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Olivier Coutelier, Issam Bliidi, Mathias Destarac. Xanthate-derived mercaptophosphonates for thiol-ene modification of styrene-butadiene rubber. *European Polymer Journal*, 2021, 151, pp.110419. 10.1016/j.eurpolymj.2021.110419 . hal-03240506

HAL Id: hal-03240506

<https://hal.science/hal-03240506v1>

Submitted on 24 Apr 2023

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Xanthate-derived mercaptophosphonates for thiol-ene modification of styrene-butadiene rubber

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Abstract:

The functionalization of elastomers by phosphonate groups remains relatively unexplored considering the great potential these polymers would represent for applications. In this paper, thiol-functional oligophosphonates were designed and coupled by a thiol-ene reaction to a styrene-butadiene rubber (SBR). We adopted a RAFT methodology with dimethyl vinylphosphonate (DMVP) and a high-temperature thermolysable xanthate, to afford the monophosphonate DMVP-SH and P(DMVP)₅-SH, a mercapto(oligophosphonate) of $DP_n=5$. We conducted a comparative study of the thiol-ene coupling reaction of DMVP-SH and P(DMVP)₅-SH with a SBR for different degrees of functionalization. We observed that P(DMVP)₅-SH was as reactive as DMVP-SH. Although only limited grafting could be achieved without alteration of the SBR structure by radical intercoupling reactions, P(DMVP)₅-SH was found superior to DMVP-SH for increasing the phosphonate content of the SBR thanks to its oligophosphonate character.

Keywords : thiol-ene, SBR, RAFT, xanthate, phosphonate

1. Introduction

Polydienes are an important class of materials accounting for more than 80% of the rubber market [1]. Their modification by introduction of functional groups allows the elaboration of materials with new or improved properties. For instance, the modification of a styrene-butadiene rubber (SBR) by alkoxy silane groups, known to promote interactions with inorganic oxide fillers, improved the mechanical performances of SBR / silica composites compared to unmodified SBR [2].

Different functionalization pathways can be envisioned, starting with the copolymerization of diene monomers with a comonomer carrying the desired function. However, the function to be introduced must be compatible with the polymerization technique, and the reactivity ratios of the monomers must be in favor of a homogeneous incorporation of the functions in the final polydiene, which requires the synthesis of specifically functionalized monomers. A second functionalization approach consists in the post-modification of the polydiene double bonds. Different post-modification strategies have been explored such as radical addition of alkyl iodides [2], hydrosilylation [3], epoxidation [4], hydroboration [5] or thiol-ene coupling [6].

Among the different functional groups of interest, phosphonates are of paramount importance owing to their specific properties such as corrosion inhibition [7], metal ligation [8], flame retardancy [9], adhesion to metallic surfaces [10] or inorganic materials [11]. Therefore, in order to confer such properties to rubbers, the possibility of introducing phosphonate groups on polydienes has caught our attention.

To our knowledge, only a few examples of phosphonated polydienes have been described in the literature. Following the former approach, Marvel et al. [12] attempted the radical copolymerization

of 1-propene-2-phosphonate with butadiene with limited success. More recently, Ajellal et al. [13] were able to produce phosphonated polydienes by radical polymerization of dimethyl-1,3-butadiene-1-phosphonate with chloroprene and isoprene in the presence of TEMPO. Following a post-modification approach, Boutevin et al. [14] functionalized a hydroxytelechelic polybutadiene by thiol-ene coupling reaction between 3-mercaptopropyl diethylphosphonate (HS-(CH₂)₃-PO₃Et₂) and the polybutadiene double bonds. Alternatively, Ajellal et al. modified a copolymer of isoprene and 1,3,7-octatriene by a rhodium-catalyzed hydrophosphorylation [15]. Finally, Intharapat et al. [16] reported an iniferter approach for the photopolymerization of dimethyl(methacryloyloxymethyl)phosphonate (DMMMP) in latex medium from *N,N*-diethyldithiocarbamate-functional natural rubber (NR) to afford NR-*g*-DMMMP graft copolymer.

Reversible Addition-Fragmentation chain Transfer (RAFT) is a very useful technique for controlling the polymerization of a wide range of complex functional monomers such as phosphonates [17–19]. Moreover, RAFT agents offer the possibility of transforming the thiocarbonylthio chain end into a thiol by simple aminolysis [18,20] or thermolysis reaction [21,22], thus giving access to thiol-ene reactions with RAFT polymers. Surprisingly, considering the extensive work on RAFT polymerization of phosphonated monomers, thiol-ene coupling of SH-terminated polyphosphonates with polydienes has not been explored yet.

In this paper, we first investigate RAFT polymerization of commercially available dimethyl vinylphosphonate (DMVP) with a xanthate, and the transformation of the resulting polymer into a thiol-terminated poly(dimethyl vinylphosphonate) (PDMVP-SH) by thermolysis/Chugaev reaction. In a second part, we study the thiol-ene coupling between PDMVP-SH and a SBR produced by anionic polymerization. The monofunctional mercaptophosphonate DMVP-SH is synthesized and evaluated in thiol-ene coupling as a basis for comparison.

