



Controlled radical polymerization of conjugated 1,3-dienes with methyl 1,3-butadiene-1-phosphonate

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ABSTRACT

Preparation of new tailor-made phosphorus-containing polydiene materials via controlled radical copolymerization of dimethyl 1,3-butadiene-1-phosphonate (BP^{M_e}) with chloroprene (CP) or isoprene (IP), by using, respectively, AIBN or an alkoxyamine derivative as initiator, is reported. The corresponding materials have been microstructurally characterized by ¹H and ³¹P NMR spectroscopies.

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1. Introduction

Owing to the numerous potential applications of rubber materials (tyres, adhesives, etc.), polymers derived from conjugated dienes are of major industrial importance [1]. Among the new materials that have been recently developed, polydienes containing phosphonate or phosphate functionalities are of particular interest, due to their modified properties (e.g., flame retardation, anti-corrosive and/or anti-oxidizing properties,...) [2]. One of the most convenient routes to phosphorylated polymers is usually radical copolymerization of conjugated dienes. However, only few examples of direct introduction of phosphonate groups by copolymerization of conjugated dienes with dialkyl 1,3-butadiene-1-phosphonate have been reported [3]. Moreover, in all cases the polymerization reaction was poorly controlled.

Recent advances in controlled (“living”) radical polymerization (CRP) have made it possible to design and synthesize at will synthetic polymers from a wide variety of monomers including nonpolar and polar, conjugated and unconjugated monomers, such as styrenics, dienes, (meth)acrylates, acrylamides and acrylonitrile [4]. The success of CRP relies on the robustness of radical chemistry and the capacity to control the polymer structure (predetermined molecular weight, narrow molecular weight distribution, well-defined end groups, and architecture) under milder experimental conditions than living ionic polymerization [5,6]. Nitroxide-based systems are among the most used CRP systems [7]. In fact,

nitroxide-mediated polymerization (NMP) is very attractive because it is metal-free and effective in the polymerization of a broad range of monomers, including conjugated dienes [7,8]. Either bimolecular or unimolecular initiators can be used in NMP [9]. The bimolecular initiation requires combining a traditional free-radical initiator (e.g., 2,2'-azobis(isobutyronitrile) (AIBN)) with a nitroxide (e.g., 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)) [10]. However, this type of systems is limited by the poorly defined structure and concentration of the initiating species. In contrast, thermolysis of a well-defined unimolecular initiator, such as an alkoxyamine, releases both the initiating radical and the nitroxide in a 1:1 molar ratio. As a result, the initiator efficiency is improved (close to unity) compared with bimolecular initiation and the structure of the chain ends is well defined.

Recently we have reported an effective preparation of new tailor-made phosphorylated polymers by combining two consecutive catalytic transformations [11]. This combination consists in the synthesis of new isoprene-co-1,3,7-octatriene copolymers by Ziegler–Natta catalysis, followed by subsequent modification of the pendant vinyl groups by regioselective Rh-catalyzed hydrophosphorylation. As an extension of our interest in this field, we have investigated, as an alternative, more direct route, the controlled radical copolymerization of chloroprene or isoprene with dimethyl 1,3-butadiene-1-phosphonate, a readily available monomer [12], by using, respectively, AIBN or an alkoxyamine derivative as initiator. We describe in this paper the one-step syntheses of the corresponding phosphonate-functionalized copolymers. The structure of the polymeric chains has been also established on the basis of detailed NMR analyses.

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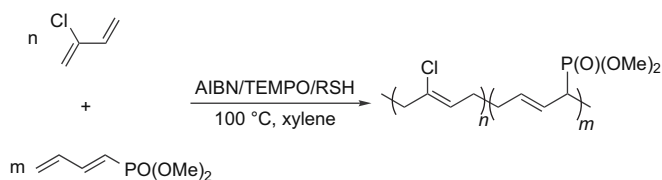
2. Results and discussion

2.1. Free-radical copolymerization of chloroprene and dimethyl *trans*-1,3-butadiene-1-phosphonate

The copolymerization of chloroprene (hereafter abbreviated CP; used as a 50 wt-% solution in xylene) and dimethyl *trans*-1,3-butadiene-1-phosphonate (BP^{Me}) was investigated with AIBN initiator, in the presence of both a transfer agent (i.e., *n*-dodecylmercaptan, RSH) [13] and a control agent (TEMPO) (Scheme 1). As our objective was the preparation of polydienes modified by few phosphonate moieties [11], an initial loading of 2–5 mol-% of BP^{Me} (vs. CP) was used in most cases [14]. All reagents were first mixed at room temperature, and the mixture was then heated at 100 °C under argon. Table 1 summarizes typical results obtained under different polymerization conditions, with variable ratios of AIBN, TEMPO and RSH [15].

