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Living Radical Polymerization of Isoprene via the RAFT Process

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ABSTRACT: The control over the polymerization of isoprene via reversible addition−fragmentation chain transfer (RAFT) is reported. The effects of RAFT agent, reaction temperature, and monomer concentration over molecular weight control and reaction kinetics were investigated. The optimized conditions were used to produce block copolymers of isoprene with styrene and *tert*-butyl acrylate.

Introduction

Since its first use in 1917 for the production of synthetic rubber,[1] isoprene and its polymers have received an ever increasing interest from both academia and industry. Polyisoprene's rubber properties make it a material of choice for the automotive industry,[2] while the presence of double bonds in the backbone or side chains also allows further chemical modification after polymerization. Polyisoprene has been widely used in a range of block copolymers to study their self-assemblies,[3−6] but also in a variety of material such as compatibilizers for natural rubber/acrylic polymer blend,[7,8] material for medical purposes,[9,10] or well-defined macromolecular core−shell nanostructure.[11,12] Isoprene polymers were obtained from anionic,[2,13,14] cationic,[15,16] coordination,[17−20] and radical polymerization,[8,21] with anionic polymerization being the technique of choice for most researchers. However, the stringent reaction conditions attached to anionic polymerization have stimulated research groups to develop alternative polymerization techniques.

In the past 20 years, living radical polymerization (LRP) has emerged as an alternative technique to control the molecular weight of polymers. LRP is based on a free radical process, and therefore it benefits from its tolerance to a wide range of functionalities and reaction conditions.[22,23] Iniferters were initially used to control the polymerization of isoprene via a radical process and led to the production of block copolymers with methyl methacrylate, but with broad polydispersity.[21] Atom transfer radical polymerization was also used to mediate isoprene polymerization, but only 5% of product yield was obtained. It was proposed that reaction temperatures and solubility of monomer and ligand in the system were the cause for such a low conversion.[24] To date, the most successful technique to control the polymerization of isoprene via a radical process has been nitroxide-mediated polymerization (NMP).[11,12,25,26] The use of nitroxide to mediate isoprene polymerization allows the production of polyisoprene with narrow PDI (typically less than 1.2) and molecular weight ranging 10 000−100 000 g/mol.[25] The successful use of NMP has led to the production of a variety of polymeric architectures using polyisoprene as building block.[11,12,26]

Reversible addition−fragmentation chain transfer (RAFT) polymerization is one of the newest of the LRP techniques.[27] The RAFT process is based on the reversible reaction of a chain transfer agent (CTA) with the propagating species. The use of thiocarbonyl thio compounds as CTA's allows to control the polymerization of a wide range of monomers, in a variety of reaction conditions, and makes RAFT one of the most versatile techniques to control vinyl monomers polymerization.[28,29] We report herein the use of the RAFT process to mediate the polymerization of isoprene, with optimized reaction conditions, to lead well-controlled polyisoprene homopolymers and block copolymers. RAFT will allow the production of a wider range of isoprene copolymers than any other techniques reported to date.

Table 1. Polymerization of Isoprene Using Different Chain Transfer Agents in Bulk at Various Temperatures and Time

RAFT agents	temp (°C)	time (h)	% conv[c]	PDI[d]	M_n[d]	M_w[d]
ETSPE	60[a]	17	4.2	1.85	1030	1900
		95	9.2	1.65	1800	3000
	120[b]	5	15.4	1.60	1100	1700
		25	39.3	1.67	4300	7200
		72	97.2	1.47	27400	40300
CPDB	60[a]	17	3.3	1.41	1000	1400
		93	14.4	1.87	6700	12 600
	120[b]	20	32.5	4.07	9400	13 400

[a] AIBN used as initiator. [b] Dicumyl peroxide used as initiator. [c] Calculated by ^{1}H NMR in $CDCl_3$. [d] Samples were measured by GPC using polystyrene standards.

Experimental Section

Materials. Isoprene (Aldrich, 99.98%) monomer was distilled before use. *tert*-Butyl acrylate (Fluka, 99.8%) was purified by passing through alumina column to remove inhibitor. 2-(2-Cyanopropyl)dithiobenzoate (CPDB)[27]and 2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester, (ETSPE)[30] were prepared following previously published routes. Dicumyl peroxide (BDH Chemicals, 99%) and *tert*-butyl peroxide (Aldrich, 98%) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich) was purified by recrystallization from methanol. All other reagents were of analytical grade and used without further purification.

