Syntheses of Triblock Polybutadiene–Polydimethylsiloxane Copolymers by Coupling Reactions

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ABSTRACT: The reaction of epoxy-telechelic polydimethylsiloxanes with polybutadienyllithium was used to prepare a series of low-molecular-weight polybutadiene-*block*-polydimethylsiloxane-*block*-polybutadiene copolymers. The copolymers were purified by repeated fractional precipitation/centrifugation and characterized with NMR, vapor pressure osmometry, size exclusion chromatography, and elemental analysis. The applicability of this method is discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3233–3240, 2006

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INTRODUCTION

Organic polymers containing siloxanes have long been intensively studied.[1–3] Some alternating, block, starlike, and grafted copolymers of siloxanes with certain alkenes, vinyl aromatic hydrocarbons, or alkadienes have been prepared.

Several synthetic strategies have been explored, the most frequent being sequential anionic polymerization of a proper organic monomer initiated with organolithium compounds followed by a reaction of the living polymer with hexamethylcyclotrisiloxane (D_3) [exceptionally with octamethyltetrasiloxane (D_4)].

A number of examples have been disclosed in patents, but mainly those reported in the original articles are cited. Of vinyl aromatics, the synthesis of polystyrene (PST)–polysiloxane copolymers has thoroughly been studied. Sequential anionic polymerization has been used to synthesize PST-*block*-poly(methylphenylsiloxane),[4] PST–polydimethylsiloxane (PDMS) copolymers,[5–8,] and polyisoprene-*block*-PST-*block*-PDMS.[9] Living lithium-bearing PDMS-*block*-PST-*block*-PDMS has been used as a precursor for the macrocyclic copolymer obtained by its reaction with dichlorodimethylsilane.[10] The side reactions of higher molecular weight linear precursors have been prevented via coupling with 2,2,5,5-tetra-2,5-disila-1-oxacyclopentane

preceding the D_3 polymerization.[10] Sequential anionic polymerization followed by D_3 ring opening and bifunctional coupling has been applied to prepare (*star*-PST)-*block*-PDMS-*block*-(*star*-PST) copolymers having relatively narrow molecular weight distributions.[11]

Besides anionic polymerization, the free-radical vinyl polymerization of styrene (ST) initiated by macroinitiators based on peroxycarbamate-terminated PDMS has been reported;[12] it yielded diblock PST–PDMS copolymers. Another macroinitiator of this type was prepared by a condensation reaction between 4,4′-azobis-4-cyanopentanoyl chloride, PDMS, and methacroyl chloride.[13]

Related to this approach are the recently reported syntheses of triblock PDMS–PST–PDMS copolymers,[14] which involve the formation of telechelic 2-pentamethyldisiloxanyl ethyl polystyrene followed by an acid-catalyzed equilibration polymerization of D_4.

A less frequently exploited method is based on the coupling of ene and siloxane units via hydrosilylation (i.e., the addition of Si—H to C=C): polyisobutylene–PDMS bicomponent networks have been prepared[15,16] by the hydrosilylation of allyl–tritelechelic polyisobutylenes with telechelic H—Si(CH$_3$)$_2$-terminated PDMS. Multiblock copolymers of α,ω-bis(hydrogenodimethylsilyl)polydimethylsiloxane with α,ω-diisoprenyloligopropylenes[17] and alternating 1,3-diisoprenylbenzene-1,1,3,3-tetramethyldisiloxane copolymers have been prepared in a similar way.[18]

Hydrosilylation coupling of commercially available difunctional PDMS, containing vinylsilyl or hydrogenosilyl terminal groups, with the corresponding hy-

drogenosilyl- or vinylsilyl-substituted benzyl chloride derivatives has been used to prepare initiators for the synthesis of triblock ST–PDMS–ST copolymers by the atom transfer radical polymerization.[19]

However, only a few studies have dealt with alkadiene–siloxane copolymers: side-loop polymers have been obtained by the hydrosilylation of polybutadiene (PBd) with a hydride-terminated PDMS,[20] and a copolymer with alternating alkadiene and dimethylsiloxane (DMS) units has been prepared by the hydrosilylation of some α,ω-alkadienes with 1,3-dihydrotetramethyldisiloxane.[21]

Sequential anionic polymerization has been employed to prepare low-molecular-weight polyisoprene–PDMS diblock copolymers, the mesomorphic phase behavior of which has been subjected to a thorough study.[22] To our knowledge, the syntheses of diblock and triblock copolymers of DMS with dienes other than isoprene have not yet been reported.