The final reaction mixtures and copolymers were analyzed by ¹H, ³¹P NMR, GPC and DSC, allowing the determination of monomers' conversion and detailed characterization of the copolymers (*vide infra*). All the copolymers were recovered as translucent gummy solids and found to contain ca. 2–3 mol-% of incorporated BP^{Me} (when an initial loading of 2–5 mol-% of BP^{Me} vs. CP was used; content determined by ¹H NMR). Considering the isolated yields of copolymers (Table 1), such phosphonate content indicates a ca. 60–70% conversion of the BP^{Me} monomer initially loaded, a conversion value which was independently confirmed by ³¹P NMR (*vide infra*) on crude reaction mixtures. Overall, whatever the conditions used for the copolymerizations, the conversion values of BP^{Me} and CP appeared quite similar, which indicates a similar reactivity of both monomers. This trend was also confirmed by an experiment with a much larger initial loading of BP^{Me} (21.0 mol-% vs. CP), which resulted in a copolymer with 12.7 mol-% of incorporated phosphonate monomer (entry 12).

A first series of reactions was performed by changing the TEMPO-to-AIBN ratio. The highest molecular weights were achieved without both control and transfer agents ($M_n \geq 42,300 \text{ g mol}^{-1}$; entries 1 and 2). In the presence of a control agent (TEMPO), but still without transfer agent, the molecular weights were somewhat lower ($M_n = 20,000\text{--}30,000 \text{ g mol}^{-1}$; entries 3–5). The corresponding molecular weight distributions were all unimodal and moderately narrow ($M_w/M_n = 1.8\text{--}2.4$). Expectedly, by using a transfer agent (RSH), lower molecular weights were obtained, along with similar polydispersity values ($M_n = 5800\text{--}7400 \text{ g mol}^{-1}$; $M_w/M_n = 1.9\text{--}2.4$, entries 6–8) [13]. Adding the whole initiator at once resulted in limited, variable monomer conversions, most presumably due to usual deactivation processes (Table 1, entries 1–8) [16]. To circumvent this limitation, we studied the effect of adding sequentially the AIBN initiator over the reaction course [17]. Although this approach is obviously incompatible with a living process, our results show that it eventually improved the polymerization efficiency and reproducibility as well, leading to significantly higher monomer conversions, and still maintaining a reasonable degree of control over the polymerization (entries 9–11). This observation is in line with common practice in commercial



Scheme 1. Preparation of CP-co-BP^{Me} copolymers via free-radical polymerization of chloroprene and dimethyl *trans*-1,3-butadiene-1-phosphonate with AIBN/TEMPO/RSH systems.

Table 1

Copolymerization of chloroprene (CP) and dimethyl *trans*-1,3-butadiene-1-phosphonate (BP^{Me}) with AIBN/TEMPO/RSH systems^a

Entry	BP ^{Me} (mol-%)	CP (mmol)	TEMPO/AIBN ^b	RSH (wt-%/CP)	Yield ^c (%)	M_n^{expd} (10^{-3} g/mol)	M_w/M_n^d	T_g^e (°C)
1	0	22.7	0	0	57	46.3	2.46	−35.9
2	2.0	22.7	0	0	56	42.3	2.25	−33.3
3	5.4	22.7	0.5	0	66	29.7	1.84	nd
4	2.5	22.7	0.5	0	50	20.3	1.94	nd
5	5.4	22.7	1.1	0	33	30.2	2.37	nd
6	2.5	11.4	1.2	2.8	69	5.8	1.92	nd
7	3.1	34.1	1.2	2.8	58	7.1	2.44	nd
8	2.9	28.4	0	2.8	61	7.4	2.10	nd
9 ^f	2.9	22.7	0	2.8	72	7.9	1.51	nd
10 ^f	2.9	22.7	1.2	2.8	79	11.8	1.60	−31.5
11 ^{fg}	2.9	22.7	1.2	2.8	80	13.6	1.71	−32.2
12	21.0	22.7	1.2	0	48	38.5	2.10	−13.2

^a AIBN: 0.5 wt-% vs. monomer, polymerization carried out at 100 °C for 24 h.

