, Sigwalt P. Polymer 1982;23:73.
[27] Obriot I, Favier JC, Sigwalt P. Polymer 1987;28: 2093.
[28] Boutillier JM, Favier JC, Hémery P, Sigwalt P. Polymer 1996;37:5197.
[29] Okamoto A, Watanabe E, Mita I. J Polym Sci Polym Chem Ed 1979;17:2483.
[30] Gourdenne A, Sigwalt P. Eur Polym J 1967;3:481.
[31] Bywater S, Johnson AF, Worsfold DJ. Can J Chem 1964;42:1255.