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Synthesis of Well-Defined 4-Miktoarm Star Quarterpolymers (4μ-SIDV) with Four Incompatible Arms: Polystyrene (S), Polyisoprene-1,4 (I), Poly(dimethylsiloxane) (D), and Poly(2-vinylpyridine) (V)

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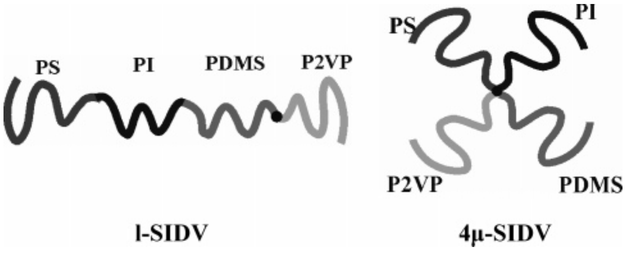
ABSTRACT: Three 4-miktoarm star quarterpolymers (4μ-SIDV), where S is polystyrene (PS), I polyisoprene-1,4 (PI), D poly(dimethylsiloxane) (PDMS), and V poly(2-vinylpyridine) (P2VP), were synthesized by anionic polymerization high-vacuum techniques. 4-(Dichloromethylsilyl)diphenylethylene (DCMSDPE), a dual-functionality compound with two SiCl groups (linking agent) and a nonhomopolymerizable double bond (diphenylethylene), was used as the nodule for the incorporation of the four incompatible arms. The synthetic approach involves selective replacement of the two chlorines of DCMSDPE with PI and PDMS by titration with the corresponding living chains, addition of the third arm PSLi to the in-chain double bond of the PI/PDMS intermediate, and finally polymerization of 2VP from the newly formed anionic site to create the fourth arm. Careful extraction/fractionation of the reaction products led to 4μ-SIDV stars with high molecular weight/compositional homogeneity, as proved by size exclusion chromatography, membrane osmometry, two-angle laser light scattering, and NMR spectroscopy. Differential scanning calorimetry (DSC) measurements confirmed the incompatibility of at least the three arms (P2VP and PS have about the same glass transition temperature, T_g).

Introduction

In contrast to miktoarm star (μ-star) co- and terpolymers (3μ-A_2B, 3μ-ABC),[1] there are only two reports dealing with the synthesis of quarterpolymers (4μ-ABCD).[2,3] Our group previously synthesized the 4μ-$SIBS_{4m}$, where S is polystyrene, I polyisoprene, B polybutadiene, and S_{4m} poly(4-methylstyrene)],[2] while Hirao et al.[3] synthesized the 4μ-$SS_{\alpha m}S_{4m}M$, where $S_{\alpha m}$ is poly(α-methylstyrene) and M poly(methyl methacrylate) or poly(*tert*-butyl methacrylate)]. The 4μ-$SIBS_{4m}$ was synthesized by anionic polymerization and selective replacement of the four chlorines of $SiCl_4$ by the four different chains, where order of the replacement was critical. The 4μ-$SS_{\alpha m}S_{4m}M$ was prepared by a new iterative methodology based on anionic polymerization and involving only two sets of reactions: (a) coupling of a benzyl bromide-functionalized polymer with a $CH_2OSiMe_2Bu^t$ diphenylethylene end-capped living PS chain and (b) transformation of $CH_2OSiMe_2Bu^t$ to CH_2Br. However, in both 4μ-ABCD quarterpolymers, a few of the arms are miscible and consequently do not form four different phases.

Recently, we published[4] the synthesis and morphology of a well-defined linear tetrablock quarterpolymer (l-SIDV) (Scheme 1) of polystyrene (PS: 30.5%), polyisoprene (PI: 23.1%), poly(dimethylsiloxane) (PDMS: 25.3%), and poly(2-vinylpyridine) (P2VP: 21.1%). The synthesis of l-SIDV achieved by sequential polymerization was based on recent advances in the controlled high-vacuum anionic polymerization of hexamethylcyclotrisiloxane (D_3)[5,6] as well as on the selective reaction of PDMSLi with the chlorosilane group of the heterofunctional linking agent (chloromethylphenyl)ethyldimethylchlorosilane (CMPDMS).[7,8] Using selective staining, we were able to observe by transmission electron microscopy (TEM) four different phases. The PI, PDMS, and P2VP form triple coaxial cylinders with hexagonal shape, packed in a hexagonal array in the PS honeycomb-shaped matrix. We present here, for the first time, the synthesis of the corresponding star quarterpolymer (4μ-SIDV star) with four immiscible arms (Scheme 1). From differential scanning calorimetry (DSC) measurements a preliminary indication of the immiscibility of at least three of the arms is obtained. Detailed morphological results are under investigation.