^b Molar ratio.

^c Yield of isolated copolymer; consistent within $\pm 5\%$ with monomer conversions determined by NMR.

^d Determined by GPC vs. PS standards.

^e Determined by DSC.

^f AIBN (0.02 mmol) added 3 times every 3 h.

^g TEMPO (0.04 mmol) added 2 times every 3 h.

polymerization processes, which often involve the addition of multiple charges of initiator during the reaction course to minimize the molecular weight broadening at high conversion [18].

GPC analyses, with dual UV and refractive index detections, evidenced that only true P(CP-co-BP^{Me}) copolymers with monodisperse distributions are produced and that the copolymers actually contain phosphonate moieties. Indeed, the UV spectrum of dimethyl *trans*-1,3-butadiene-1-phosphonate in methanol features a maximum absorption at 250 nm, attributed to the P=O bond. In contrast, polychloroprene does not absorb around this wavelength. For instance, GPC analysis of a representative copolymer (Table 1, entry 10) by using dual UV/RI detection showed that the phosphonate group (detected by UV) is equally distributed over the whole polymer distribution (detected by RI) (Fig. 1).

The copolymers were also characterized by ¹H and ³¹P{¹H} NMR spectroscopies. The BP^{Me} content in the copolymers was readily determined by ¹H NMR, from the relative integration between the vinyl hydrogens of CP units (δ 5.44 ppm) and the methoxy group of BP^{Me} units (δ 3.7–3.8 ppm). NMR data show that the polychloroprene backbone in those P(CP-co-BP^{Me}) copolymers retain more than 95% of 1,4-microstructure (mixture of 1,4-*trans* and 1,4-*cis*, with head-to-head (hh), head-to-tail (ht) and tail-to-tail (tt) enchainments) (Fig. 2) [19]. As regards the inserted BP^{Me} monomer, the most noticeable NMR features include the appearance of two groups of resonances in the ³¹P{¹H} NMR spectrum, showing each

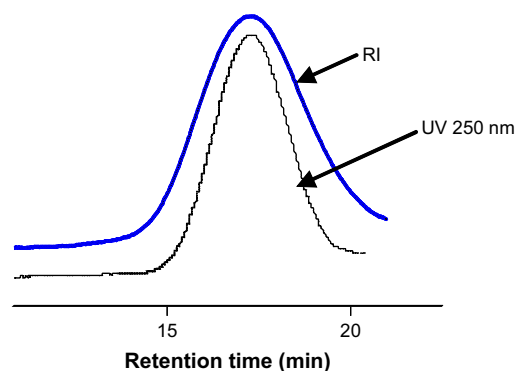


Fig. 1. Typical GPC traces (THF, 25 °C) with dual UV/RI detections of a P(CP-co-BP^{Me}) copolymer produced by AIBN/*n*-C₁₂H₂₅SH/TEMPO (Table 1, entry 10).

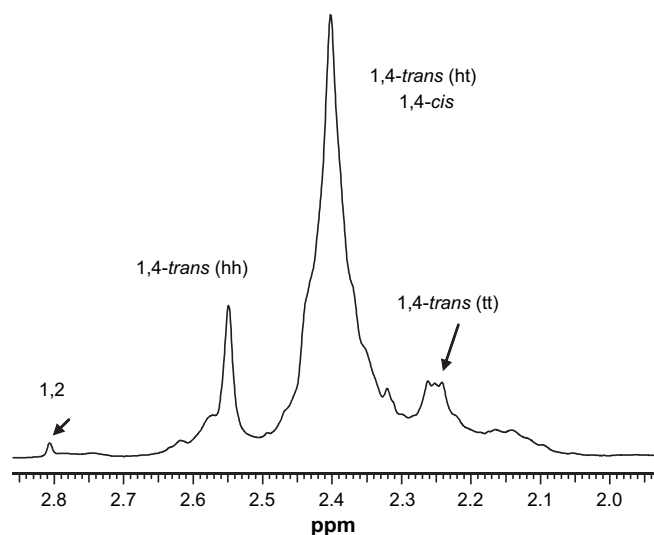


Fig. 2. Methylene region of the ^1H NMR spectrum (300 MHz, CDCl_3 , 20°C) of a P(CP-co-BP $^{\text{Me}}$) copolymer (Table 1, entry 4).