2. Materials and Methods

2.1. Materials

SBR ($M_{n,PS} = 235900 \text{ g mol}^{-1}$, $D = 1.24$, styrene / butadiene = 25 / 75 molar ratio, 1,2-/1,4- butadiene units (%) = 60/40) was synthesized by anionic polymerization. AIBN (99%, Sigma Aldrich) was recrystallized in methanol. Dilauroyl peroxide (DLP) (97%, Sigma Aldrich), bromoacetonitrile (99%, Sigma Aldrich), 3-methylbutan-2-ol (99%, SAFC), *n*-Butyllithium (*n*-BuLi, 1.6 M in hexane) (Sigma Aldrich), carbone disulfide (99,9%, Sigma Aldrich), 2,2'-methylene bis(4-methyl-6-tert-butylphenol) (Sigma Aldrich), dimethyl vinylphosphonate (DMVP) (98%, Alfa Aesar) and solvents were used as received. Dry THF was prepared by distillation over Na.

2.2. Synthesis of xanthate X1

3-methylbutan-2-ol (6g, 68.1 mmol) is solubilized with dry THF (45 mL) in a 500 mL round-bottom flask equipped with a magnetic stir bar under argon. 46.5 mL (74.4 mmol) of a 1.6 M *n*-BuLi solution in hexane is added dropwise to the reaction mixture at 0°C and stirred for 30 min, then CS₂ (30 mL, 0.496 mol) is added dropwise at 0°C, stirred for another 30 min and finally bromoacetonitrile (11.6g, 136.2 mmol) is added dropwise. The reaction mixture is allowed to warm up to room temperature and stirred for 15 h. Solvent is removed under vacuum, and the crude mixture extracted with CH₂Cl₂. The organic layer is dried over MgSO₄ and evaporated under vacuum. The residue is purified by column chromatography on silica gel (petroleum ether/ethyl acetate: 95/5 v/v). The product is obtained as a yellow oil with a yield of 86%.

^1H NMR (300 MHz, CDCl_3 , δ = ppm) : 5,58 (1H, m, O-CHCH₃), 3,85 (2H, s, NC-CH₂-S-C=S), 2,02 (1H, m, (-CH(CH₃)₂), 1,33(3H, d, O-CHCH₃), 0,96 (6H, d, (-CH(CH₃)₂).

^{13}C NMR (300 MHz, CDCl_3 , δ = ppm) : 208,6 (S=C-SCH-), 115,5 (NC-CH₂-S-C=S), 87,8 (O-CHCH₃), 32,7 ((-CH(CH₃)₂), 21,1 (NC-CH₂-S-C=S), 18,1 (-CH(CH₃)₂), 17,9 (O-CHCH₃), 15,8 (O-CHCH₃).

2.3. Synthesis of DMVP-X1 monoadduct

In a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stir bar are successively added xanthate X1 (2.76 g, 13.59 mmol), DMVP (1g, 7.35 mmol) and 1,2-dichloroethane (6 mL). The reaction mixture is degassed with argon for 15 min and the reaction mixture heated at 95°C. DLP (145 mg, 0.364 mmol) is added every hour for a period of 5 h, and the reaction is kept at 95°C for another 2h. The reaction mixture is cooled down to room temperature, the solvent removed under vacuum and the residue purified by column chromatography over silica gel with ethyl acetate as eluent. After evaporation of the solvent, the DMVP-X1 is obtained as an oil with a yield of 78%.

^1H NMR (300 MHz, CDCl_3 , δ = ppm) : 5,58 (1H, m, O-CHCH₃), 4,35 (1H, m, NC-CH₂-CH₂-CH-S-C=S), 3,82 (3H, s, P=(OCH₃)₂), 2,62 (2H, m, NC-CH₂-CH₂-CH(P(O)(OCH₃)₂-S-C=S), 2,45-2,21 (2H, m, NC-CH₂-CH₂-CH(P(O)(OCH₃)₂-S-C=S), 2,03 (-CH(CH₃)₂), 1,35 (3H, d, O-CHCH₃), 0,95 (6H, d, (-CH(CH₃)₂).

^{31}P NMR (121.49 MHz, CDCl_3 , δ = ppm) : 25 (1P, s, P=(OCH₃)₂), 25.1 (1P, s, P=(OCH₃)₂).

^{13}C NMR (75.47 MHz, CDCl_3 , δ = ppm) : 210,7 (S=C-SCH-), 119,1 (NC-CH₂-CH₂-CH(P(O)(OCH₃)₂-S-C=S), 88,0 (O-CHCH₃), 54,2 (P=(OCH₃)₂), 44,4 et 42,6 (NC-CH₂-CH₂-CH(P(O)(OCH₃)₂-S-C=S), 32,7 ((-CH(CH₃)₂), 26,6 (NC-CH₂-CH₂-CH(P(O)(OCH₃)₂-S-C=S), 19,1 (-CH(CH₃)₂), 16,4 (O-CHCH₃), 15,1 (NC-CH₂-CH₂-CH(P(O)(OCH₃)₂-S-C=S).

