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Design and Synthesis of Functionalized Styrene-Butadiene Copolymers by Means of Living Anionic Polymerization

Mayumi Hayashi

Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 2-1 Kitasode, Sodegaura-city, Chiba Pref. 299-0295, Japan
Tel: (+)-81-438-62-1276; Fax: (+)-81-438-63-6754

Summary: Styrene-butadiene copolymers (SBR) end-functionalized with dimethylamino groups at the initiating and terminating chain-ends were successfully synthesized by a one-step methodology based on living anionic polymerization using 1-(4-dimethylaminophenyl)-1-phenylethylene. The expected structures of the resulting copolymers were confirmed by ^{1}H-NMR, SEC, and SLS analyses, titration, and model reactions. Furthermore, the possible synthesis of tri-functionalized styrene-butadiene copolymer with dimethylamino groups in a chain by extending the methodology is described.

Keywords: anionic copolymerization; dimethylamino group; living polymerization; SBR; telechelics

Introduction

Chain-end-functionalized polymers such as telechelic polymers and macromonomers are industrially very important materials for preparing multi-block and graft copolymers and cross linked polymers with network structures.[1-4] Recently, these polymers have been utilized as precursory polymers for the synthesis of rod-coil block copolymers, specially shaped, branched polymers, cyclic polymers, and regular and asymmetric star-branched polymers.[5,6]

The methodology of living anionic polymerization is particularly suitable for the synthesis of well-defined chain-end-functionalized polymers with controllable molecular weights, narrow molecular weight distributions, and quantitative degrees of end-functionalizations.[4] Functional groups are generally introduced at either initiating or terminating chain-ends by using functionalized initiators or terminating agents. For this purpose, 1,1-diphenylethylene (DPE) and its derivatives are very useful and convenient compounds. They can react efficiently with carbanionic species like organolithium compounds as well as living anionic polymers of styrene

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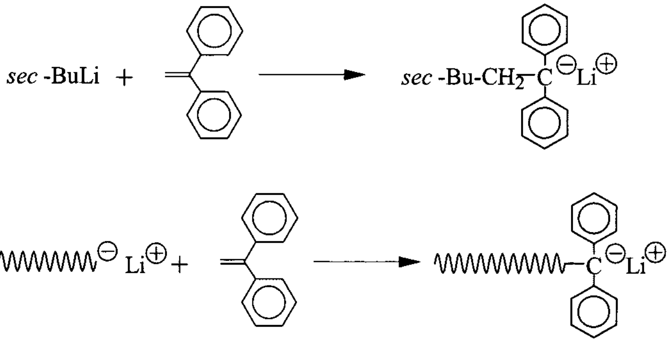
and 1,3-diene monomers in a monoaddition manner to quantitatively afford 1:1 adduct 1,1-diphenylalkyl anions (Scheme 1). Thus, they can be used as not only initiators but also terminators.

Scheme 1



Quirk and his coworkers have greatly developed the methodology of using functionalized DPE derivatives to synthesize well-defined chain-functionalized polymers.[7-10] They demonstrated for the first time that 1,1-diphenylalkyl anions derived from functionalized DPE derivatives, often used as functionalized initiators in the polymerization of alkyl methacrylates and ethylene oxide, can also be used as effective initiators for the living anionic polymerization of less reactive styrene and 1,3-diene monomers. By this success, polystyrenes and poly(1,3-diene)s can be functionalized at both initiating and terminating chain ends. Asymmetric chain-end-functionalized polymers can also be synthesized by the use of different DPE derivatives at initiation and termination steps. Furthermore, in-chain-functionalized homopolymers and block copolymers have been synthesized by terminating living anionic polymers with functionalized DPE derivatives, followed by initiating the polymerization of the same or different monomers with the generated anions at the chain ends. Thus, functionalized DPE derivatives potentially offer a versatile methodology for the synthesis of various chain-functionalized polymers. However, one limitation of this methodology is that rigid stoichiometry is required in the addition reaction between DPE derivative and either initiator or propagating chain-end anion. If an excess of the DPE derivative is used, it may be incorporated into the polymer chain, resulting in the introduction of extra functional groups. If the anionic species is used in excess, unfunctionalized polymer chains are produced.