one main singlet of similar intensity at δ 21.4 ppm and 31.5 ppm (vs. δ 19.65 ppm for BP $^{\text{Me}}$ monomer) (Fig. 3) [20]. The 2D HMQC ^1H - ^{31}P NMR spectrum of P(CP-co-BP $^{\text{Me}}$) copolymers shows the presence of correlation cross-peaks between the main phosphorus resonance at δ 21.4 ppm with the vinyl hydrogens of BP $^{\text{Me}}$ at δ 5.5 and 6.5 ppm, and between the main phosphorus resonance at δ 31.5 ppm with the aliphatic hydrogens at 2.7–3.0 ppm region (Fig. 4). This observation indicates that BP $^{\text{Me}}$ units are inserted in the polychloroprene main chain in two strongly different manners: about the half of the phosphonate moieties (δ 31.5 ppm) are connected to a C(sp 3), which is consistent with the expected 1,4-*trans* and 1,4-*cis* microstructures (Chart 1), while the other half of the phosphonate moieties (δ 21.4 ppm) are connected to a C(sp 2); the latter situation can be accounted by a 3,4-microstructure, as commonly observed in the free-radical polymerization of 1-substituted-1,3-dienes [21], and/or a “tautomerized” 1,4-microstructure in which the C=C bond would be conjugated with the phosphonate moiety (Chart 1) [22].

DSC analyses showed that introduction of 2–3 mol-% of BP $^{\text{Me}}$ in polychloroprene had a limited influence on the glass transition temperatures of these polymers. The T_g values of these P(CP-co-BP $^{\text{Me}}$) copolymers were found in the range -33 to -31°C , that is a minimal increase as compared to the glass transition temperature (-36°C) of a polychloroprene prepared under similar conditions (Table 1). Consistently, the incorporation of a large amount of phosphonate monomer (12.7 mol-%) led to a more noticeable increase of the T_g value (-13°C , entry 12).

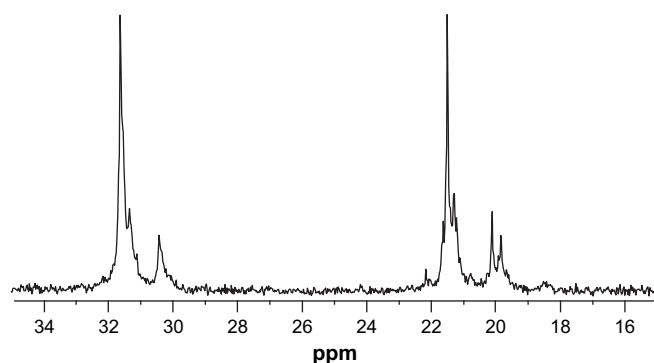


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.5 MHz, CDCl_3 , 20°C) of a P(CP-co-BP $^{\text{Me}}$) copolymer initiated by AIBN/TEMPO/ n -C $_{12}$ H $_{25}$ SH (Table 1, entry 10).