2.4. Synthesis of P(DMVP)₅-X1

In a Schlenk tube are successively added xanthate X1 (470 mg, 2.31 mmol), DMVP (3 g, 22 mmol), AIBN (72 mg, 0.438 mmol) and 1,4-dioxane (4.4.47 mL). The solution is degassed with argon for 15 min and heated at 70°C for 24 h. The reaction mixture is cooled down to room temperature and the solvent removed under vacuum. The residue is triturated in dichloromethane to remove residual DMVP and 1,4-dioxane. PDMVP-X1 is filtered off, and dried under vacuum. Monomer conversion=50% (determined by ^{31}P NMR, Fig. S6, ESI). $M_{n,NMR} = 840 \text{ g mol}^{-1}$ ($M_{n,th} = 850 \text{ g mol}^{-1}$), which corresponds to $DP_n=5$ is obtained by ^{31}P NMR analysis (Fig. S6, ESI).

2.5. Synthesis of DMVP-SH

In a round-bottom flask equipped with a reflux condenser are successively added DMVP-X1 (250 mg, 0.737mmol) and 1,2-dichlorobenzene (3 mL). The reaction mixture is degassed with argon for 5 min, protected from light with aluminum foil and heated at 210°C for 10 min. ^{31}P NMR analysis of the crude mixture revealed a nearly quantitative conversion of DMVP-X1 and formation of DMVP-SH. The molar fraction of the target product was estimated to 72% based on the relative integration of its signal at 26 ppm and all the other signals in the ^{31}P NMR spectrum. The product was used without further purification.

^{31}P NMR (121.49 MHz, CDCl_3 , $\delta = \text{ppm}$) : 26,3 (1P, s, $\text{P}=\text{O}(\text{OCH}_3)_2$)

2.6. Synthesis of $\text{P}(\text{DMVP})_5\text{-SH}$

In a round-bottom flask equipped with a reflux condenser are successively added $\text{P}(\text{DMVP})_5\text{-X1}$ (250 mg, 29.7 mmol) and 1,2-dichlorobenzene (3 mL). The reaction mixture is degassed with argon for 5 min, protected from light with aluminum foil and heated at 210°C for 15 min to yield $\text{P}(\text{DMVP})_5\text{-SH}$.

^{31}P NMR (121.49 MHz, CDCl_3 , $\delta = \text{ppm}$) : 32-36 (4P, m, $\text{P}=\text{O}(\text{OCH}_3)_2$) and 26-29 (1P, m, $\text{P}=\text{O}(\text{OCH}_3)_2$)

2.7. General procedure for thiol-ene coupling between DMVP-SH and SBR

In a 50 mL two-neck round-bottom flask protected from light with aluminum foil, and equipped with a reflux condenser are added DMVP-X1 (26 mg, 0.0766 mmol), corresponding to a maximum percentage of modified double bonds of butadiene units equal to 1.36%) and 3 mL of 1,2 dichlorobenzene. The solution is degassed with argon for 15 min, heated at 210°C for 10 min to yield DMVP-SH , and cooled down to room temperature. Then, a solution of SBR (500 mg, $M_{n,PS} = 235900 \text{ g mol}^{-1}$, $2.12 \cdot 10^{-6} \text{ mol}$) in methylcyclohexane (15 mL) degassed with argon for 15 min is added to the previous one. An aliquot is taken for ^1H NMR analysis and the reaction mixture heated at 75°C . A degassed solution of DLP (10 mg, 0.025 mmol) in methylcyclohexane (20 mL) is added dropwise to the reaction mixture. After 3 h the reaction mixture is cooled down to room temperature and precipitated in methanol (200 mL), filtered off and stabilized with 1 mL of a solution of 2,2'-methylene bis(4-methyl-6-tert-butylphenol) at a concentration of 10 g L^{-1} in dichloromethane. The resulting SBR-g-DMVP is dried at 60°C in a vacuum oven.

A grafting yield of 68% is determined by ^1H NMR by comparing the relative integration of the OMe signal of DMVP-SH before reaction with that of purified SBR-g-DMVP , using the integration of the aromatic signals of SBR as internal reference (Fig. S8, ESI).

2.8. General procedure for the thiol-ene coupling between $\text{P}(\text{DMVP})_5\text{-SH}$ and SBR

In a 50 mL two-neck round-bottom flask, protected from light with aluminum foil, and equipped with a reflux condenser are added $\text{P}(\text{DMVP})_5\text{-X1}$ ($M_{n,NMR} = 840 \text{ g mol}^{-1}$, 312 mg, 0.372 mmol, corresponding to a maximum percentage of modified double bonds of butadiene units equal to 6.6%) and 3 mL of 1,2 dichlorobenzene. The solution is degassed with argon for 15 min and heated at 210°C for 15 min and cooled down to room temperature. Then, a solution of SBR (500 mg, $M_{n,PS} = 235900 \text{ g mol}^{-1}$, $2.12 \cdot 10^{-3} \text{ mmol}$) in methylcyclohexane (15 mL) degassed with argon for 15 min is added to the previous one. An aliquot is taken for ^1H NMR analysis and the reaction mixture heated at 75°C . A solution of DLP (10 mg) in methylcyclohexane (20 mL) degassed with argon for 15 min is added dropwise to the reaction mixture. After 3 h the reaction mixture is cooled down to room temperature and precipitated in methanol (200 mL) filtered off and stabilized with 1 mL of a solution of 2,2'-methylene bis(4-methyl-6-tert-butylphenol) at 10 g L^{-1} in dichloromethane. $\text{P}(\text{DMVP})_5\text{-grafted-SBR}$ is dried at 60°C in a vacuum oven.