We herein report on a new, simple one-step methodology based on living anionic polymerization and DPE chemistry for the synthesis of chain-end-functionalized styrene-butadiene copolymers with dimethylamino groups at both initiating and terminating chain-ends. Although such functionalized polymers can be synthesized by the method of Quirk using two steps involving initiation and termination reactions, the same functionalized polymers can be synthesized by a one-step reaction in our new methodology. Furthermore, the possible synthesis of tri-functionalized styrene-butadiene copolymers with dimethylamino groups at desired positions in a chain by extending the methodology is described. Finally, the influence of number and position of dimethylamino groups on the physical properties of the resulting rubbery copolymers is discussed.

Experimental

Materials. Hexane, cyclohexane, styrene and 1,3-butadiene were purified to the level of anionic polymerization according to the literature procedures.[11] The functionalized 1,1-diphenylalkylanion used as an initiator was prepared by the reaction of appropriate amounts of 1-(4-dimethylaminophenyl)-1-phenylethylene (**1**)[7] with *sec*-BuLi in cyclohexane at 25 °C for 0.5 h under nitrogen.

α,ω-Functionalized Copolymers with Dimethylamino Groups. The anionic copolymerization of styrene and 1,3-butadiene was carried out in a mixture of hexane and cyclohexane at 60 °C in the presence of 15.2 mL of THF and 1.0 mL of 1,2-dimethoxyethane. The copolymerization was started by adding the functionalized initiator from a 2.1-fold excess of **1** (5.25 mmol) and *sec*-BuLi (1.0 M cyclohexane solution, 2.50 mL, 2.50 mmol) in cyclohexane (7.0 mL) to a mixture of styrene (58 g) and 1,3-butadiene (142 g) in hexane solution (3.5 L) in a 5L autoclave with stirring. Styrene (87 g) and 1,3-butadiene (213 g) were further fed for 1 h and 1.5 h, respectively throughout the polymerization. During stirring for 30 min after the copolymerization, an orange color characteristic to the 1,1-diphenylalkyl anion derived from **1** gradually developed. The polymer solution was stirred for an additional 1 h and quenched with degassed methanol. The resulting polymer was precipitated in methanol and purified by reprecipitation three times. It was finally dried under reduced pressure at 55 °C for 12 h.

Chain-Functionalized Copolymers with Three Dimethylamino Groups. The functionalized initiator prepared from a 3.1-fold excess of **1** (7.75 mmol), *sec*-BuLi (1.0 M cyclohexane solution, 2.50 mL, 2.50 mmol) and cyclohexane (7.0 mL) was used in this case. The copolymerization was first carried out under conditions identical to those described above. During the first stage of copolymerization, styrene (43.5 g) and 1,3-butadiene (106.5 g) were fed for 1 h and 1.5 h, respectively, and the polymerization mixture was stirred for additional 1.5 h. Then, the same amounts of styrene and 1.3-butadiene were again fed for 1 h and 1.5 h at the second stage of copolymerization, and the mixture was allowed to stir for an additional 1.5 h. The resulting polymer was precipitated in methanol and purified by reprecipitation three times. It was finally dried under reduced pressure at 55 °C for 12 h.

Polymer Characterization. Size-exclusion chromatography (SEC) was obtained at 40 °C with a TOSOH HLC 8020 instrument with UV (254nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 0.6 mL/min. A calibration curve was made using standard polystyrenes. ^{1}H NMR spectra were recorded on JEOL instrument at 270 MHz in $CDCl_3$. The measurement by static light scattering (SLS) was performed with an Otsuka Electronics SLS-600R instrument equipped with a He-Ne laser (633 nm) in THF at 25 °C. Infrared spectra were measured on a PERKIN ELMER FT-IR Spectrometer 1720X in order to determine the 1,2-vinyl content of butadiene unit. The styrene content was measured by the refractive index method.