Characterization. ^{1}H (400 MHz) nuclear magnetic resonance (NMR) spectra of polymer products were recorded on a Bruker 400 UltraShield spectrometer using $CDCl_3$ and tetramethylsilane as solvent and an internal reference, respectively. The molecular weight and polydispersity indexes were determined on SEC equipped with a LC 1120 HPLC pump ((Polymer Laboratories, UK), a MIDAS (type 830) autosampler (Spark Holland, Netherlands), a differential refractive index (DRI) detector (Shodex, RI-101), a 5.0 μm bead-size guard column (50 × 7.5 mm), and two PLgel 5.0 μm MIXED-C columns (300 × 7.5 mm) in series (Polymer Laboratories, UK). THF was used as the eluent at a flow rate of 1 mL min^{-1} at ambient temperature, and toluene was used as a flow rate marker. The SEC system was calibrated with

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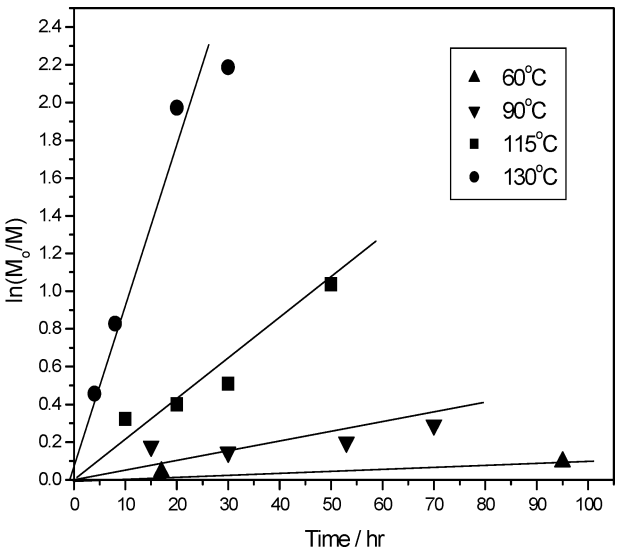


Figure 1. Semilogarithmic plot for the RAFT polymerization of isoprene mediated by 2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester (ETSPE) at various temperatures, in the presence of AIBN at 60 °C, dicumyl peroxide at 90 and 115 °C, and *tert*-butyl peroxide at 130 °C.

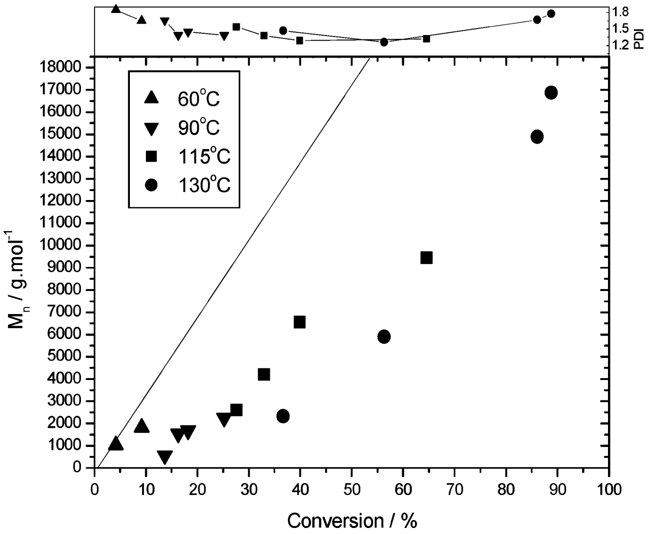


Figure 2. Evolution of molecular weight with conversion for the RAFT polymerization of isoprene mediated by 2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester (ETSPE) at various temperatures, in the presence of AIBN at 60 °C, dicumyl peroxide at 90 and 115 °C, and *tert*-butyl peroxide at 130 °C (straight line represents the predicted M_n).

polystyrene standards (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7 500 000 g mol^{-1}.