A grafting yield of 48.5% is determined by ^1H NMR as described in section 2.7.

2.9. Characterizations

Average molecular weights (M_n , M_w) and dispersity (\mathcal{D}) were determined by size exclusion chromatography (SEC). SEC was equipped with a Waters 2414 refractive index (RI) detector, and a set

of 2 columns (Shodex KF-802.5 and KF-804) thermostated at 35°C. THF was used as eluent with a flow rate of 1.0 mL min⁻¹.

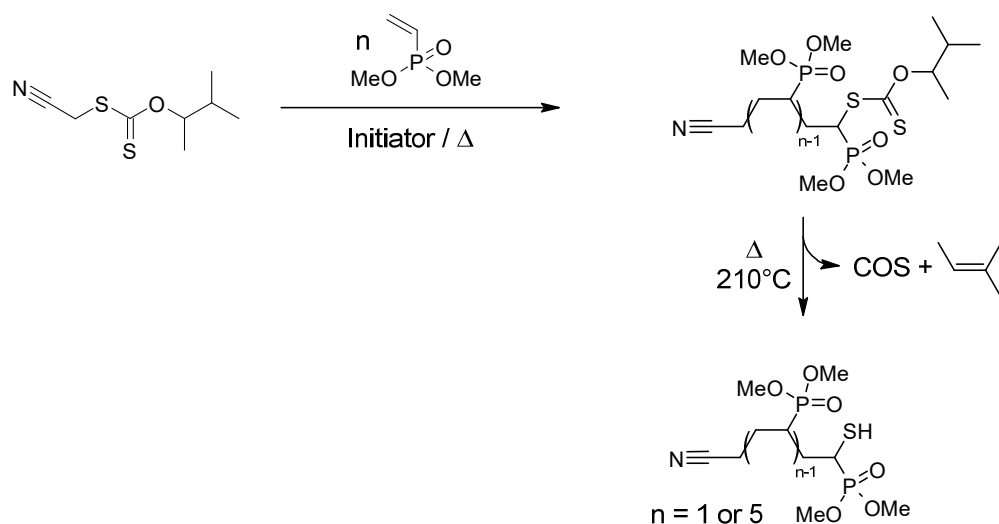
¹H NMR, ¹³C NMR and ³¹P NMR analyses were recorded on a 300 MHz Bruker spectrometer using CDCl₃ as solvent at room temperature and chemical shifts were reported in ppm.

3. Results and discussion

3.1. Synthesis of mercaptophosphonates

In order to propose an original series of phosphonate precursors for thiol-ene reactions, we took the following into consideration: i) xanthates are reactive chain transfer agents (CTAs) in RAFT polymerization of vinyl phosphonates, ii) like other RAFT agents, xanthates are a direct source of terminal thiol group on RAFT polymers. While RAFT polymerization of vinyl phosphonic acid (VPA) with xanthate CTAs has been well documented by our group over the last decade [17,23–27], very limited focus has been put on vinyl phosphonate esters, in particular dimethyl vinylphosphonate (DMVP) [28,29]. However, the latter candidate was chosen for our study, anticipating solubility issues of VPA derivatives for direct SBR modification. For xanthate transformation into thiol, we opted for thermal decomposition through intramolecular elimination (Chugaev reaction), [21,30] thereby avoiding unnecessary manipulation of sensitive thiols towards oxidation, and tedious purification steps. The general reaction pathway is shown in Scheme 1.

Xanthate X1 (*S*-cyanomethyl *O*-3-methylbutan-2-yl carbonodithioate) was considered owing to the established effectiveness of the cyanomethyl RAFT leaving group for less-activated vinyl monomers [31], and the capacity of secondary *O*-alkyl xanthates to cleanly decompose into a thiol at elevated temperature with only carbonyl sulfide and 2-methyl-2-butene volatiles as side products (Scheme 1) [32].



Scheme 1. General concept for the synthesis of mercaptophosphonates

At first, we attempted the polymerization of DMVP in the presence of X1 with a DMVP/X1 molar ratio of 10/1, at 70°C in presence of AIBN. After 24h of reaction, the DMVP conversion reached 50%, leading to P(DMVP)₅-X1 oligomer of DP_n=5. ³¹P NMR was the analysis of choice for the polymerization of DMVP, as it allows the determination of both monomer conversion (Fig. S6) and number-average degree of polymerization DP_{n,NMR} (Fig. 1, bottom and Fig. S6).