Scheme 1. Linear Tetrablock Quarterpolymer, l-SIDV, and 4-Miktoarm Star Quarterpolymer (4μ-SIDV) of Four Immiscible Blocks: Polystyrene (S), Polyisoprene-1,4 (I), Poly(dimethylsiloxane) (PDMS), and Poly(2-vinylpyridine) (V)



Experimental Section

Materials. Isoprene (Aldrich, 99%), styrene (Aldrich, 99%), all solvents [tetrahydrofuran (THF), benzene, and hexane, all reagent grade], the terminating agent (methanol), and trichloromethylsilane (Aldrich, >99%) were purified by high-vacuum techniques and standard procedures described in detail elsewhere.[6] The PDMS monomer hexamethylcyclotrisiloxane, D_3 (Aldrich, 99%), was melted, transferred into a flask, diluted with an equal volume of purified benzene, and stirred over CaH_2 overnight. The next day the benzene and the D_3 were distilled/sublimed into a flask containing polystyryllithium (PS^-Li^+), stirred for 2 h at room temperature, then distilled/sublimed into a cylinder, and finally split in precalibrated ampules. 2-Vinylpyridine (2VP) (Aldrich, 98%) was dried over CaH_2 overnight, exposed to Na mirror for a few minutes, and finally distilled over trioctylaluminum. *sec*-Butyl chloride (Aldrich, 99.9%), dried over CaH_2 overnight, degassed, and distilled in a vacuum line, was reacted, in a suitable high-

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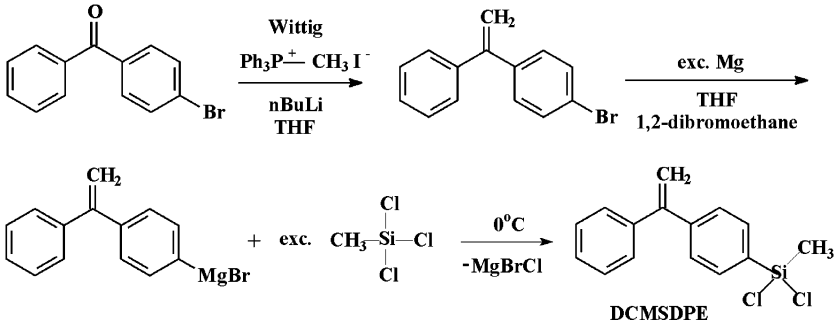
Scheme 2. General Reactions for the Synthesis of 4-(Dichloromethylsilyl)Diphenylethylene



vacuum apparatus, with excess Li (99% high sodium, Aldrich) in hexane to produce the initiator, *sec*-BuLi.[6]

Methyltriphenylphosphonium iodide (97%, Aldrich), *n*-BuLi (1.6 M in hexane, Aldrich), 4-bromobenzophenone (98%, Aldrich), and $MgSO_4$ were used as received. Magnesium turnings (Aldrich) were activated by sequential washings with 0.1 N HCl solution, distilled water, diethyl ether, and acetone and dried in a vacuum oven until constant weight.

Synthesis of 4-(Dichloromethylsilyl)diphenylethylene. 4-(Dichloromethylsilyl)diphenylethylene (DCMSDPE) was prepared from the Grignard reagent of 4-bromodiphenylethylene and trichlorodimethylsilane, using high-vacuum techniques and appropriate apparatuses. 4-Bromodiphenylethylene was obtained from the Wittig reaction of 4-bromobenzophenone and methyltriphenylphosphonium iodide in the presence of *n*-BuLi.[9] The route followed for the synthesis of DCMSDPE is given in Scheme 2.

Methyltriphenylphosphonium iodide (31 g, 76 mmol) was suspended in dry THF (200 mL) under a nitrogen atmosphere. *n*-BuLi (47.5 mL of 1.6 M in hexane, 76 mmol) was added to the suspension at room temperature, and the solution was stirred for 30 min. 4-Bromobenzophenone (20 g, 76 mmol) was then added dropwise under vigorous stirring at room temperature and was left overnight. The solution was diluted in a chloroform/hydrochloric acid aqueous solution (0.1 N) mixture (v/v 1:1). The organic phase was collected, washed, and dried over $MgSO_4$. The solvent was evaporated and hexane was added. Filtration in order to remove the precipitate, condensation of the solution, and new addition of hexane were repeated several times until no precipitation took place after the addition of hexane. The resulting residue was purified by chromatography on silica gel using *n*-hexane as the eluent to yield 4-bromo-DPE as a yellow oil.