Isoprene Homopolymerization. For the general procedures, all polymerization were carried out in a dry ampules equipped with a magnetic stirring bar. A typical polymerization is as follows: the reaction solution was prepared using a ratio monomer:CTA:initiator = 500:1:0.5, by adding to isoprene monomer (4.292 g, 63.0 mmol) ETSPE as CTA (0.030 g, 0.126 mmol) and 2,2′-azobis(isobutyronitrile) (0.010 g, 0.063 mmol) in an ampule. The solution were degassed and sealed off under a nitrogen atmosphere. The solution mixture was placed in an oil bath for the desired time and temperature. The reaction was stopped by cooling in an ice bath. Determination of monomer conversion and molecular weight properties was performed by ^{1}H NMR and GPC measurements, respectively. The ^{1}H NMR spectrum of polyisoprene was recorded in $CDCl_3$ at room temperature. The integration of the monomer C═C−H resonance at around 6.5 ppm was compared with the −C*H*═CH$_2$ of 1,2-addition polymerization around 5.6−5.9 ppm, the −C*H*═C(CH$_3$)− of 1,4-addition polymerization around 5.0−5.5 ppm, and the mixture of −CH═C*H*$_2$ of 1,2-addition and −C(CH$_3$)═C*H*$_2$ of 3,4-addition polymerization around 4.4−5.0 ppm.

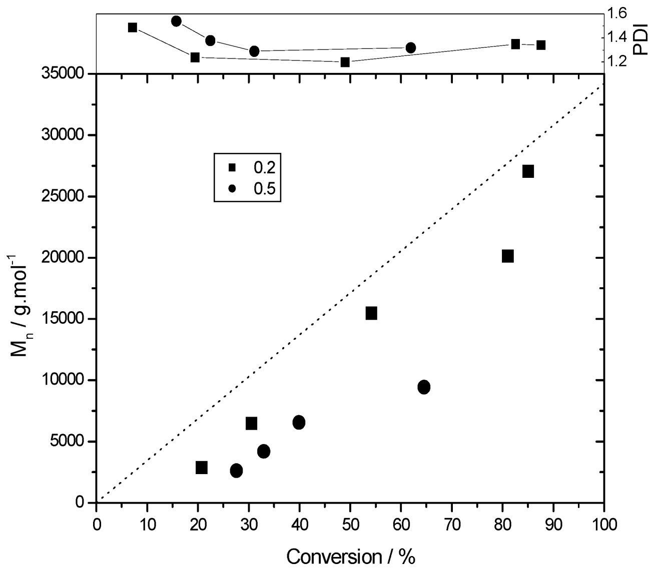


Figure 3. Evolution of molecular weight with conversion for the RAFT polymerization of isoprene mediated by 2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester (ETSPE) at 115 °C using dicumyl peroxide as initiator in a ratio ETSPE/initiator = 1/0.2 (■) and 1/0.5 (●) (···, theoretical M_n).

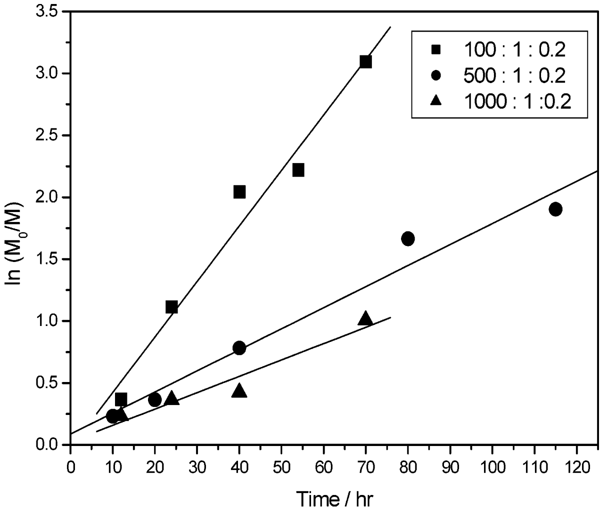


Figure 4. Semilogarithmic plot for the RAFT polymerization of isoprene mediated by 2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester (ETSPE) at 115 °C using dicumyl peroxide as initiator in a ratio isoprene/ETSPE = 1000 (▲), 500 (●), and 100 (■).

Chain Extension. A similar procedure as that highlighted above was used, with the isoprene monomer (3.1131 g, 45.7 mmol), macrochain transfer agent (0.2233 g, 0.046 mmol), and dicumyl peroxide (0.0025 g, 0.009 mmol) added into a dry ampule and degassed under a nitrogen atmosphere.