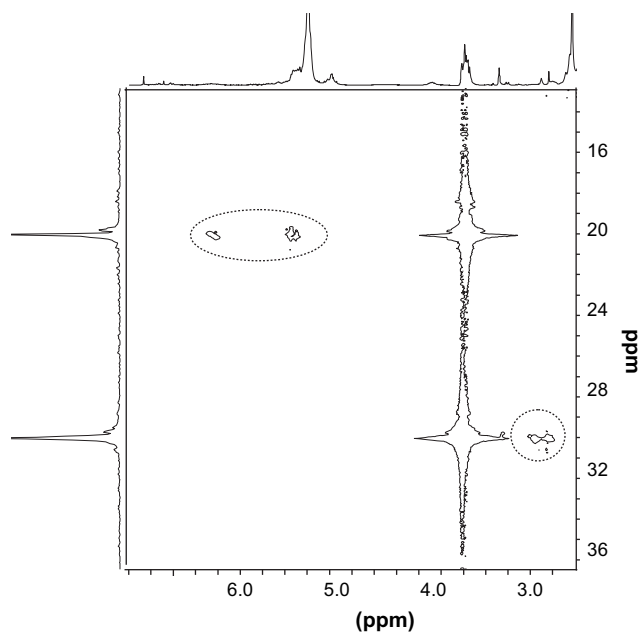


Fig. 4. ^1H - ^{31}P HMQC spectrum (CDCl_3 , 20°C) of a P(CP-co-BP $^{\text{Me}}$) copolymer (Table 1, entry 10).

2.2. Controlled-living radical copolymerization of isoprene with dimethyl *trans*-1,3-butadiene-1-phosphonate

Initial attempts at copolymerizing dimethyl *trans*-1,3-butadiene-1-phosphonate (BP $^{\text{Me}}$) with isoprene (IP) using the same system as the one used above for CP led to poor monomer conversion and recovery of a quite low molecular weight polymer [23]. These results reflect the known poor ability of AIBN/TEMPO systems to promote the polymerization of conjugated dienes in general (*vide supra*).

The controlled-living polymerization of isoprene mediated by an alkoxyamine was reported by Hawker and coworkers [8b]. We therefore selected this alkoxyamine initiator (**1**) to investigate the copolymerization of isoprene (IP) with dimethyl *trans*-1,3-butadiene-1-phosphonate (BP $^{\text{Me}}$) (Scheme 2). The alkoxyamine **1** was mixed at room temperature with bulk reagents (i.e., IP and BP $^{\text{Me}}$; no solvent), and then heated at 125°C under argon in a Teflon-valved glass reactor. Table 2 summarizes representative results obtained under different polymerization conditions. In all cases, with 2.5–2.7 mol-% of BP $^{\text{Me}}$ (vs. IP) initially engaged, the formed copolymers contained approximately the same amount of incorporated BP $^{\text{Me}}$ (2.2–2.6 mol-%) (Table 2, entries 1–5) [15].

Preliminary experiments were first carried out by adding the alkoxyamine **1** at once. However, under these reaction conditions, the yield did not exceed 46%, and the experimental M_n values did

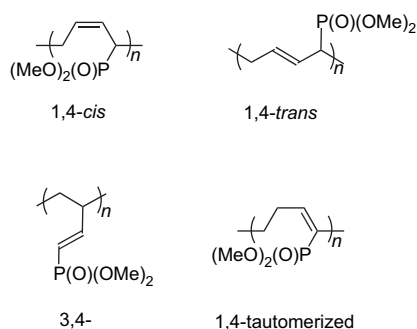
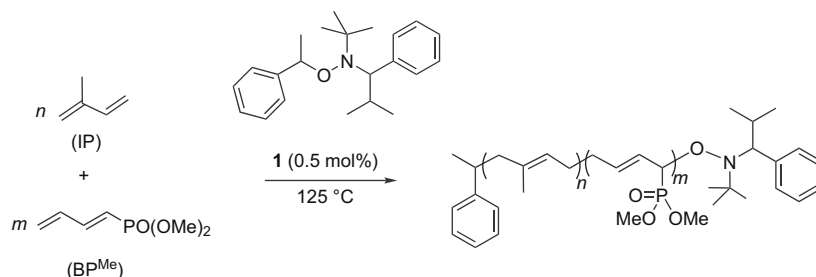


Chart 1. Possible microstructures for BP $^{\text{Me}}$ units in P(CP-co-BP $^{\text{Me}}$) copolymers.



Scheme 2. Preparation of P(IP-co-BP^{Me}) copolymers via alkoxyamine-mediated controlled-living copolymerization of isoprene with dimethyl *trans*-1,3-butadiene-1-phosphonate.