In this work, we report what we believe is the first example of PBd-*block*-PDMS-*block*-PBd copolymers. For this purpose, we decided to employ a novel synthetic approach based on the coupling of living polybutadienyllithium (PBd–Li) with a telechelic α,ω-diepoxy-terminated PDMS macromonomer as the precursor of the middle segment.

EXPERIMENTAL

Materials

1,3-Butadiene (Kaučuk a.s., Kralupy nad Vltavou, Czech Republic) was stored in a glass pressure bottles and used as received. Butyllithium (BuLi; $1.6M$ solution in hexanes; Sigma–Aldrich, Prague, Czech Republic), propylene oxide (99%; Kaučuk, Bruker Biospin GmbH, Rheinstetted, Germany), and glycidyloxypropyl-telechelic PDMS [Sigma–Aldrich; number-average molecular weight (M_n) = 718, as determined by vapor pressure osmometry (VPO) in this laboratory] were commercial products, as indicated. *tert*-Butyl methyl ether (Kaučuk) was dried with sodium bis(2-methoxyethoxy)aluminum hydride (a 70% solution in toluene), redistilled, and kept under argon.

Size exclusion chromatography (SEC)

The SEC separation system consisted of a Deltachrom SDS 030 (Watrex, Prague, Czech Republic) pump operating at a flow rate of 0.5 mL/min, a Midas (Spark, Emmen, Holland) autosampler, two PLgel 10-μm mixed-B LS columns separating (according to the producer, Polymer Laboratories, Shropshire, UK) in the molecular weight range of approximately $300 < M < 10^7$ (related to PST standards), and a PL-ELS 1000 evaporative light scattering detector (Polymer Laboratories). The temperatures of the nebulizer and evapo-

rator were 47 and 80°C, respectively. Tetrahydrofuran (Fluka, Buchs, Switzerland) at the ambient temperature was used as the mobile phase. The calibration curve for hydroxy-semitelechelic polybutadiene (PBd–OH) was constructed with four samples, their molecular weights ranging from 628 to 1787.

VPO

The M_n values of the samples were determined by VPO (model K-7000, Knauer, Berlin, Germany). Calibration with PST standards (Polymer Standards Service, Mainz, Germany) and measurements of the samples were carried out under the same conditions: tetrahydrofuran as the solvent, 45°C as the cell temperature, 1.5 min as the time of measurement, and 16 (gain). Each sample was measured with four different concentrations ranging from 0.5 to 5 wt %, and the data were extrapolated to zero concentration.

NMR spectroscopy

For the regioselectivity study, ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were measured in deuteriobenzene on a Varian Mercury 300 NMR spectrometer (Varian Inc., Palo Alto, CA). A total of 1% hexamethyldisiloxane added to deuteriobenzene served as a reference for ^{1}H-NMR (δ = 0.04) and ^{29}Si-NMR (δ = −19.79). ^{13}C-NMR spectra were referenced to a central line of the solvent (δ = 128.7). ^{29}Si-NMR spectra were measured with a 10-s relaxation delay by an insensitive nuclea enhanced by polarization transfer method (INEPT) pulse sequence optimized for polarization transfer through [2]J (^{1}H and [29]Si) = 6.7 Hz in CH₃—Si fragments.

The copolymer compositions were determined from ^{1}H-NMR spectra measured in CDCl₃ solutions with a Bruker Avance DPX-300 spectrometer at 300.1 MHz and room temperature. No internal standard was added to the solutions, and the signal of residual CHCl₃ at δ = 7.26 was used as a reference. The copolymer compositions were calculated from the intensities of the signals of olefinic protons of 1,2- and 1,4-PBd units[23] (δ = 4.9–6.0) and from the signal intensity of PDMS units (δ = 0.06).