Results and Discussion

We initially investigated the effect of two types of chain transfer agents, a dithiobenzoate derivative (2-(2-cyanopropyl) dithiobenzoate, CPDB) and a trithiocarbonate derivative (2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester, ETSPE) at 60 and 120 °C, using a ratio monomer:RAFT agent: initiator = 500:1:0.5. From Table 1, we observe that both polymerizations at 60 °C show low percent conversion and relatively broad polydispersity. Upon increase of temperature

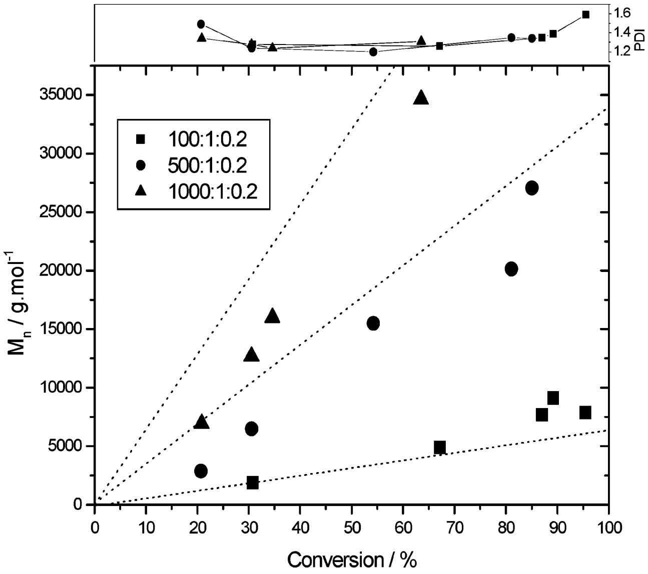


Figure 5. Evolution of molecular weight with conversion for the RAFT polymerization of isoprene mediated by ETSPE at 115 °C using dicumyl peroxide as initiator in a ratio isoprene/ETSPE = 1000 (▲), 500 (●), and 100 (■) (···, theoretical M_n).

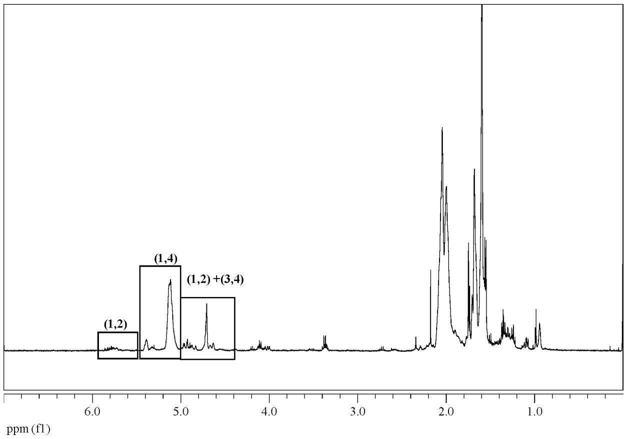


Figure 6. ^{1}H NMR spectrum in $CDCl_3$ with partial assignments for polyisoprene sample prepared by RAFT polymerization.

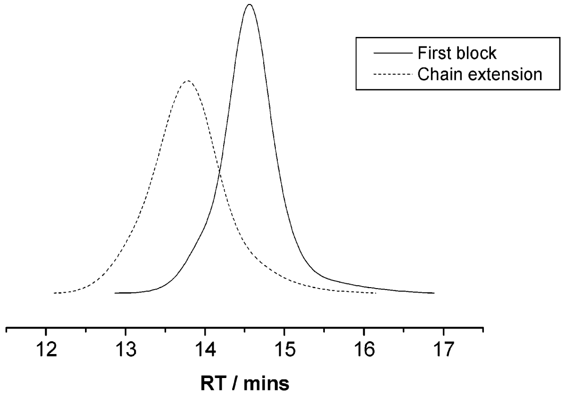


Figure 7. SEC traces signal of polyisoprene obtained before and after chain extension.