Table 2
Copolymerization of isoprene (IP) and dimethyl *trans*-1,3-butadiene-1-phosphonate (BP^{Me})^a

Entry	[IP]/[1]	BP ^{Me} (mol-%)	Reac. time (h)	Yield (%)	BP ^{Me} ^b (mol-%)	$M_{n,theo}^c$ (10^{-3} g/mol)	$M_{n,exp}^d$ (10^{-3} g/mol)	M_w/M_n^d	1,4- <i>cis</i> (%)	1,4- <i>trans</i> (%)	3,4 (%)	T_g^e (°C)
1	260	2.7	72	33	2.6	5.8	18.7	1.21	36	60	4	−54.8
2	200	2.5	96	40	2.2	5.4	18.5	1.32	36	56.5	7.5	nd
3 ^f	250	2.5	72	78	2.4	13.3	16.8	1.24	35	55	10	−53.6
4 ^f	200	2.5	72	76	2.4	10.5	12.3	1.16	35	58	7	nd
5 ^f	300	0	72	82	0	18.0	21.5	1.20	32	60	8	−57.9
6 ^{f,g}	200 ^g	100 ^g	72	15	100	4.7	1.2	1.25	nd	nd	nd	nd

^a Polymerization carried out at 125 °C in a Teflon-valved glass reactor.

^b Comonomer content determined by ¹H NMR in CDCl₃.

^c Average number molecular weight in g mol^{−1} calculated from the relation: [IP]/[cat] × % conv × 68.

^d Experimental average number molecular weight in g mol^{−1} determined by GPC vs. PS standards.

^e Determined by DSC.

^f **1** (10.9 mg, 0.03 mmol, 3 times) added initially and every 24 h.

^g Homopolymerization of BP^{Me}; no isoprene introduced.

not correspond well with the calculated M_n values (Table 2, entries 1 and 2). To tackle this issue, we added the initiator in several portions over the reaction course. By this way, higher monomer conversions were obtained; also, the polymers produced still exhibited narrow molecular weight distributions ($M_w/M_n = 1.1$ – 1.4) and experimental number-average molecular masses (M_n) close to the theoretical ones (Table 2, entries 3 and 4). Homopolymerization of BP^{Me} proceeded more slowly under these conditions, resulting in modest monomer conversion and recovery of a low molecular weight polymer (Table 2, entry 6).

As described above for the P(CP-co-BP^{Me}) copolymers, GPC analyses of our P(IP-co-BP^{Me}) polymers using dual UV/RI detection demonstrated the formation of true copolymers containing phosphonate moieties; no contamination by homopolymers was detected in crude copolymers prepared under adequate conditions [24]. The resulting copolymers were also characterized by ¹H and ³¹P NMR spectroscopies. The BP^{Me} content in the copolymers was readily determined by ¹H NMR, from the relative integration of the methoxy group of BP^{Me} (δ 3.7–3.8 ppm) and the singlet resonance for the methylene hydrogens of 1,4-polyisoprene (δ 1.67 ppm) (see supplementary data). NMR data show that the polyisoprene backbone in those P(IP-co-BP^{Me}) copolymers contains 55–60% of 1,4-*trans*- and ca. 35% of 1,4-*cis*-units. Essentially the same microstructure was observed for a homopolyisoprene prepared under similar conditions (entry 5). As regards the inserted BP^{Me} monomer, the most noticeable NMR features include the appearance of three major singlet resonances in the ³¹P{¹H} NMR spectrum at δ 22.86, 23.50 and 33.76 ppm (vs. 19.65 ppm for BP^{Me}) (Fig. 5). Those resonances have close chemical shifts to those determined for P(CP-co-BP^{Me}) copolymers (*vide supra*), and suggest that BP^{Me} units inserted in a PI backbone adopt similar microstructures as those inserted in a PCP backbone (Chart 1).