Determination of the epoxy groups in the presence of lithium

The procedure reported by Jay[24] was modified in the following way.[25] To 15 mL of chloroform and 15 mL of aqueous $0.2M$ H₃BO₃, a sample containing 0.05–1.0 mmol of epoxy groups was added, and the mixture was shaken for 3 min. The chloroform layer was transferred into a 50-mL beaker, to which 15 mL of glacial acetic acid and 3 g of tetrabutylammonium bromide were added, and the content of epoxy groups was determined by potentiometric titration with $0.5M$

TABLE I
Characterization of PBd–OH

Sample	M_n (VPO)	SEC	
		M_n	M_w/M_n
PBd–OH/1	530	575	1.05
PBd–OH/2	910	908	1.08
PBd–OH/3	970	1122	1.04
PBd–OH/4	1650	1679	1.06

HClO$_4$ in glacial acetic acid (glass and calomel electrode).

Determination of the OH functionality of PBd end-quenched with propylene oxide

The OH functionality of PBd, expressed as the average number of OH groups per PBd molecule, was determined in the Analytical Department of the Synthetic Rubber Research Institute (Kralupy nad Vltavou, Czech Republic) by liquid adsorption chromatography (for details, see ref. 26).

Synthesis of the triblock butadiene (Bd)–siloxane copolymers: a typical procedure

First, living PBd–Li was prepared by anionic polymerization. A three-necked, round-bottom flask equipped with a magnetic stirrer, an inlet/outlet tube, a dropping funnel, and a condenser topped with a mercury seal was evacuated, filled with argon, and charged with dry *tert*-butyl methyl ether. A calculated volume of 1.6*M* BuLi was added to the stirred solvent by a microsyringe. Bd was then gradually introduced from a volumetric flask via the inlet tube immersed in the solution at the rate at which it was consumed. The polymerization was carried out at 15–20°C and was complete within 1–1.5 h.

A defined part of the solution was transferred to a pressure-equalizing dropping funnel connected to a separate reaction flask containing α,ω-diglycidyloxypropyl polydimethylsiloxane (PDMS–DG) cooled to 12°C. Then, the living polymer solution was added dropwise with stirring. When the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred for an additional 8 h. The block copolymer that formed was isolated in the following way. Its solution was shaken in a separator funnel, first with a dilute phosphoric acid and then with water until a neutral reaction was achieved. (The acid should be removed quantitatively because it catalyzes the reaction between the hydroxyl groups formed between the blocks and the oxirane groups on residual, unreacted PDMS–DG precursor molecules or diblock copolymer molecules and leads to branched structures.) The organic layer was separated and dried

with anhydrous magnesium sulfate, the solvent was evaporated, and the product was transferred to a screw-top vial under a stream of argon. The procedure was tested on a 20–50-mmol scale with stoichiometric amounts of BuLi and PDMS–DG. The characterization of the products is given in the Results and Discussion section.

Synthesis of PBd–OH

Another portion of PBd–Li was end-quenched by an addition of excess propylene oxide. After the completion of the reaction (10 min), PBd–OH was obtained by the workup described in the previous paragraph. The characterization of these products is presented next (Table I).

RESULTS AND DISCUSSION

Coupling reactions

The synthesis of PBd-*block*-PDMS-*block*-PBd copolymers through the coupling of diepoxy-terminated PDMS with living PBd is shown in Scheme 1, where Bu is the butyl group incorporated (from the initiator), Bd represents a butadiene unit (regardless of its structure), and *m* and *n* are the average numbers of Bd and DMS units in the chains.

The equation describes only tentatively the course of the coupling reaction because its regioselectivity is not known. Our attempt at investigating the structure of PBd to the PDMS linkage by ^{29}Si- and ^{1}H-NMR analyses of several copolymers failed because potential structure-significant signals in the C–alkyl region were too weak to allow an unambiguous assignment to be made.

As for the structure of the Si block of the copolymer, its ^{29}Si-NMR spectrum, which is practically identical to that of the starting PDMS, has been taken as evidence for a selective attack of the living polymer on the oxirane ring. In contrast to low-molecular-weight
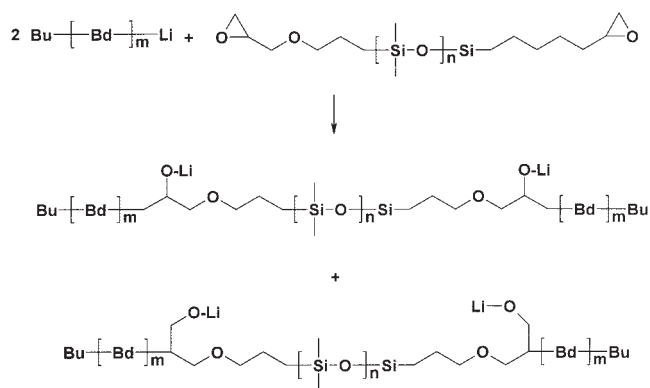
Scheme 1