Preparation of Vulcanized Rubber. The rubber composites listed in Table 1 were prepared from the resulting polymer (Mw .200kg/mol) by mechanical mixing. The mixing conditions were as follows: the dried copolymer was masticated in labo plastomill at 70 °C for 0.5 min, and then well-dried silica and the silane coupling agent were mixed with the resulting masticated polymer at 110 °C for 1.5 min. Furthermore, zinc oxide, stearic acid, and the antioxidant were mixed with the silica-filled rubber composites thus prepared at 120 °C for 3.5 min (first step). The master batch obtained at the first step was then mixed with sulfur and the accelerator at 70 °C for 3 min, followed by cooling to room temperature (second step). Finally, the resulting master batch was vulcanized at 160 °C for 45 min to prepare test pieces. Hardness, 300% modulus, and resilience of the resulting vulcanized polymers were measured according to ASTM STANDARD.[12]

Table 1. Composition of silica-filled rubber composite (weight per hundred rubber).

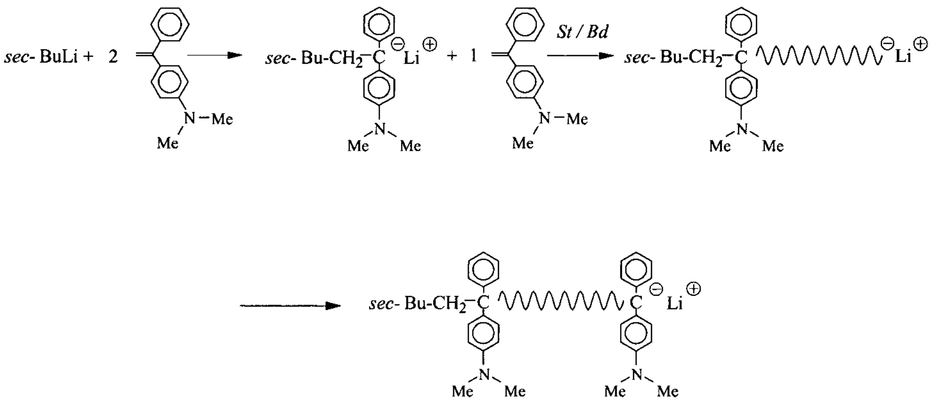
Copolymer	100	Antioxidant 6C	1.5
Silica	75	Accelerator CZ	1
Coupling agent	5	Accelerator DPG	1
Zinc Oxide	3	Sulfur	1.5
Stearic acid	2		

Results and Discussion

Synthesis of α,ω-Functionalized Copolymer with Dimethylamino Groups. We previously synthesized chain-end-functionalized styrene-butadiene copolymer with dimethylamino groups by the anionic copolymerization of styrene with 1,3-butadiene in a mixture of cyclohexane and hexane at 60 °C for 2.5 h with the functionalized initiator prepared from a 1.2-fold excess of **1** and *sec*-BuLi. Therefore, 0.2 equivalents of **1** remained after the preparation of the initiator. As described in experimental section, the copolymerization was performed by feeding two monomers throughout the polymerization. Since the weight ratio of 1,3-butadiene to styrene was 3/7 and 1,3-butadiene was fed longer, a pale yellow color of the poly(1,3-butadienyl) anion was always observed during the copolymerization, as expected. After the copolymerization, the polymerization mixture was allowed to stir for 30 min. Very surprisingly, the color gradually changed from pale yellow to bright orange color of the 1,1-diphenylalkyl anion presumably generated from **1** and the chain-end anion. This strongly suggests that the residual 0.2 equivalents of **1** are not incorporated into the copolymer, but remain intact during the course of the copolymerization and then react gradually with the propagating chain-end anion after the copolymerization.

This unexpected result prompted us to investigate the reaction pattern of **1** on the living anionic copolymerization of styrene and 1,3-butadiene in more detail with hope that a chain-end-functionalized styrene-butadiene copolymer having two dimethylamino groups at both initiating and terminating chain-ends can be synthesized as illustrated in Scheme 2. For this purpose, we prepared the dimethylamino-functionalized initiator from a 2.1-fold excess of **1** and *sec*-BuLi, and used it for the anionic copolymerization of styrene and 1,3-butadiene under the conditions

Scheme 2



mentioned above. Again, the pale yellow color was observed throughout the copolymerization, and the characteristic orange color gradually appeared after the copolymerization.