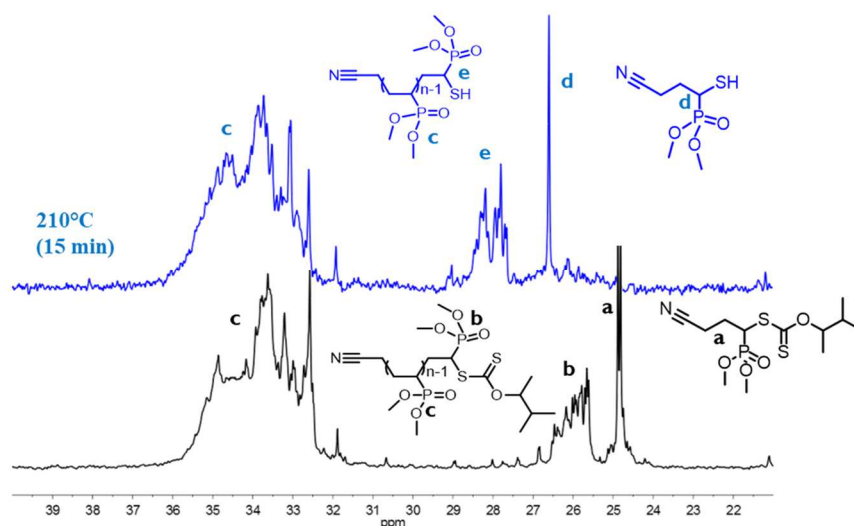


Fig. 1. ^{31}P NMR of $\text{P}(\text{DMVP})_5\text{-X1}$ (bottom) and its thermolysis product, $\text{P}(\text{DMVP})_5\text{-SH}$ (top)

As we can observe in the bottom part of Fig. 1, there is a clear difference of chemical shifts between the phosphonates of the polymer main chain (signal c, 32-36 ppm) and the one of the last monomer unit (signal b, 25.5-26.5 ppm) next to the xanthate function. A signal characteristic of the X1:DMVP monoadduct (signal a, 24.6 ppm) is still present after 50% conversion, highlighting the slow reactivation of the DMVP-xanthate group. All these observations were very similar to the ones observed in our previous study of the RAFT polymerization of VPA [17]. M_n values determined by SEC ($M_{n\text{ SEC}}=940\text{ g mol}^{-1}$) and ^{31}P NMR ($M_{n\text{ NMR}}=840\text{ g mol}^{-1}$) were in excellent agreement with that expected for a controlled RAFT oligomerization ($M_{n\text{ th}}=850\text{ g mol}^{-1}$).

Then, taking advantage of the initialization process first brought out by Klumperman et al. for some xanthate/monomer systems [33] and later observed by us [17] for VPA, we adapted the experimental conditions to selectively obtain a DMVP/xanthate monoadduct [32]. By reaction of 1 eq of DMVP with 1.8 eq of X1 in the presence of DLP in dichloroethane at 95°C , we were able to selectively obtain a monoadduct DMVP-X1 with a yield of 78%. ^{31}P NMR analysis of DMVP-X1 revealed a set of two signals corresponding to the different diastereoisomers at 25 and 25.1 ppm (Fig. 2, bottom and Fig. S5).

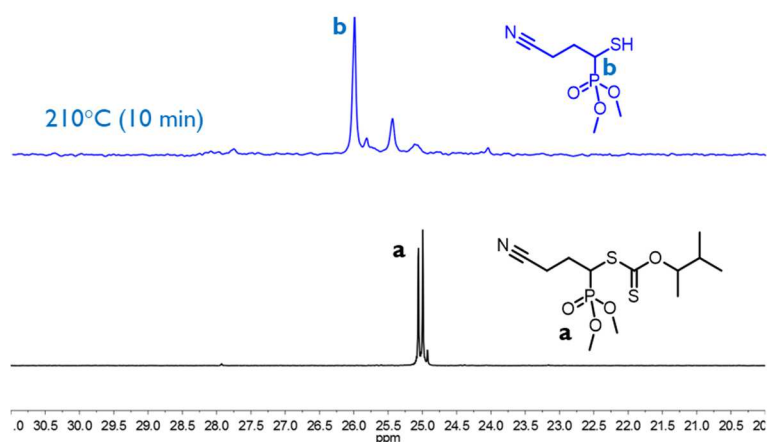


Fig. 2. ^{31}P NMR analysis of DMVP-X1 (bottom) and its thermolysis product, DMVP-SH.

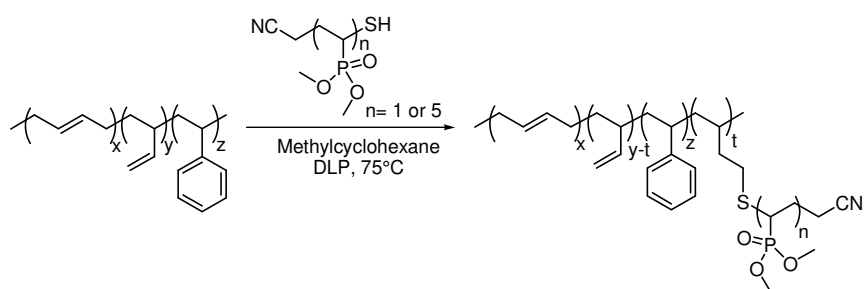
The best conditions for thermal decomposition of the xanthate end group into thiol were determined by studying DMVP-X1 as a model compound. A 10 min thermolysis in dichlorobenzene at 210°C under argon was found to be the best compromise for a total decomposition of the xanthate into the corresponding thiol as main product, with only a small amount of undetermined side products based on ^{31}P NMR (Fig. 1, top). ^{31}P NMR analysis clearly shows the complete disappearance of the initial two signals for DMVP-X1 at 25 and 25.1 ppm, and the rise of a new singlet at 26 ppm corresponding to target DMVP-SH, as well as small minor peaks. Integration of different phosphorous signals indicated a nearly quantitative transformation of starting DMVP-X1, with an estimated molar fraction of 72% in DMVP-SH based on signal integrations. This result corresponds to the highest rate of DMVP-SH we could get with these experimental conditions. The product was used as such for the rest of the study.