organolithium compounds, which have long been known to react readily with siloxanes (cf. refs. 27 and 28), PBd–Li, under the reaction conditions used, does not cleave significantly the Si—O—Si group. Such a cleavage would ultimately lead to a redistribution of the Si—O—Si skeleton, a molecular weight reduction, and a broader molecular weight distribution of the product. The absence of such a process is indeed one of the conditions for a successful application of the aforementioned coupling reaction for the preparation of block copolymers with well-defined structures.

In this context, we hoped to obtain some information on the regioselectivity of the oxirane ring cleavage by reacting PDMS–DG with BuLi. However, as deduced from the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra, the expected reaction was accompanied by a cleavage of Si—O—Si and C—O bonds, yielding a multicomponent product, the analysis of which did not give conclusive results.

Unlike the aforementioned reaction components, living polymers prepared by the anionic polymerization of ST and isoprene were found to attack selectively the oxirane ring of monomeric (3-glycidyloxypropyl)trimethoxysilane, giving presumably linear semitelechelic alkoxysilyl-substituted oligomers.[29] We believe that the coupling of PDMS–DG with living PBd–Li proceeds in a similar way.

In contrast to the PDMS block, the microstructure of the PBd block can vary widely, depending on the specific conditions applied in anionic polymerization, which affect both the 1,2-isomerism versus 1,4-isomerism[30,31] and the stereoregularity (1,2-atactic and syndiotactic PBd; cf. ref. 9). In this work, *tert*-butyl methyl ether was used as a solvent for the preparation of living PBTd and led to a medium content of pending vinyls[32] (60% 1,2, 15% 1,4-cis, and 25% 1,4-trans monomer units).

The synthesis of triblock PBd-*block*-PDMS-*block*-PBd copolymers is described in detail in the Experimental section and deserves only a short comment.

First, the course of the polymerization was followed by the end capping of part of the living polymer with propylene oxide (Table I), which yielded PBd–OH. The samples thus prepared were used to determine the molecular weights of the corresponding PBd blocks and their molecular weight distribution, as well as the selectivity of the living polymer formation (i.e., potential presence of byproducts). The values of the weight-average molecular weight/number-average molecular weight ratio (M_w/M_n) of PBd–OH demonstrate that, as expected, the chosen polymerization conditions ensure the formation of a PBd block with a narrow molecular weight distribution. In addition, several samples were tested for their OH-functionality values, which, in all cases, were close to 0.97, as obtained by the adsorption high-performance-liquid-chromatography method cited in the Experimental
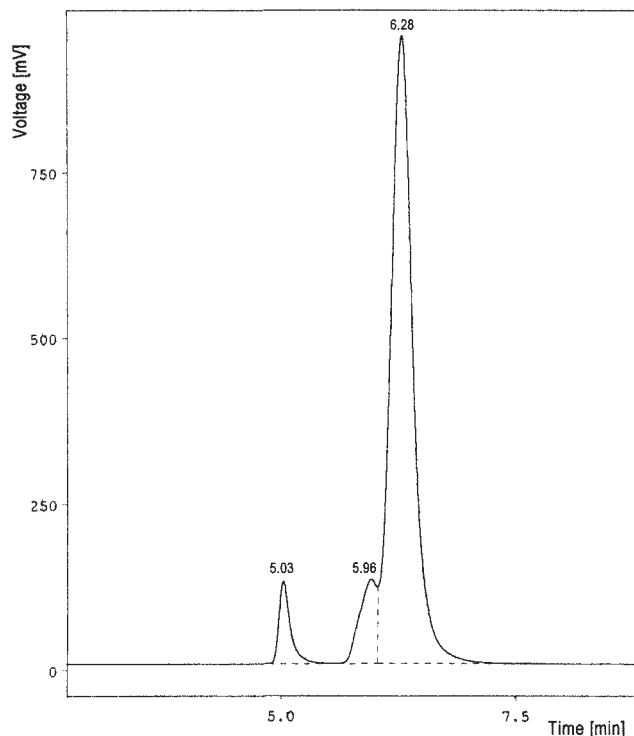