After introducing magnesium turnings (1.9 g, 78.2 mmol) in a special designed glass apparatus, a solution of a few drops of 1,2-dibromoethane in THF was added to the flask, and the mixture was stirred for a few minutes to activate the magnesium. The produced ethane was eliminated, and 4-bromo-DPE (5 g, 19.3 mmol) in THF (30 mL) was introduced dropwise to the flask while maintaining the reflux of THF. The reaction mixture was allowed to stir for an additional 5 h at 45 °C. The Grignard reagent was added dropwise in trichloromethylsilane (5.8 g, 38.8 mmol) diluted in THF (20 mL) solution at 0 °C and was allowed to stir for 1 h. The crude product of the reaction was condensed in the vacuum line to eliminate the volatile compounds, and hexane was distilled into the apparatus. The solution was kept at −20 °C for 2 days until the partial precipitation of MgBrCl and was filtered. The product was left in the vacuum line, under stirring at 40 °C, to remove the solvent.

DCMSDPE was distilled into ampules at ~110 °C in the high-vacuum line, diluted in benzene, and stored at −20 °C. The ^1H NMR spectrum confirms the successful synthesis of DCMSDPE. ^1H NMR ($CDCl_3$): δ 7.7−7.8 (2H, d, Ar−H), 7.46−7.52 (2H, d, Ar−H), 7.37 (5H, m, Ar−H), 5.55−5.62 (2H, d, $C{=}CH_2$), 2.34 (1H, m, Si−OH from the hydrolysis of the Si−Cl bonds), 1.1 (3H, m, Si−CH_3). Integration gave the expected ratios of the protons.

Synthesis of 4*μ*-SIDV. All synthetic manipulations were conducted with classic high-vacuum techniques. Polymerizations were carried out in evacuated, *n*-BuLi-washed, and solvent-rinsed glass reactors equipped with break-seals for the addition of reagents and constrictions for the removal of intermediate products. Full details regarding apparatuses and techniques used have been reported elsewhere.[6]

The synthetic approach involves the selective replacement of the two chlorines of DCMSDPE with PI and PDMS by titration, addition of the third living arm PSLi to the in-chain double bond of the PI/PDMS intermediate, and finally polymerization of 2VP from the newly created anionic site to create the fourth arm. As an example, the synthesis of 4*μ*-SIDV-1 [M_n(PI): 25.0K, M_n(PDMS): 20.0K, M_w(PS): 19.3K, M_n(P2VP): 16.0K] is given. Living polyisoprene [M_n(MO) = 25.0 kg/mol] was synthesized by polymerization of isoprene (3 g, 4.41×10^{-2} mol) with *sec*-BuLi (0.12 mmol) in benzene (30 mL) at room temperature for 18 h. Living PDMS was obtained by (a) polymerization of D_3 (2.6 g, 1.17×10^{-2} mol) with *sec*-BuLi (0.13 mmol) in benzene (30 mL) for 2 days, (b) addition of 30 mL of THF to make a 1/1 (v/v) mixture with benzene and reaction for 2 h at room temperature (~50% conversion), and finally (c) lowering the temperature to −20 °C and allowing the polymerization to proceed for one more week [M_n(^1H NMR) = 20.0 kg/mol].

The living polyisoprene (10% w/v) was added dropwise to the reactor containing DCMSDPE (0.035 g, 0.12 mmol) in benzene (10 mL) under vigorous stirring. The ~5% w/v solution of $PDMS^-Li^+$ was subsequently added dropwise in the same reactor to form the PI/PDMS intermediate having in-chain double bond.

The flask with the in-chain double bond product was attached to a new reactor (Figure 1). The anionic polymerization of styrene (2.2 g, 0.12 mmol) in THF (50 mL) was carried out with *n*-BuLi as initiator (1.18×10^{-4} mol) for 30 min under vigorous stirring at −78 °C. The appropriate amount of the (PDMS)(PI)Si-DPE reagent having the in-chain double bond ([Li]/[DPE] 1/1) was then added to the living PSLi [M_w(TALLS) = 19.3 kg/mol] solution and stirred for ~3 h. Finally, the 2VP monomer (2 g of 2VP, 0.12 mmol) was distilled into the reactor under vigorous stirring at −78 °C for 30 min to afford the fourth arm, P2VP [M_n(calcd) = 16.0 kg/mol]. The living chains were terminated with methanol after the quantitative polymerization of 2VP.