The resulting copolymer showed a sharp monomodal SEC distribution, the M_w/M_n value being 1.08. The absolute M_w value of 205 kg/mol determined by SLS agreed well with that calculated (200 kg/mol). The ^{1}H NMR spectrum of the reaction mixture showed the characteristic resonance at 2.90 ppm assigned to methyl protons of the dimethylamino groups introduced into the polymer chain. In addition, a small resonance at 2.97 ppm corresponding to methyl protons of the dimethyl amino group of **1** was also present in this mixture. The ratio of two peak intensities of 2.0/0.1 is exactly the same as the ratio assuming that two dimethylamino groups are introduced at both the initiating and terminating chain-ends and 0.1 equivalent of **1** remains unreacted as illustrated in Scheme 2. The copolymer was purified by reprecipitation three times. The resonance at 2.90 ppm remained almost unchanged and the degree of dimethylamino-functionalization was 2.0 ± 0.1 using methyl benzoate (3.90 ppm) as an internal standard. The functionalization degree was also determined by titration, using $HClO_4$ with crystal violet as an indicator, to be 2.0 ± 0.05. These results showed that two dimethylamino groups were introduced into the polymer chain and the residual 0.1 equivalent of **1** remains intact after the copolymerization.

In our copolymerization system, one dimethylamino group is definitely introduced at the initiating chain-end *via* the initiation step with the functionalized 1,1-diphenylalkyl anion. It is therefore indicated that the second dimethylamino group may be introduced at the terminating chain-end by the reaction of the propagating chain-end anion with **1** after the copolymerization. Since the resulting 1,1-diphenylalkyl anion cannot further react with **1**, it is reasonable that 0.1 equivalent of **1** remains unreacted. Two more reactions have been performed to prove the fact that the resulting copolymer chain-end anion is completely converted from butadienyl anion to the 1,1-diphenylalkyl anion derived from **1**.

As the first reaction, we have reacted methyl 4-dimetylaminobenzoate (**2**) with a model poly(1,3-butadienyl) anion (A), the reaction product of (A) with **1** (B), and the polymer anion (C) prepared by our one-step methodology and compared the reaction products. The polymer anion (A) was prepared by the anionic copolymerization of styrene and 1,3-butadiene with *sec*-BuLi under conditions similar to (C). The polymer anion (B) was prepared by adding a 2.0-fold excess of **1** to the anion (A). The three polymer anions thus prepared were reacted with **2** at 60 °C for 1 h. SEC profiles of the reaction mixtures are shown in Figure 1. In all cases, there were only two sharp peaks. Lower molecular weight peaks represent the 1:1 ketonic products of **2** with polymer