Figure 1 SEC chromatogram (adsorption mode) of the product of the living polymer with propylene oxide. The peak at the retention time of 5.03 min corresponds to PBd (functionality 0), and the peaks at 5.96 and 6.28 min correspond to two regioisomers of 2-hydroxypropyl-terminated PBd (functionality 1). For the analytical method, see ref. 26.

section; that is, more than 97% of the PBd chains were OH-semitelechelic, the rest being PBd chains with no OH end groups. This situation is illustrated by a corresponding chromatogram in Figure 1. Furthermore, the two peaks in the region of OH-semitelechelic chains (at retention times of 5.95 and 6.25 min) demonstrate that the reaction of the living polymer with propylene oxide led to two OH regioisomers, one of which was predominant (the main OH-terminated product constituted about 90% of the mixture, as estimated from integrated peak areas).

Second, the structure of the terminal groups of the predominant PBd–OH regioisomer was determined by NMR spectroscopy. [13]C distortionless enhancement by polarization transfer experimentation with multiplicity assessment revealed roughly three lines pertaining to the CH—O groups, their chemical shifts being 65.86, 66.90, and 67.89 ppm. The presence of the CH$_2$—O groups was not detected. [1]H homonuclear selective decoupling confirmed the presence of the CH$_3$—CH—O group (signals in the 3.55–3.65 ppm range for the CH—O protons and at 0.98 and 1.02 ppm for the CH$_3$ protons). On the basis of these findings, the main product can be assigned to the structure of semitelechelic 2-hydroxypropyl-terminated polybutadiene [PBd–CH$_2$CH(OH)CH$_3$].

Third, the molar ratio of the initiator (BuLi) to PDMS–DG should strictly be adjusted to 2 to avoid the contamination of the triblock copolymer with PBd and/or unreacted PDMS–DG. For that reason, we developed an efficient method for product purification.

Because with increasing molecular weight of the precursor blocks the concentration of the reactive end groups decreases, the rate of the coupling reaction between the carbanion of PBd–Li and the oxirane ring of PDMS–DG also decreases; this causes a higher risk of contamination of the product. No systematic study of such an effect of the molecular weights of the constituent blocks was performed, but it can be expected that higher molecular weights would demand stricter experimental conditions of the coupling reactions and longer reaction times.

Purification and characterization of the triblock copolymers

The triblock copolymers were synthesized as model substances for a study of microphase separation and mesoscopic structures,[33] the results of which will be the subject of a forthcoming article. The combination of PBd and polysiloxane blocks was chosen because they are known to be extremely incompatible. Theory predicts that, at the siloxane unit concentration of about 21 wt %, there will be a phase transition between two entirely different morphologies, one with cubic symmetry and the other with hexagonal symmetry. Hence, we synthesized four samples of the triblock copolymer differing in their chemical composition, which was expressed as the weight fraction of DMS units (w_{DMS}). For one of them, w_{DMS} assumed the transition value of 0.21; another one had its w_{DMS} above this value, and the remaining two had values below it.

Obviously, for such a physical study, the model samples should be well defined and characterized and free of undesirable impurities such as starting homopolymers and/or diblock structures. SEC shows that such admixtures are always present in the crude product, their peaks appearing in the region of molecular weights lower than that of the main peak. Therefore, a purification/fractionation procedure had to be applied, consisting of a repeated precipitation/centrifugation procedure described by us earlier.[34] *t*-Butyl methyl ether was used as the solvent, and methanol with 5 vol % water was used as the precipitant. SEC analyses have demonstrated (for a typical example of such a procedure, see Fig. 2) that individual purification cycles gradually enrich the product with the desirable triblock copolymer.

Because an evaporative light scattering detector was used in the SEC instrument applied to follow this purification procedure, the ratios of integrated individual peaks in the same chromatogram matched the
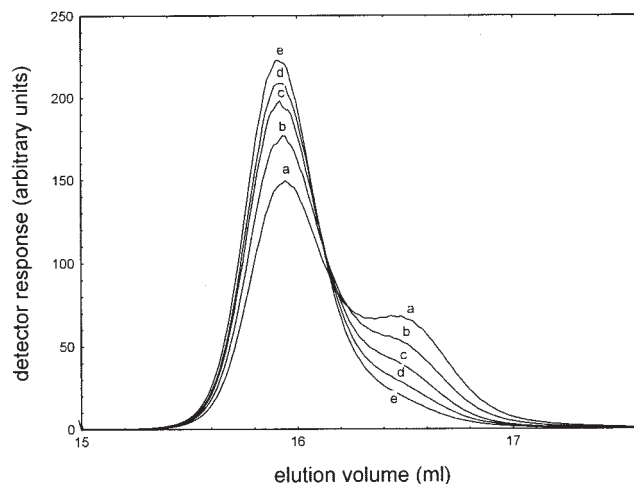
Figure 2 SEC chromatograms of a typical example of the repeated precipitation/centrifugation procedure (for sample C4): peaks after (a) 0, (b) 4, (c) 8, (d) 12, and (e) 16 purification cycles. Individual chromatograms were transformed to have identical integrated areas.