Measurements. The molecular weight distributions of the final and intermediate products were obtained by size exclusion chromatography (SEC). SEC experiments were performed at 35 °C in two separated setups. Both setups were equipped with a Waters model 510 pump, a Waters model 410 differential refractometer, and three Styragel columns with a porosity range of 10^3−10^6 Å. The carrier solvent in one setup was THF and in the other a mixture of chloroform/triethylamine (95/5, v/v) at a flow rate of 1.0 mL/min. In both cases calibrations were carried out with PS standards at a range of M_n from 1.5×10^3 to 9×10^5 at the same flow rate.

Multidetector SEC analysis [size exclusion chromatography/refractive index (at 633 nm) and size exclusion chromatography/two-angle laser light scattering (SEC-TALLS) with laser power at 10 mw], using a Waters system equipped with a Waters 1525 high-pressure liquid chromatography pump, Waters Ultrastyragel columns (HR-2, HR-4, HR-5E, and HR-6E having pore sizes 10^2, 10^4, 10^5, and 10^6 Å), a Waters 2410 differential refractometer detector, and a Precision PD 2020 two-angle (15°, 90°) light scattering

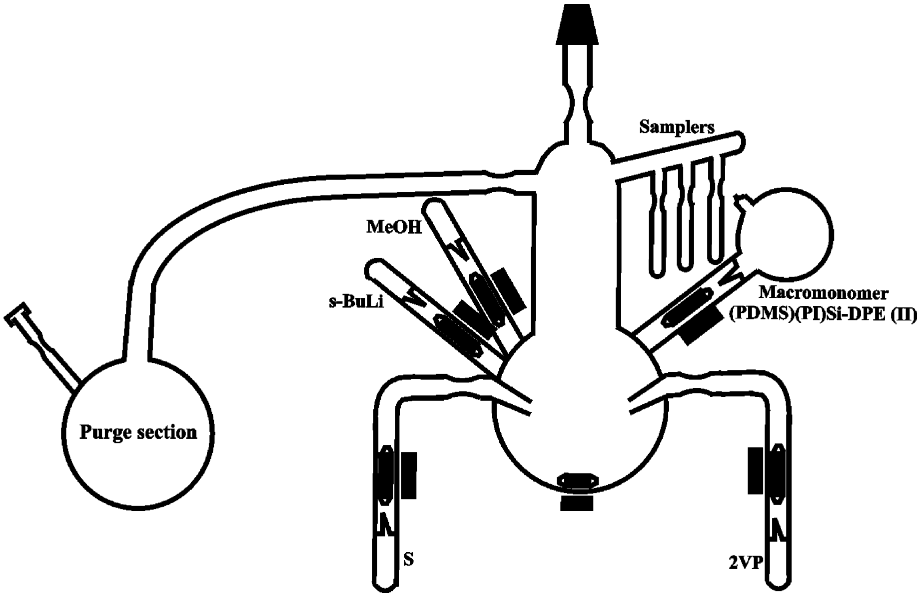
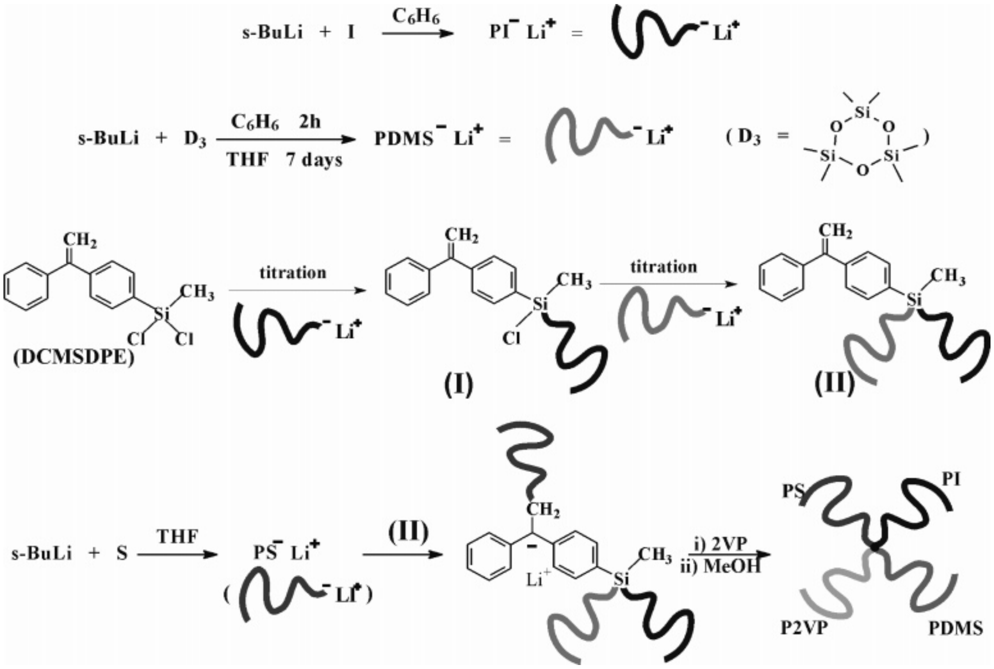


Figure 1. Main reactor for the synthesis of the 4-miktoarm star quarterpolymers (PS)(PI)(PDMS)(P2VP) (4μ-SIDV) from the in-chain double bond (PDMS)(PI)Si-DPE (II) (Scheme 3).