As described above for the P(CP-co-BP^{Me}) copolymers, DSC analyses showed that introduction of 2–3 mol-% of BP^{Me} in polyisoprene had also only a limited influence on the glass transition

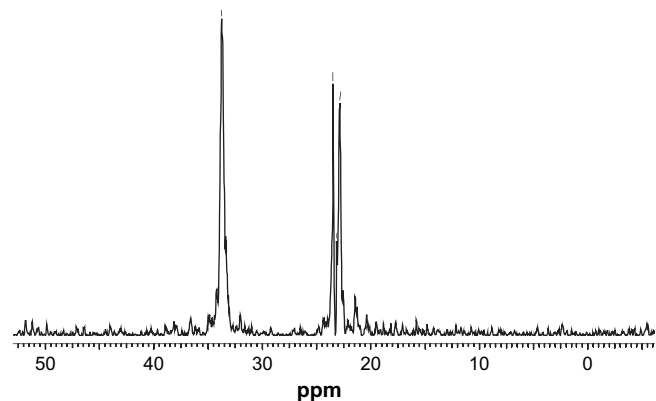


Fig. 5. ³¹P{¹H} NMR spectrum (121.5 MHz, CDCl₃, 20 °C) of a P(IP-co-BP^{Me}) copolymer initiated by the alkoxyamine **1** (Table 2, entry 2).

temperatures of these polymers. The T_g values of these P(IP-co-BP^{Me}) copolymers were found in the range −55 to −53 °C, that is a small increase as compared to the glass transition temperature (−58 °C) of a polyisoprene prepared under similar conditions (Table 2). It is interesting to note that these T_g values compare well those determined for related phosphonated polyisoprene materials ($T_g = -57$ to -52 °C for 2–5 mol-% phosphonate contents) prepared by Rh-catalyzed hydrophosphorylation of isoprene-*co*-1,3,7-octatriene copolymers initially obtained by Ziegler–Natta catalysis [11].

3. Conclusion

In conclusion we have demonstrated the possibility to prepare tailor-made phosphorylated polymers by controlled radical polymerization. New chloroprene-*co*-dimethyl *trans*-1,3-butadiene-1-phosphonate copolymers and isoprene-*co*-dimethyl-*trans*-1,3-butadiene-1-phosphonate copolymers were prepared, respectively,

by bimolecular and unimolecular initiators. In particular, the results obtained by using an alkoxyamine as the initiator suggest a number of new avenues for functionalized copolymerization.

4. Experimental section

4.1. General conditions

All manipulations requiring dry atmosphere were performed under purified argon by use of standard Schlenk techniques. Chloroprene (50 wt-% solution in xylene), TEMPO and *n*-dodecylmercaptan were purchased from Aldrich and used as-received. Azobisisobutyronitrile (AIBN) was purified via recrystallisation in diethyl ether. Isoprene (99.98%) was distilled over CaH₂ prior to use. Dimethyl *trans*-1,3-butadiene-1-phosphonate (BP^{Me}) [12] and 2,2,5-trimethyl-3-(1'-phenylethoxy)-4-phenyl-3-azahexane (**1**) [8b] were prepared according to the literature procedures.

¹H (200 and 300 MHz) and ³¹P (121.5 MHz) NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers at ambient probe temperature. ¹H NMR chemical shifts are reported in ppm vs. SiMe₄ and were determined by reference to the residual solvent peaks. ³¹P{¹H} NMR chemical shifts were referenced to external H₃PO₄. Molecular weights of copolymers were determined by gel permeation chromatography (GPC) at room temperature on a Waters 600 apparatus equipped with five PL gel columns (Polymer Laboratories Ltd), an autosampler Waters WISP 717, a differential refractometer Shimadzu RID 6A and an UV Shimadzu detector. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹. Polystyrene standards were used for molecular weight universal calibration.

4.2. Preparation of poly[(chloroprene)-co-(dimethyl *trans*-1,3-butadiene-1-phosphonate)] and poly[(isoprene)-co-(dimethyl *trans*-1,3-butadiene-1-phosphonate)]

A typical procedure in the case of chloroprene is as follows (Table 1, entry 10): a mixture of AIBN (3.3 mg, 0.2 wt-% vs. monomers), chloroprene (4.00 g of a 50 wt-% in xylenes, 22.7 mmol), BP^{Me} (0.11 g, 0.70 mmol), TEMPO (5.5 mg, 0.04 mmol), and *n*-dodecylmercaptan (59.0 mg, 2.8 wt-% vs. monomers) was introduced in a Teflon-valved Schlenk flask with a magnetic stir bar. The homogenous solution was degassed by 3 freeze/thaw cycles, placed under argon and heated at 100 °C. Additional AIBN (3.3 mg, 0.2 wt-% vs. monomers) and TEMPO (5.5 mg, 0.04 mmol) were re-loaded each 3 h under argon, after cooling the reaction mixture to room temperature and opening the glass reactor under argon. After the desired polymerization time, the reaction was quenched by adding a methanol solution acidified with 10% HCl (ca. 1 mL), and methanol (ca. 10 mL) was further added. The supernatant was removed, and the polymer was washed with methanol and dried under vacuum at 40 °C for 8 h. The polymer was then dissolved in dichloromethane (5 mL) and precipitated (twice) into methanol (100 mL). The colorless gummy translucent precipitate was then collected and further dried in vacuum.