Table 2. Block Copolymerization of Isoprene Using Different Macro-Chain-Transfer Agents

macro-CTA	$M_{n,macro-CTA}$ (PDI)[a]	$M_{n,block}$ (PDI)[a]
polyisoprene	4500 g/mol (1.23)	12300 g/mol (1.30)
poly(*tert*-butyl acrylate)	10900 g/mol (1.05)	21500 g/mol (1.20)
polystyrene	34000 g/mol (1.13)	44300 g/mol (1.19)

[a] Samples were measured by GPC using polystyrene standards.

to 120 °C, the polymerizations mediated by CPDB show a loss of color during reaction and lead to uncontrolled polymeric chains, suggesting the decomposition of the CTA at this temperature. On the other hand, ETSPE seems to remain stable throughout the reaction, although broad polydispersities were also observed.

In order to clarify the effect of temperature over reaction time, molecular weight control, and polydispersity, we focused our study on polymerizations mediated by ETSPE, as it appeared to be the most stable CTA. A ratio monomer:RAFT agent: initiator = 500:1:0.5 was used (Figures 1 and 2).

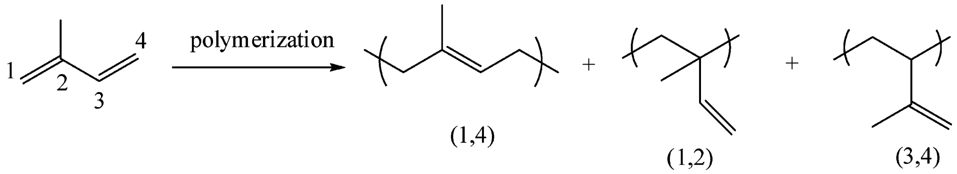
A striking observation of these results is the slow rate of polymerization of isoprene when mediated by RAFT. At 130 °C, 90% conversion is reached within 30 h, while reactions at 60, 90, and 115 °C yield 5, 14, and 40% conversion, respectively, within the same time. An increase in temperature allows for faster reactions but also leads to a loss of control. Indeed, when comparing molecular weight evolution with conversion for the polymerization at 130 and 115 °C, we observe that the highest temperature leads to polymers with higher polydispersities at high conversion (above 85%, see Figure 2). In all cases, the molecular weight seems lower than that expected. Although the molecular weight was determined via SEC, using polystyrene as standards, the large discrepancy between targeted and experimental molecular weights cannot be explained solely by the use of the wrong calibration samples. Therefore, it appears that side reactions, such as conventional chain transfer, occur during polymerization. In order to minimize these side reactions, the concentration of free radical initiator was lowered. All reactions were undertaken at 115 °C, as this temperature offers the best compromise in terms of molecular weight control and reaction time.

The initiator-to-CTA ratio plays an important role in controlling the molecular weight of polymerization mediated by RAFT. In order to improve the control over the molecular weight of the polymerization isoprene mediated by ETSPE at 115 °C, the ETSPE:DCP ratio was lowered from 0.5 to 0.2 (Figure 3). In the cases of the polymerization with low initiator ratio, polymers with well-controlled molecular weight and PDI's lower than 1.3 were obtained. A slight discrepancy exists between theoretical and experimental molecular weight values, which can be explained by the use of polystyrene standards to calibrate the GPC system. Furthermore, as often observed in RAFT polymerization, longer reaction time was needed to reach high conversions (Figure 4).

In order to verify the control over the polymerization, reactions at various monomer loading were undertaken at 115 °C, keeping a ratio ETSPE:DCP of 1:0.2 (monomer:ETSPE = 100, 500, and 1000). All reactions follow a first-order kinetic plot up to high conversion, as expected from a living system (Figure 4). In the case of ratios monomer:RAFT agent = 500:1 and 1000:1, the kinetics of polymerization are very similar, as expected for RAFT polymerizations mediated by a trithiocarbonate.[28,29] On the other hand, the polymerizations are relatively faster for a ratio monomer:RAFT agent = 100:1. All polymerizations were well controlled, as illustrated by the linear molecular weight evolution with conversion, with PDI remaining below 1.3 up to 90% conversion (Figure 5).

The polymerization of isoprene proceeds via three types of addition, namely 1,2-addition, (1,2), 1,4-addition, (1,4), and 3,4-addition, (3,4) as shown in Scheme 1.