Scheme 3. General Reactions for the Synthesis of 4-Miktoarm Star Quarterpolymers of Polystyrene (PS), Polyisoprene (PI), Poly(dimethylsiloxane) (PDMS), and Poly(2-vinylpyridine) (P2VP)



detector, was also performed to characterize the intermediate products.

The number-average molecular weight (M_n) of the precursors and the final products were measured with a Jupiter model 231 recording membrane osmometer (MO) at 40 °C. Toluene was used as a solvent and distilled from CaH_2 before use. The M_n values from MO were obtained from the corresponding $(\pi/c)^{1/2}$ vs c plots, where π is the osmotic pressure and c is the concentration in g/mL. In all cases, the correlation coefficient was better than 0.99.

Nuclear magnetic resonance (NMR) spectra were generated with a Bruker 400-MHz instrument with $CDCl_3$ as a solvent, at 25 °C.

A TA Instruments 2910 modulated DSC (differential scanning calorimetry), calibrated with indium ($T_m = 165.65$ °C), was used to obtain preliminary information about the microphase separation of the 4-miktoarm star quarterpolymers.

All samples (~50 mg) were annealed by increasing their temperature at a rate of 20 °C/min to 140 °C and maintaining it for 10 min. The measurements were taken during the second heating cycle, which was executed at the same heating rate. The T_g value was determined at the midpoint, defined as the temperature axis value halfway between the onset and end of the step transition region.

Results and Discussion

The synthesis of the 4-miktoarm star quartepolymers (4μ-SIDV) with four immiscible arms, i.e., polystyrene (PS), polyisoprene (PI), poly(dimethylsiloxane) (PDMS), and poly(2-vinylpyridine) (P2VP), was achieved according to the general reactions, given in Scheme 3.

The initial step of the synthesis involved the titration of the two chlorines with PILi and PDMSLi. The living polyisoprene in benzene (10% w/v) was added dropwise to the reactor containing DCMSDPE in benzene (3.5×10^{-3}% w/v), under

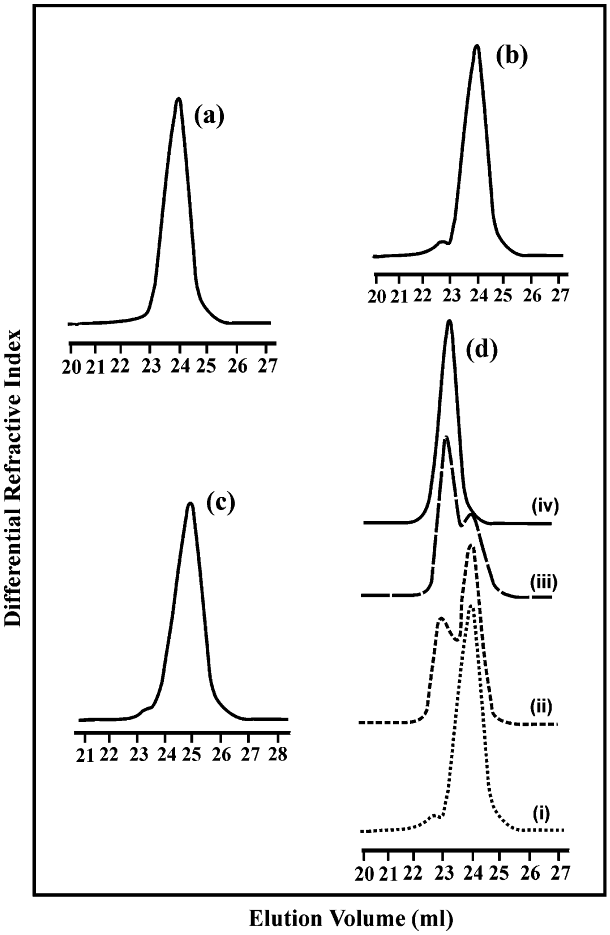


Figure 2. Monitoring the first steps of the synthesis of (PS)(PI)(PDMS)(P2VP) 4μ-SIDV-1 (Scheme 3) by size exclusion chromatography, SEC: (a) living polyisoprenyllithium, $PI^{-}Li^{+}$; (b) off-chain double bond product (I); (c) living polydimethylsiloxanyllithium, $PDMS^{-}Li^{+}$; (d) in-chain double bond product (II): conversion (i) 0%, (ii) 30%, (iii) 70%, (iv) 100%.