Thermolysis of $\text{P}(\text{DMVP})_5\text{-X1}$ was also performed in dichlorobenzene at 210°C under argon, but required 15 min for a total decomposition of the xanthate to form a thiol. ^{31}P NMR analysis after thermolysis revealed a total disappearance of the signals corresponding to the last monomer unit next to xanthate for $\text{P}(\text{DMVP})_5\text{-X1}$ at 25.5-26.5 ppm (signals b, Fig. 1), and the rise of new signals corresponding to phosphorus next to a thiol at 27.5-28.5 ppm (signal e, Fig. 1). Residual DMVP-X1 with characteristic phosphorous signals at 24.5-25 ppm (signal a, Fig. 1) is also totally converted to its corresponding thiol at 26.5 ppm (signal d, Fig. 1).

RAFT oligomerization of DMVP with X1 followed by a fast thermolysis step was found to be a very efficient technique to easily access thiol-terminated oligophosphonates.

3.2. Thiol-ene coupling of mercapto(oligophosphonates) with SBR

The SBR used for this study was obtained by anionic polymerization and had a S/B molar composition of 25/75 (Fig. S7). SEC analysis gave a $M_{n\text{-SEC}} = 235900 \text{ g mol}^{-1}$ for a dispersity $\mathcal{D} = 1.24$.



Scheme 2. General scheme for the thiol-ene coupling of DMVP-SH ($n=1$) and $\text{P}(\text{DMVP})_5\text{-SH}$ to SBR

Radical addition of freshly prepared DMVP-SH to the butadiene double bonds of the SBR was conducted in methylcyclohexane at 75°C in presence of DLP as a radical source, to afford SBR-*g*-DMVP (Scheme 2). In order to investigate the scope and limitations of this coupling reaction, we targeted two different degrees of grafting, corresponding to the modification of 1.36% and 12.50% of butadiene double bonds. After reaction, the crude mixture is precipitated in methanol to separate the SBR-*g*-DMVP (insoluble) from unreacted DMVP-SH. ^1H NMR analysis of SBR-*g*-DMVP revealed the

presence of a new signal at 3.8 ppm corresponding to the methylphosphonate groups, confirming the thiol-ene coupling of DMVP-SH onto the SBR (Fig. 4). The grafting yield was also determined by ^1H NMR, by using the integration of the methylphosphonate before and after reaction and using the aromatic signals of the SBR as an internal standard (Fig. S8). ^1H NMR analysis also allowed us to calculate the consumption of the butadiene double bonds after thiol-ene reaction (Fig. S8).

Table 1. Thiol-ene coupling between SBR and mercaptophosphonates

Entry	Thiol	Targeted degree of grafting (%)	Grafting yield (%)	Double bonds conv. (%)	DMVP content (mol. %) ^a	$M_{n,SEC}^b$ (kg mol ⁻¹)	\mathcal{D}
1	-	-	-	-	-	235.9	1.24
2	DMVP-SH	1.36	68	2.9	0.7	250.8	1.23
3	DMVP-SH	12.50	37.5	16.3	3.5	400.6	1.44
4	P(DMVP) ₅ -SH	1.05	66.5	2.2	2.6	239.8	1.25
5	P(DMVP) ₅ -SH	6.60	48.5	8.1	11.9	243.0	1.26

^a DMVP content (mol. %)= (0.75 x targeted degree of grafting x grafting yield x DP_n)/100, ^b Polystyrene calibration