weight ratios of the corresponding components in the injected sample. An attempt was therefore made at deconvoluting the overlapping peaks to obtain the weight fractions of the components. It failed, however, because the smaller peaks (Fig. 2) always proved to be a mixture of several entities, that is, PBd, unreacted PDMS–DG, and the diblock copolymer (formed by the reaction of only one oxirane ring of PDMS–DG).

Because the molecular weights of the individual blocks are quite low, the groups of atoms located on the chain in the two boundaries between the three blocks (joints), as well as the Bu groups remaining at both chain ends as a residue of the initiator, must be taken into account for the molecular characterization of the triblock copolymer.

Although ^{1}H-NMR yields the pure content of the Bd and DMS units in the chain (as if Bu and joints are absent), elemental analysis and VPO yield values that include both Bu and joints. (The values of the copolymer composition from ^{1}H-NMR will be used for microphase-separation studies.) Corresponding equations needed to calculate expected values of M_n, w_{DMS}, and the C percentage have been derived and are given in the appendix. The results of the characterizations of the PBd–OH homopolymers and the corresponding triblock copolymers are presented in Tables I and II, respectively. Here, the OH-telechelic polybutadiene PBd–OH/1 corresponds to the triblock copolymer coded C-1. From the data, it follows that

1. The M_n values of PBd–OH obtained from SEC and VPO match within the limits of experimental error (Table I). Such good agreement is achieved only if direct calibration of the SEC

TABLE II
Characterization of the Triblock Copolymers

	M_n		w_{DMS}			% C		
Sample	VPO	Eq. (7)	NMR	$(w_{DMS})_{p'}$ eq. (A.6)	$(w_{DMS})_{g'}$ eq. (A.8)	eq. (A.9)[a]	eqs. (A.7) and (A.9)	Elemental analysis
C1	1400	1704	0.318	0.359	0.286	83.83	68.8	71.43
C2	1920	2420	0.216	0.235	0.202	94.25[b]	74.78	76.37
C3	2420	2692	0.198	0.208	0.181	84.68	76.13	77.21
C4	—[c]	3930	0.112	0.136	0.128	—[c]	80.20	82.56

[a] In eq. (9), the value of M_n from VPO was used.
[b] Higher than physically possible.
[c] Not obtained because of the insufficient amount of the sample.

columns by PBd–OH samples is used; universal calibration (see ref. 35) yields substantially larger differences. SEC is related to PBd–OH only (there was no proper calibration available for the copolymers).

2. The M_n values of the copolymer calculated as a sum of the M_n values of the blocks (including joints and Bu groups) are systematically higher than those from VPO, probably because the VPO values are reduced by the presence of some solvent residue (Table II).

3. Rather surprisingly, the values of w_{DMS} obtained from ^{1}H-NMR measurements are much closer to those calculated from eq. (A.8) (joints and Bu groups are included in the M_n values of the copolymer) than to those calculated from eq. (A.6) (joints and Bu groups are excluded). This can be explained by a possible small systematic error in the quantitative analysis of the ^{1}H-NMR spectra and/or in the M_n values from VPO (Table II).

4. Experimental values of the C percentage obtained from elemental analysis and those obtained with eq. (A.9) are much closer to each other if M_n is calculated from eq. (A.7) than if experimental (VPO) M_n values are used, probably because VPO underestimates the M_n values of the copolymer (Table II).

CONCLUSIONS

A novel method for preparing PBd-*block*-PDMS-*block*-PBd triblock copolymers of relatively narrow molecular weight distributions, consisting of the coupling of living PBd with epoxy-telechelic PDMS, was designed and tested. Only low-molecular-weight triblock copolymers, having their compositions in a relatively narrow range, were synthesized as model substances for the study of mesoscopic structures. Commercial PDMS–DG was used as a precursor of the middle PDMS block. A rather narrow choice of commercial PDMS–DGs represents the only limitation to a wider application of the method.