vigorous stirring. The reaction must be carried out slowly in order to avoid local excess of the living PI chains; otherwise, a portion of the second chlorines will be replaced by other PI chains leading to 4μ-SI_2V tetrablock terpolymer instead of 4μ-SIDV. Although both chlorine atoms are initially equal in reactivity, after the replacement of the first chlorine the reactivity of the second one is lower due to the steric hindrance imposed by the already incorporated PI chain. The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC. An example is provided in Figure 2. The SEC chromatogram (Figure 2b) of the reaction product (Scheme 3, I) is indistinguishable from the PI chain added (Figure 2a), meaning that almost all of the product is the desired one (Scheme 3, I). The small peak (Figure 2b) at lower elution volume (double molecular weight) serves to detect the end point of the titration and indicates the complete replacement of only one chlorine by PI.

A ~10% w/v solution of $PDMS^{-}Li^{+}$ was then added dropwise into the (I) solution (Scheme 3). The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC. The peak of product (II) having the in-chain double bond increased while that of (I) decreased (Figure 2d). The disappearance of the peak corresponding to (I) indicated the end of the titration.

In a new reactor the anionic polymerization of styrene in THF (~5% w/v) was carried out for 30 min under vigorous stirring at −78 °C. The success of the polymerization was indicated by the orange color of $PS^{-}Li^{+}$. When the polymerization of styrene was complete, an appropriate amount of the intermediate (II) ([Li]/[II] 1/1) was added, and the solution was stirred for ~3 h. The success of the incorporation of the living $PS^{-}Li^{+}$ in (II) was confirmed by the immediate change of the solution color from orange to dark red, indicating the opening of the double bond of the diphenylethylene. Moreover, using a DPE (nonhomopolymerizable) derivative ensured the incorporation of one DPE unit in the living chain. The conversion after 1 h was 75% and 95% after 3 h, as shown in Figure 3b.

Finally, the 2VP monomer was distilled into the reactor under vigorous stirring at −78 °C. The polymerization was allowed to proceed for 30 min and was then terminated with methanol. The solvents were evaporated, and the final product was extracted to remove the residual intermediates (5−10% of the final products) PI/PDMS in-chain double bond product and PS.

The isolation of the 4μ-SIDV from the residual intermediates was extremely difficult due to the different solubility parameters of the four different components. Classic fractionation techniques were not feasible for these products, since no common solvent/nonsolvent system could be found. After many trials we concluded that only extraction in a Soxhlet apparatus was effective for separation. Because of the different composition of the 4μ-SIDV products synthesized, the extractions were carried out with different solvents (~1% w/v) in order to match the solubility either of the 4μ-star or the residual intermediates. For 4μ-SIDV-1 methanol, solvent for the P2VP but nonsolvent for the other chains, was used to extract the neat 4μ-star, leaving behind the residues insoluble. For 4μ-SIDV-2 hexane, solvent for PI and PDMS but nonsolvent for the other chains, was in

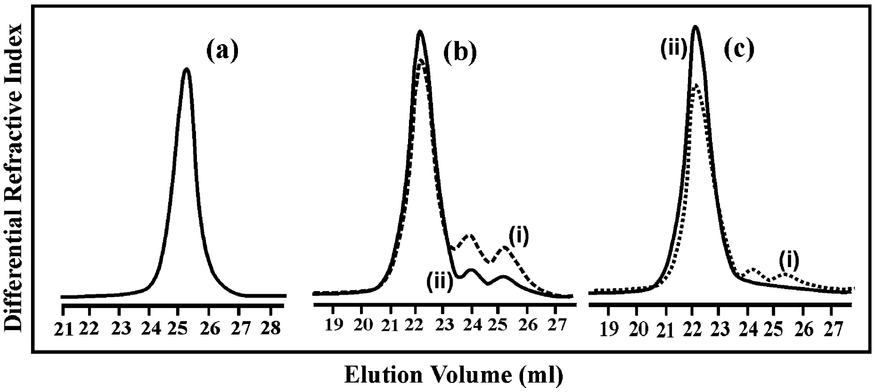


Figure 3. Monitoring the final steps of the synthesis of (PS)(PI)(PDMS)(P2VP) 4μ-SIDV-1 (Scheme 3) by size exclusion chromatography, SEC: (a) living polystyryllithium, $PS^{-}Li^{+}$; (b) living 3-miktoarm terpolymer at different reaction times: conversion (i) 1 h 75%, (ii) 3 h 95%; (c) (i) unpurified and (ii) purified 4-miktoarm star quaterpolymer, 4μ-SIDV.