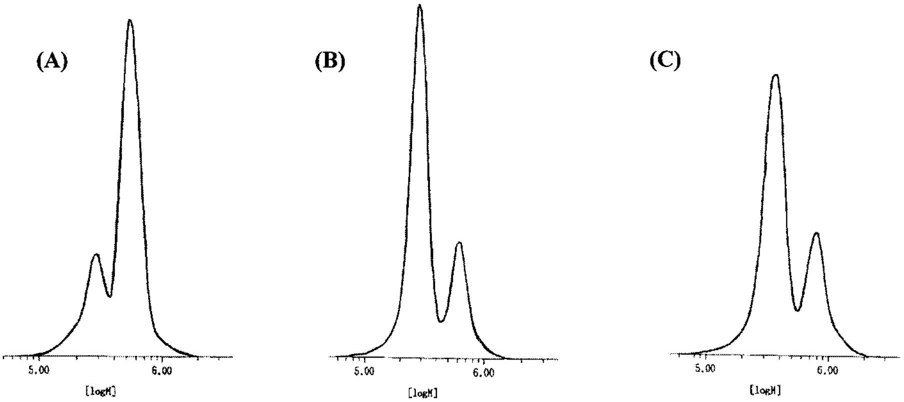
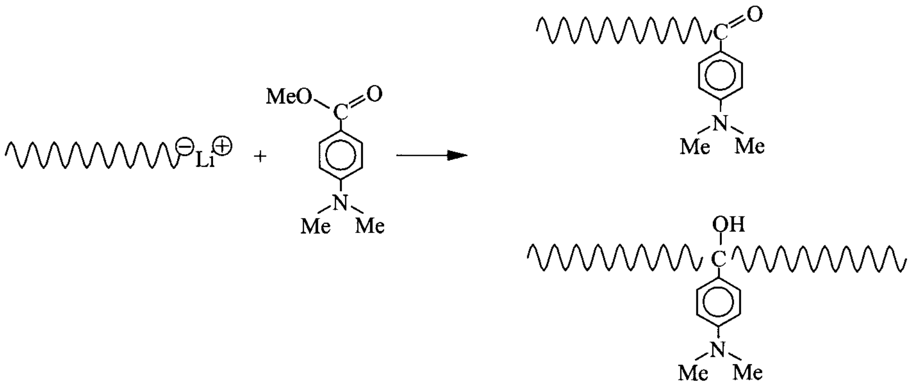


Figure 1. SEC profiles of the reaction mixtures of **2** with the model poly (1,3-butadienyl)anion **(A)**, the model 1,1-diphenylalkyl anion derived from **1** **(B)** and the polymer anion **(C)** prepared by our one-step methodology.

anions, while higher ones at double the molecular weight may possibly be dimeric alcohols as illustated in Equation 1. The area ratios of the two peaks were 25/75, 75/25, and 74/26 in the reactions of **2** with polymer anions, (A), (B), and (C), respectively. Since the ratio obtained by the reaction of **2** with (C) was consistent with that obtained by the reaction of **2** with (B), the anion (C) prepared by our one-step methodology proved to be the 1,1-diphenylalkyl anion derived from **1**.

Equation 1

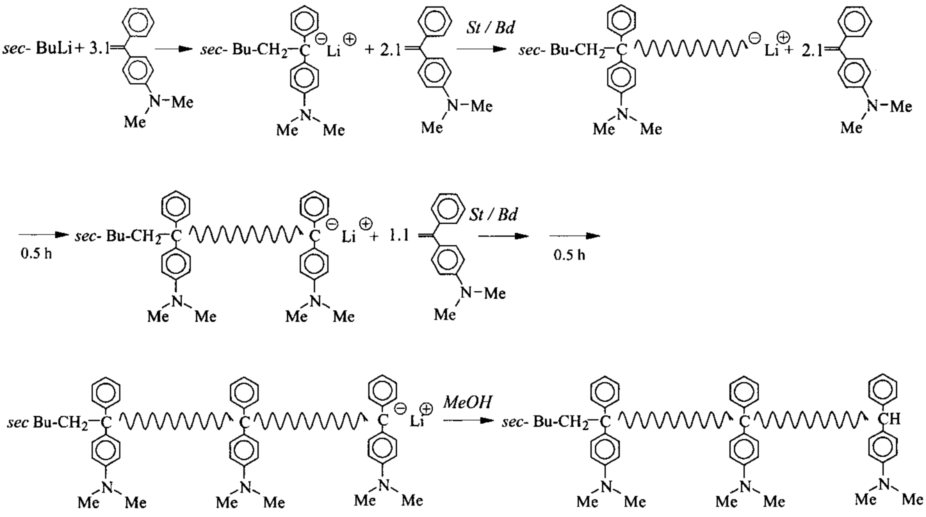


In order to further evaluate the structure of the terminal anion, we have reacted 1-(*N*-morpholinophenyl)-1-phenylethylene (**3**) with (A), (B), and (C) at 60 °C for 10 h. The introduction of morpholino group was observed in the copolymer obtained by the reaction of **3** with (A), while morpholino group was not present in the copolymers obtained by the reactions of **3** with (B) and (C). As it is well established that no addition reaction of DPE to 1,1-diphenylalkyl anion occurs under normal conditions, the result of the reaction of **3** with (B) is reasonable. Since the same result occurred for the reaction of **3** with (C), we conclude that (C) is terminated by the 1,1-diphenylalkyl anion from **1**.