Preparation of poly[(isoprene)-co-(dimethyl *trans*-1,3-butadiene-1-phosphonate)] was carried out in a similar way, starting from alkoxyamine **1** (32.7 mg, 0.10 mmol), isoprene (1.33 g, 19.5 mmol), and dimethyl *trans*-1,3-butadiene-1-phosphonate (81.0 mg, 0.50 mmol). Alkoxyamine **1** (32.7 mg, 0.10 mmol) was re-loaded twice each 24 h.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.07.059.

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- [13] The ¹H and ³¹P NMR spectra (as well as the T_g values, Table 1) of CP-co-BP^{Me} copolymers obtained in the absence and in the presence of *n*-dodecylmercaptan were essentially similar, arguing against significant thiol-ene reaction under these conditions. These results indicate that *n*-dodecylmercaptan behaves essentially as a chain transfer agent in those systems. This was independently confirmed by the treatment of a sample of poly(CP) with *n*-dodecylmercaptan (0.1 equiv vs. monomer unit) in the presence of AIBN, which produced under our conditions sluggishly minimal amounts of the corresponding thiol adduct, as revealed by the slow disappearance of the resonances for the internal C=CH group in the ¹H NMR spectra.
- [14] Homopolymerization of BP^{Me} with AIBN (0.5 wt-%) at 100–120 °C, either in bulk or benzene solution, led to modest monomer conversions (27–36% after

- 24 h). ESI-MS analyses of the recovered oily products indicated that they mostly consist of dimers and trimers of BP^{Me}.
- [15] For comparison purposes, the copolymerization of CP with BP^{Me} was also carried out with alkoxyamine **1**, under similar conditions than those used for the copolymerization of BP^{Me} with isoprene ([CP]/[**1**] = 200; 2.5 mol-% initial loading of BP^{Me} vs. CP, 100 °C, 72 h). A copolymer with 1.7 mol-% incorporated BP^{Me}, $M_n = 8500$ g/mol, and $M_w/M_n = 1.45$, was recovered in 35% yield. This copolymer featured a microstructure similar to that of copolymers produced with AIBN/TEMPO/RSH combinations, as indicated by ¹H and ³¹P NMR spectroscopies.
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- [20] The observation of several singlet resonances in those two groups (beside the main ones at δ 21.4 and 31.5 ppm) likely accounts for the differences in regioselectivity/microstructure of the BP^{Me} and CP units.
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- [22] Calculated (Chemoffice Ultra 8.0) ¹H NMR chemical shifts for the vinylic hydrogens of the 3,4-BP^{Me} microstructure: $\delta(H_\alpha) = 6.14\text{--}6.33$ ppm; $\delta(H_\beta) = 6.41\text{--}6.65$ ppm; 1,4-“tautomerized” BP^{Me} microstructure: $\delta(H_\beta) = 5.46\text{--}5.75$ ppm; these values are all consistent with the observed chemical shifts.
- [23] Copolymerization was attempted using 2.9 mol-% of BP^{Me} with 22.7 mmol of IP in the presence of AIBN (0.020 mmol) and TEMPO (0.024 mmol) at 100 °C for 24 h. A copolymer, with phosphonate content of 2 mol-%, $M_n = 2600$ g/mol and $M_w/M_n = 1.95$, was recovered in 22% yield.
- [24] Only minor contamination (<10 wt-%) by homopolyisoprene was evidenced by a small shoulder at high molecular weights in the GPC-RI trace for copolymers prepared by adding alkoxyamine **1** only once at the beginning of the reaction course (Table 2, entry 1).