Table 1. Molecular Characteristics of 4-Miktoarm Star Quarterpolymers, 4μ-SIDV

sample	$M_n{}^a$PI × 10^{-3} (g/mol)	$M_n{}^b$PDMS ×10^{-3} (g/mol)	$M_w{}^c$PS ×10^{-3} (g/mol)	$M_n{}^d$P2VP × 10^{-3} (g/mol)	$M_n{}^a$total ×10^{-3} (g/mol)	I^e (M_w/M_n)	(% w/w)^f (I/DMS/S/2VP)	(% w/w)^b (I/DMS/S/2VP)
4μ-SIDV-1	25.0 ($M_w{}^c$ = 26.9K)	20.0	19.3	16.0	78.5	1.08	31.8/25.5/22.3/20.4	33.0/27.8/20.7/18.5
4μ-SIDV-2	25.0 ($M_w{}^c$ = 26.9K)	13.0	54.5 ($M_n{}^a$ = 50.2K)	61.5^b		1.11		16.7/8.2/34.0/41.1
4μ-SIDV-3	25.0 ($M_w{}^c$ = 26.9K)	13.0	14.1	25.1	75.9	1.06	32.9/17.1/16.9/33.1	33.6/16.0/16.6/33.8

[a] Number-average molecular weight (M_n) obtained by membrane osmometry, MO, in toluene at 40 °C. [b] Calculated by ^{1}H NMR spectra in $CHCl_3$. [c] Weight-average molecular weight (M_w) obtained by size exclusion chromatography equipped with light scattering detector, SEC-TALLS in tetrahydrofuran, THF, at 35 °C. [d] Calculated using the equation $M_n(P2VP) = M_n(total) - M_n(PI) - M_n(PDMS) - M_n(PS)$. [e] Size exclusion chromatography, SEC, in tetrahydrofuran, THF, at 35 °C. [f] Calculated from the molecular weights of the arms. PI = polyisoprene, PS = polystyrene, PDMS = poly(dimethylsiloxane), P2VP = poly(2-vinylpyridine).