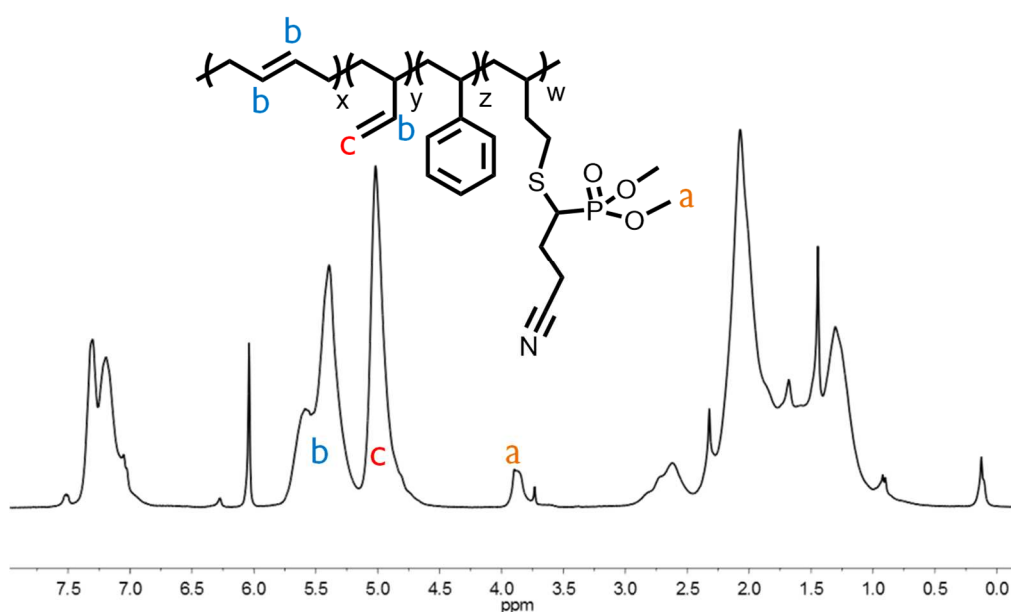


Fig. 3. ^1H NMR spectrum of a SBR-g-DMVP (entry 2, Table 1)

A grafting yield of 68% was obtained for a targeted degree of grafting of 1.36%, which corresponds to 0.69 mol. % of DMVP units relative to the whole SBR. We also observed by ^1H NMR that more double bonds were consumed (2.9%) than functionalized (Table 1, Entry 2), indicating the presence of radical side reactions (for 68.7% of the converted double bonds based on data of Table 1) during thiol-ene coupling. We assumed that secondary reactions consist in the formation of 5- or 6-membered rings by an intramolecular radical reaction between two double bonds, as already reported by Justynska et al [34].

When increasing the targeted degree of grafting to 12.5% of the double bonds (Table 1, entry 2), the grafting yield dropped to 37.5%, corresponding to 3.5 mol. % DMVP in copolymer. Here again, in addition to thiol-ene coupling of DMVP-SH, a large proportion of the 16.3% consumed double bonds underwent side reactions (71.3%), in slightly higher proportion than for the lower degree of grafting.

The SEC-RI trace of the modified SBR-*g*-DMVP with the lowest degree of grafting (0.7 mol.% DMVP) was almost identical to the one of the initial SBR, with an increase of M_{n-SEC} to 250.8 kg mol⁻¹ but a similar dispersity at \mathcal{D} =1.23 which was expected for a minor modification of the initial SBR (Table 1, entry 2). In contrast, the SEC-RI trace of SBR-*g*-DMVP with the highest degree of grafting (3.5 mol.% DMVP) was shifted to much higher molecular weight values, with M_{n-SEC} = 400.6 kg mol⁻¹ and an increased dispersity \mathcal{D} = 1.44 (Table 1, entry 3 and Fig. 4). Such an increase in molar mass and dispersity cannot be explained by the sole grafting of few percents of DMVP on the SBR backbone. This evolution can be ascribed to radical cross-coupling reactions of SBR chains occurring during thiol-ene coupling of DMVP-SH, because of the too high radical concentration required for the highest rates of SBR modification with DMVP.

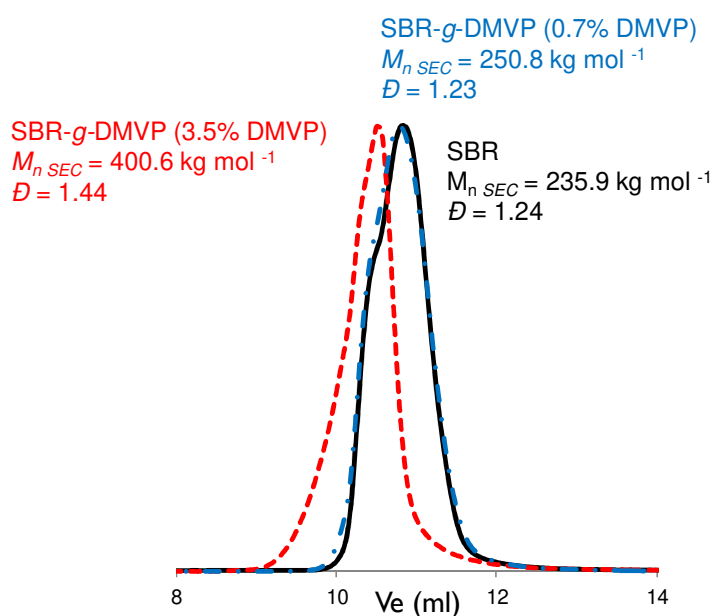


Fig. 4. SEC-RI traces of the initial SBR (black line) and SBR-*g*-DMVP with targeted low and high degrees of phosphonate grafting.

These results clearly indicate that the thiol-ene coupling of DMVP-SH with SBR, in our conditions, is limited to the functionalization of a few percent of the double bonds. The free-radical nature of the coupling reaction presents serious limitations when higher levels of phosphonate incorporation are desired. Consequently, with a view to increase the phosphonate content on modified SBR while keeping a sufficiently low level of double bond conversion in order to avoid interchain coupling side reactions, the thiol-ene coupling of P(DMVP)₅-SH was then considered (Scheme 2).