All of these results confirm the expectation that styrene and 1,3-butadiene copolymerize with the dimethylamino-functionalized initiator and the resulting polymer anion reacts with the residual **1** after the copolymerization to afford an α,ω-functionalized copolymer with two dimethylamino groups at both the initiating and terminating chain-ends. It should be however mentioned that **1** undergoes copolymerization with styrene and 1,3-butadiene if a relatively large amount of **1** exists. Quirk and his co-workers[13] previously reported that **1** indeed copolymerized with either styrene or 1,3-butadiene to afford copolymers with many dimethylamino groups. These results suggest that the polymerization in the presence of **1** is very sensitive and depends significantly on changes of the applied concentration and reactivity of **1**, the reaction solvent, temperature and so on.

Synthesis of Chain-Functionalized Styrene-Butadiene Copolymer with Three Dimethyl-amino Groups. The copolymer chain-end anion prepared by the one-step methodology developed herein is still active and can reinitiate the copolymerization to extend a new polymer chain by the addition of monomers. If residual **1** is present in the system, it is expected that the new polymer chain-end anion reacts with **1** to introduce the third dimethylamino group at the chain-end as illustrated in Scheme 3.

Scheme 3



To test the possibility of this type of functionalized copolymer synthesis, the functionalized 1,1-diphenylethylene anion was newly prepared from a 3.1 molar ratio of **1** to *sec*-BuLi. The first copolymerization was similarly carried out with the initiator thus prepared under conditions identical to those employed for the one-step methodology. The color of the resulting polymer solution became gradually bright orange by allowing the polymerization mixture to stir for an additional 30 min after the copolymerization. The second copolymerization was started by feeding both styrene and 1,3-butadiene in the same manner. The color of the polymerization mixture instantaneously changed from bright orange to pale yellow and the pale yellow color remained stable as the copolymerization proceeded. After the polymerization, the reaction mixture was allowed to stir for 30 min and the color gradually changed again to bright orange with time.

The copolymers obtained at the first and second polymerization stages exhibit sharp monomodal SEC distributions, and the SEC peak of the first copolymer moves to a higher molecular weight side while maintaining a narrow molecular weight distribution, as shown in Figure 2. The characteristic resonance at 2.90 ppm for methyl protons of the dimethylamino group was observed in both copolymers. The degree of dimethylamino functionalization of the second copolymer was 3.0 ± 0.15. It was proved by the reactions with **2** and **3** that the copolymer chain-end anion after the second copolymerization is the 1,1-diphenylalkyl anion derived from **1**. These results in addition to the bright orange coloration in each copolymerization stage strongly indicate that the methodology works satisfactorily as illustrated in Scheme 3 to afford a special chain-functionalized styrene-butadiene copolymer with three dimethylamino groups, including

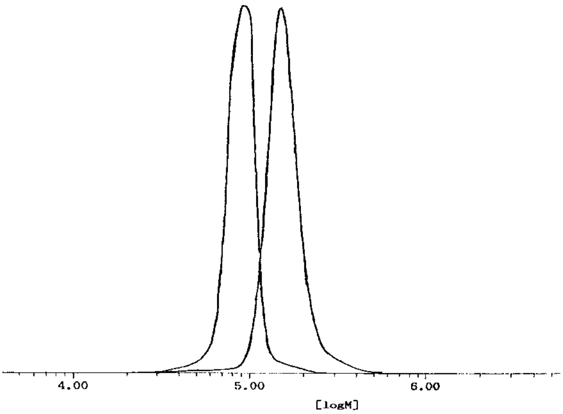


Figure 2. SEC profiles of the first and the second copolymers.

one each at the initiating and terminating chain ends as well as in the chain. Thus, we were successful in extending the one-step methodology to the synthesis of chain-functionalized styrene-butadiene copolymer with three dimethylamino groups. Although the influence of changes in molecular weight, copolymer composition, and reaction variables have to be studied in detail, the developed one-step methodology provides a promising tool for the design and synthesis of well-defined chain-functionalized styrene-butadiene copolymers with multiple dimethylamino groups. We are now investigating an extension of this one-step methodology to the introduction of more dimethylamino groups into copolymer chains.