Scheme 1. Isomeric Repeating Units Produced from the Polymerization of Isoprene



The use of catalyst based on rare-earth complexes such as neodymium[18] and mixed alumimum−magnesium with lanthanide allyl[17] leads to polyisoprene with a high proportion of the (1,4)-addition product. The cis or trans configuration of the (1,4) chain structure was found to depend on the type of metal and reaction conditions. The use of supramolecular complexes of alkali metals anionic polymerization leads to only 37% of the product from (1,4)-addition, and this was explained by the occurrence of an anionic mechanism during polymerization. NMP produces a polyisoprene with 80% (1,4)-addition, with the ratio of (3,4)-chain structure and (1,2)-chain structure varying from 15−5% to 10−10% depending on the reaction conditions.[11,12,25,26] In order to estimate the ratio between the various addition pathways, we used ^{1}H NMR spectroscopy to characterize the products of each addition (5.6−5.9 ppm for 1 H of $-\mathrm{C}\mathit{H}{=}\mathrm{CH_2}$ from the 1,2-addition, 5.0−5.5 ppm for 1 H of $\mathrm{C}\mathit{H}{=}\mathrm{C(CH_3)_3}-$ from the 1,4-addition, and 4.4−5.0 ppm for 4 H of $-\mathrm{CH}{=}\mathrm{C}\mathit{H}_2$ (1,2-addition) and $-\mathrm{C(CH_3)_3}{=}\mathrm{C}\mathit{H}_2$ (3,4-addition) (Figure 6).

The ratio of each isomer was calculated throughout the polymerization, and a ratio 75% (1,4), 5%, (1,2) and 20% (3,4) was obtained independently of the monomer conversion.

For all experiments, the molecular weight distributions show a shoulder toward high molecular weight values at percent conversion ~85%. This is also observed by the increase of PDI at high conversion, and we observe that the concentration of these high molecular weight species increase with reaction temperatures. For instance, the reaction at 115 °C, using a ratio monomer:CTA:initiator = 500:1:0.2 shows the presence of high molecular weight species from 81% conversion (PDI = 1.35), while at the same temperature, the reaction using a ratio 100:1:0.2 leads to high molecular weights species appearing at a monomer conversion of 87% (PDI = 1.35). When increasing the reaction temperature to 130 °C, high molecular weight species appears after 86% conversion, but in higher concentration (PDI = 1.67). The same observation was made by Benoit et al. when polymerizing isoprene via NMP at conversions higher than 85%.[25] The authors attributed this shoulder to the presence of dead polymeric chains of high molecular weight, formed via termination reactions by combination. In order to produce block copolymers, Benoit et al. stopped all their polymerization at 80%. Another potential explanation for the increase in polydispersity may be due to increased chain−chain coupling or cross-linking reactions involving allylic hydrogens and polyisoprene double bond.[31] Indeed, for reaction at high conversion (>95%) we observed the formation of some insoluble material. This material could be formed via reaction of radical propagating species with vinyl bonds present in polyisoprene, which become more reactive toward radical addition at low concentration in monomers (i.e., high conversion).

In order to prove the livingness of the system, a reaction of chain extension was undertaken on a polyisoprene sample. In order to minimized potential termination and cross-linking reactions, a polyisoprene was produced up to 85% conversion and isolated (M_n = 4500 g/mol, PDI = 1.23). The polyisoprene was then used as macro-chain-transfer agent to mediate isoprene polymerization and led to a polymer with M_n = 12 300 g/mol and PDI = 1.30. Figure 7 illustrates the clear shift of molecular weight distribution after chain extension.

Living radical polymerization allows the easy production of block copolymers. In order to demonstrate the preparation of block copolymers based on isoprene, a poly(*tert*-butyl acrylate (M_n = 10 900 g/mol and PDI = 1.05) and a polystyrene (M_n = 34 000 g/mol and PDI = 1.13) were synthesized via RAFT and isolated. Both polymers were then used as macro-chain-transfer agents to mediate the polymerization of isoprene, following the optimized reaction conditions described above. Table 2 shows that the block copolymerization was successful, and well-defined block copolymers were obtained.

Conclusion

We have demonstrated the use of RAFT to control the polymerization of isoprene. We found that the use of trithiocarbonate (2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester, ETSPE) at 115 °C with a ratio chain transfer agent:AIBN = 1:0.2 leads to a good control over molecular weight and low PDI. These conditions were used to produced block copolymers of polyisoprene with polystyrene and poly(*tert*-butyl acrylate).

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