APPENDIX

Polysiloxane precursor

The number-average molecular weight of the polysiloxane precursor, that is, the oxirane-telechelic PDMS PDMS–DG ($M_{PDMS-DG}$ = 718 by VPO; supplied by Aldrich; for the structural formula, see Scheme A.1), can be expressed as the sum of the number-average molecular weight of the siloxane chain (M_{PDMS}) and the molecular weights of the two glycidyloxypropyl groups serving as joints to outer blocks (M_j = 115):

$$M_{PDMS-DG} = M_{PDMS} + 2M_j \qquad (A.1)$$

Accordingly, the average number of DMS repeating units per chain [i.e., number-average degree of polymerization (P_{PDMS})] can be calculated with eq. (A.2):

$$P_{PDMS} = (M_{PDMS-DG} - 2M_j)/M_{DMS} \qquad (A.2)$$

where M_{DMS} = 74 is the molecular weight of the DMS repeating unit. Thus, P_{PDMS} is 6.6 (hexamer to heptamer).

The expected content of carbon in this precursor [$C_{PDMS-DG}$ (%)] is obtained with eq. (A.3):

$$C_{PDMS-DG} = 100A_C\sum C_{PDMS-DG}/M_{PDMS-DG} \qquad (A.3)$$

where A_C = 12 is the atomic weight of carbon and $\sum C_{PDMS-DG}$ is the average overall number of carbon atoms in the precursor chain, for which it holds that

$$\sum C_{PDMS-DG} = 2\sum C_j + (\sum C_{DMS})P_{PDMS} \qquad (A.4)$$
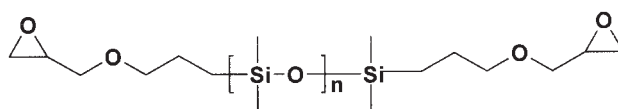
Scheme A.1

In eq. (A.4), $\Sigma C_j = 6$ and $\Sigma C_{DMS} = 2$ are the number of carbon atoms in a single joint and the number of carbon atoms in a DMS repeating unit, respectively.

Thus, eq. (A.3) yields $C_{PDMS-DG} = 42.10$, which is somewhat higher than the experimental value, 40.05. This discrepancy can be explained by a slight underestimation of $M_{PDMS-DG}$, as obtained by VPO.

PBd precursors

As mentioned in the Experimental section, the batch of living PBd–Li was always divided into two parts.

One was quenched by propylene oxide and yielded an OH-semitelechelic structure given in Scheme A.2, where the symbol Bd stands for a butadiene monomer unit, regardless of its isomerism. Its number-average molecular weight (M_{PBdOH}) consists of three parts:

$$M_{PBdOH} = M_{bu} + M_{PBd} + M_t \qquad (A.5)$$

The values for individual samples are given in Table I. In eq. (A.5), $M_{bu} = 57$ and $M_t = 59$ are the molecular weights of the Bu group (the incorporated residue of the initiator) and the terminal 2-hydroxypropyl group from propylene oxide, respectively, and M_{PBd} corresponds to the pure PBd chain.

The other part of the batch was coupled with the PDMS precursor. Naturally, the triblock thus formed lacked the 2-hydroxypropyl group.

Triblock copolymers

Individual copolymer samples differ in the lengths of their PBd (outer) blocks only, and their structure is given by a general formula in Scheme A.3.

Unlike other methods for the determination of the chemical composition, such as elemental analysis, ^{1}H-NMR spectroscopy is able to yield the pure molar fraction of DMS [$(x_{DMS})_p$], which, with the familiar relation, can be transformed to the pure weight fraction [$(w_{DMS})_p$], its values ignoring the presence of the Bu groups at the chain ends, as well as the joints between the blocks.