Properties of Functionalized Styrene-Butadiene Copolymers

In this study, well-defined functionalized styrene-butadiene copolymers with one, two, or three dimethylamino groups were synthesized by one-step methodology. By testing physical properties of these polymers, the influence of the number and position of dimethylamino groups on the properties can be discussed. The samples and the results are listed in Table 2. As shown in the Table, the modulus of 300 % elongation becomes a bit higher with increasing number of dimethylamino groups. However, both hardness and resilience were independent of the number of dimethylamino groups. The influence of the number and position of dimethylamino groups on other properties is now under investigation.

Table 2. Properties of Functionalized Styrene-Butadiene Copolymers.

Polymer (number of -NMe_2)	Styrene (%)	Vinyl (%)	ML $_{1+4}$ 100℃ 1)	Hs 2) (Duro-A)	M300 3) (Mpa)	Resilience 60℃ 4) (%)
1	28.9	42.9	67	69	7.42	53
2	28.9	42.3	70	70	7.59	54
3	29.1	44.3	72	69	7.75	54

1) Measured according to ISO 289:1985
2) Measured according to ISO 48:1994
3) Measured according to ISO 37:1977
4) Measured according to ISO 4662:1986

Conclusions

We have developed a promising new one-step methodology for the synthesis of well-defined chain-functionalized styrene-butadiene copolymers with dimethylamino groups at both initiating and terminating chain-ends. By extending this methodology with the functionalized initiator prepared from 1 and *sec*-BuLi in a 3.1:1 molar ratio, a chain-functionalized styrene-butadiene copolymer with three dimethylamino groups could be synthesized. The simplicity and efficiency of this methodology makes it an attractive candidate for preparing multi-functionalized styrene-butadiene copolymers (SBR).

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[1] F. W. Harris, H. J. Spinelli, *Reactive Oligomers*, ACS Symposium Series, No. 282, Am. Chem. Soc., Washington D.C. **1985**
[2] E. J. Goethals, *Telechelic Polymers: Synthesis and Applications*, CRC Press, Boca Raton, Florida **1989**
[3] Y. Yamashita, *Chemistry and Industry of Macromonomers*, Marcel Dekker, Inc., Huthing & Wepf, Heidelberg **1993**
[4] H. L. Hsieh, R. P. Quirk, *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker, New York **1996**
[5] References are cited in A. Hirao, M. Hayashi, *Acta Polym.* **1999**, *50*, 219
[6] A. Hirao, M. Hayashi, Y. Tokuda, N. Haraguchi, T. Higashihara, S-W. Ryu, *Polymer J.* **2002**, *34*, 633
[7] R. P. Quirk, L-F. Zhu, *British Polym. J.* **1990**, *23*, 47
[8] R. P. Quirk, J. Yin, S-H. Guo, X-W. Hu, G. J. Summers, J. Kim, L-F. Zhu, J-J. Ma, T. Takizawa, T. Lynch, *Rubber Chem. Tech.* **1991**, *64*, 648
[9] R. P. Quirk, *Macromol. Chem., Macromol. Symp.* **1992**, *63*, 259
[10] R. P. Quirk, T. Yoo, Y. Lee, J. Kim, B. Lee, *Adv. Polym. Sci.* **2000**, *153*, 67
[11] N. Hadjichristidis, H. Iatrou, S. Pispas, M. Pitsikalis, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 3211
[12] Annual Book of ASTM STANDARDS, Vol. 09.01, **1990**
[13] R. P. Quirk, L-F. Zhu, *Polymer International* **1992**, *27*, 1