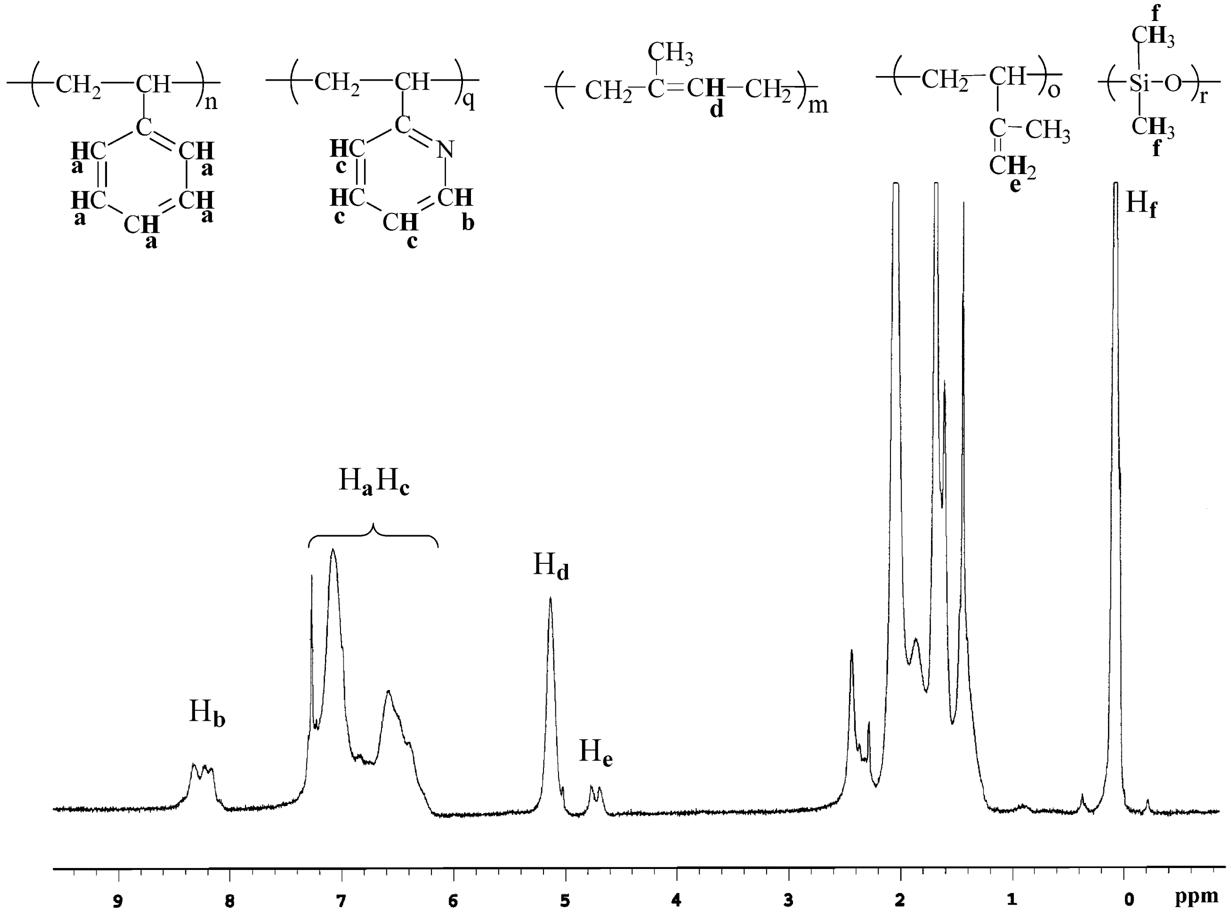


Figure 4. ^{1}H NMR spectrum of the (PS)(PI)(PDMS)(P2VP) 4μ-SIDV-1 in $CDCl_3$ (Ar protons of polystyrene, PS: 6.8−7.2 ppm, Ar protons of poly(2-vinylpyridine), P2VP: 6.3−8.4 ppm, olefin protons of polyisoprene, PI 1,4 and PI 3,4: 5.2 ppm and 4.8 ppm, respectively, and methyl protons of poly(dimethylsiloxane), PDMS: 0 ppm).

this case an effective solvent for the residues, leaving behind the neat 4μ-star. Finally, the neat 4μ-SIDV-3 was extracted from the residues with acetone, solvent for P2VP and nonsolvent for the other chains, leaving behind the residues.

The molecular characteristics of the precursors and the neat 4-miktoarm star quarterpolymer are given in Table 1. The composition of the 4-miktoarm star quaterpolymer was obtained from ^{1}H NMR spectra. A representative example of a ^{1}H NMR spectrum is given in Figure 4.

In the case of the 4μ-SIDV-2 the determination of the M_n with membrane osmometry in toluene was impossible, since toluene is not a solvent for the 4μ-star in this composition, causing the formation of micelles.

The DSC measurements obtained indicate the microphase separation of the 4-miktoarm star quarterpolymers. A representative DSC thermograph of 4μ-SIDV is shown in Figure 5. The

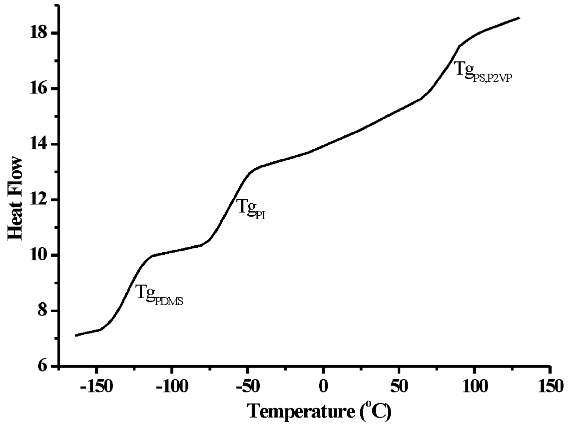


Figure 5. Differential scanning calorimetry (DSC) thermograph of (PS)(PI)(PDMS)(P2VP) 4μ-SIDV-1.

existence of three glass transition temperatures detected: $T_{g1} \sim -127$ °C, $T_{g2} \sim -60$ °C, and $T_{g3} \sim 100$ °C, corresponding to PDMS, PI, and PS/P2VP homopolymers (same T_g), respectively, suggests that the system is well microphase separated. Even though three T_g are seen, four different are expected, since P2VP and PS have same T_g despite the fact that are not miscible.[4,10] The microphase separation of these novel star quarterpolymers is under investigation and will be published in a forthcoming paper.[11]

Conclusions

In conclusion, the combined characterization results indicate that well-defined 4-miktoarm star quarterpolymers, 4μ-SIDV, with four immiscible arms: polystyrene, polyisoprene-1,4, poly(dimethylsiloxane), and poly(2-vinylpyridine) can be synthesized by anionic polymerization high-vacuum techniques and 4-(dichloromethylsilyl)diphenylethylene. DCMSDPE is a dual-functionality compound, with two SiCl groups (linking agent) and a nonhomopolymerizable double bond (diphenylethylene).

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