If the molecular weights of individual parts of the structure in Scheme A.3 are known, it is possible to calculate $(w_{DMS})_p$ according to eq. (A.6):

$$(w_{DMS})_p = M_{PDMS} / (M_{PDMS} + 2M_{PBd}) \qquad (A.6)$$
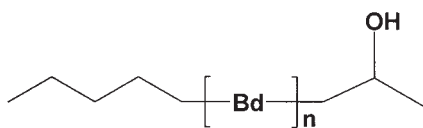
Scheme A.2
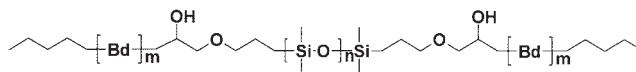
Scheme A.3

Similarly, it is possible to obtain also the gross weight fraction of DMS [$(w_{DMS})_g$] with respect to the whole copolymer molecule; its M_n value is given by eq. (A.7):

$$M_n = M_{PDMS} + 2M_{PBd} + 2M_t + 2M_j \qquad (A.7)$$

Then

$$(w_{DMS})_g = M_{PDMS} / (M_{PDMS} + 2M_{PBd} + 2M_t + 2M_j) \qquad (A.8)$$

As a typical example, calculating $(w_{DMS})_p$ and $(w_{DMS})_g$ for sample C1 (Table II) gave 0.359 and 0.286, respectively, which clearly show that the effect of the terminal and interphase joining groups is non-negligible.

The theoretical C percentage for the copolymer is given by eq. (A.9):

$$C = (100A_C/M_n)[2\sum C_{bu} + 2P_{PBd}\sum C_{Bd}$$
$$+ P_{PDMS}\sum C_{DMS} + 2\sum C_j] \qquad (A.9)$$

where $P_{PBd} = M_{PBd}/M_{Bd}$ is the number of Bd monomer units in one PBd block; $M_{Bd} = 54$ and $\Sigma C_{Bd} = 4$ are the molecular weight of and number of carbon atoms in a single Bd monomer unit, respectively; and $\Sigma C_{bu} = 4$ is the number of carbon atoms in the Bu group.

NOMENCLATURE

A_C	atomic number of carbon
Bd	butadiene
Bu	butyl
BuLi	butyllithium
$C_{PDMS-DG}$	expected content of carbon in α,ω-diglycidyloxypropyl polydimethylsiloxane (%)
D_3	hexamethylcyclotrisiloxane
D_4	octamethyltetrasiloxane
DMS	dimethylsiloxane
m	average number of butadiene units in the chains
M_{Bd}	molecular weight of a butadiene monomer unit
M_{bu}	molecular weight of butyl
M_{DMS}	molecular weight of a dimethylsiloxane repeating unit
M_j	molecular weight of a glycidyloxypropyl group (joint)

M_n	number-average molecular weight of the copolymer
M_{PBd}	number-average molecular weight of a pure polybutadiene chain (excluding the butyl and 2-hydroxypropyl groups)
M_{PBdOH}	number-average molecular weight of hydroxy-semitelechelic polybutadiene
M_{PDMS}	number-average molecular weight of a pure polysiloxane chain (excluding the joints)
$M_{PDMS-DG}$	number-average molecular weight of α,ω-diglycidyloxypropyl polydimethylsiloxane (precursor)
M_t	molecular weight of a polybutadiene terminal group from propylene oxide
M_w	weight-average molecular weight
n	average number of DMS units in the chains
PBd	polybutadiene
PBd–Li	polybutadienyllithium
PBd–OH	hydroxy-semitelechelic polybutadiene
PDMS	polydimethylsiloxane
PDMS–DG	α,ω-diglycidyloxypropyl polydimethylsiloxane
P_{PBd}	average number of butadiene monomer units in a polybutadiene block
P_{PDMS}	average number of dimethylsiloxane repeating units in a chain
PST	polystyrene
ΣC_{Bd}	number of carbon atoms in a single butadiene monomer unit
ΣC_{DMS}	number of carbon atoms in a dimethylsiloxane repeating unit
ΣC_j	number of carbon atoms in a single glycidyloxypropyl joint
$\Sigma C_{PDMS-DG}$	average overall number of carbon atoms in α,ω-diglycidyloxypropyl polydimethylsiloxane
SEC	size exclusion chromatography
ST	styrene
VPO	vapor pressure osmometry
w_{DMS}	weight fraction of dimethylsiloxane units
$(w_{DMS})_g$	gross weight fraction of dimethylsiloxane units in the copolymer (excluding joints and butyls)
$(w_{DMS})_p$	pure weight fraction of dimethylsiloxane units in the copolymer (excluding joints and butyls)
$(x_{DMS})_p$	pure molar fraction of dimethylsiloxane units

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