A grafting yield of 66.5% of P(DMVP)₅-SH was obtained for a targeted degree of grafting of 1.05% (Table 1, entry 4), which is a similar result to that obtained with DMVP-SH. However, the oligomeric nature of the mercaptophosphonate allowed an increase of the fraction of DMVP in the SBR composition by a factor of five (2.6 mol.%). For a targeted degree of grafting of 6.6% (Table 1, entry 5), the yield slightly decreased to 48.5% but allowed us to reach a high phosphonate content of

11.8% in modified SBR (Table 1, entry 5). To a similar extent than for DMVP-SH, only a minor fraction of the consumed double bonds reacted with P(DMVP)₅-SH (respectively 31.7 and 39.5% for two low and high degrees of grafting of the mercaptophosphonate oligomer).

Due to the relatively high content of phosphonate groups (11.8%) in SBR-*g*-P(DMVP)₅, ³¹P NMR analysis of the purified polymer allowed us to clearly observe all the characteristic signals of PDMVP grafts (Fig. 5), confirming the presence of the oligophosphonate onto the SBR.

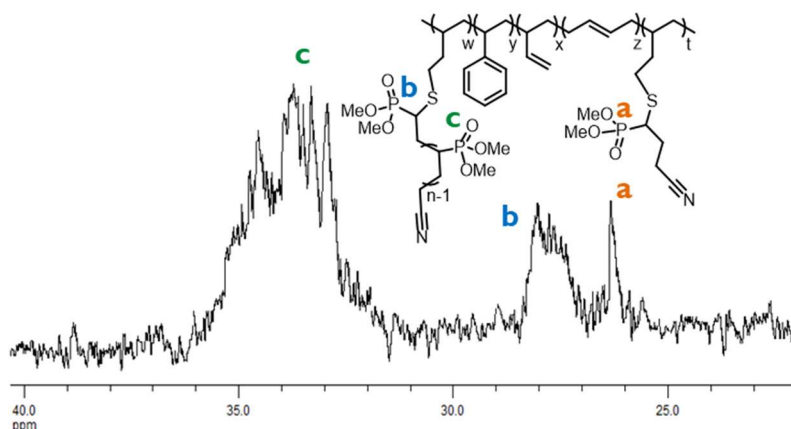


Fig. 5. ³¹P NMR analysis of SBR-*g*-P(DMVP)₅ (Table 1, entry 5).

SEC-RI analysis of the two SBR-*g*-P(DMVP)₅ with DMVP composition of 2.6 and 11.9 mol% revealed a slight displacement of the traces towards higher molar masses (Fig. 6), as expected after modification of few percents of double bonds. Most importantly, the overall shape of the chromatograms looks similar before and after modification, with identical dispersities. This result supports the absence of inter-chain coupling encountered for the highest degrees of grafting with model mercaptophosphonate.

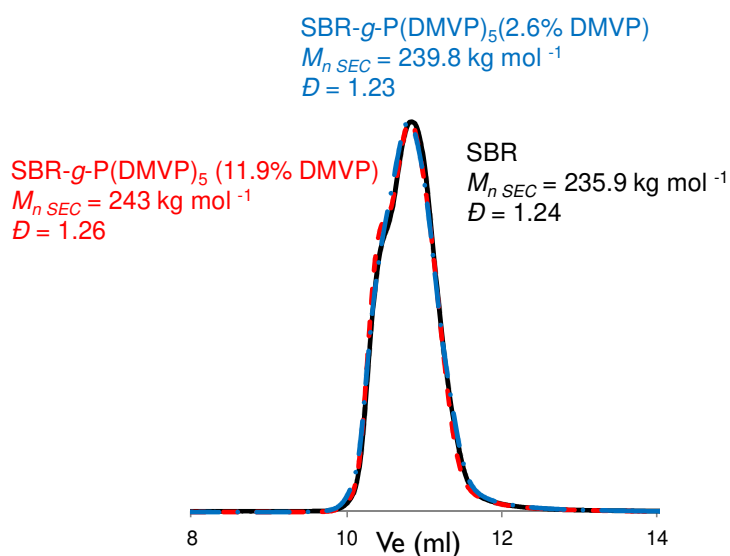


Fig.7. SEC-RI traces of SBR and SBR-*g*-P(DMVP)₅ with targeted low and high degrees of phosphonate grafting.

4. Conclusions

Phosphonate-functionalized SBRs were obtained by thiol-ene coupling between the double bonds of the SBR and thiols carrying phosphonate functions. We used a RAFT approach for dimethyl vinylphosphonate in the presence of a thermolysable xanthate to access both a DMVP-SH model compound and a SH-terminated DMVP oligomer of $DP_n=5$. The thiol-ene reaction of DMVP-SH allowed us to functionalize the SBR with very satisfactory grafting yields but only for a low percentage (~1%) of modified butadiene double bonds. For the higher degree of grafting considered, undesired radical coupling between SBR chains was observed. Thanks to the polyphosphonate character of P(DMVP)₅-SH, we were able to strongly increase the amount of phosphonate functions incorporated in the SBR while maintaining low grafting rates, without noticeable radical coupling reactions between SBR chains.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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Xanthate-derived mercaptophosphonates for thiol-ene modification of styrene-butadiene rubber

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