Star Polymers with Alternating Arms from Miktofunctional μ-Initiators Using Consecutive Atom Transfer Radical Polymerization and Ring-Opening Polymerization

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ABSTRACT: The synthesis of unique miktofunctional μ-initiators, combining initiator sites for both controlled ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) arranged in an alternating fashion, is described. This initiator was used to prepare miktoarm star block copolymers in a core-out approach utilizing consecutive ATRP and ROP processes. NMR and GPC studies on the block copolymers comprising poly(methyl methacrylate) (PMMA) and poly(caprolactone) (PCL) confirm the versatility of this approach which is independent of the order of polymerization. Furthermore, amphiphilic alternating arm block copolymers containing poly(caprolactone) and poly(acrylic acid) blocks were also prepared by this method.

Introduction

The combination of different "living" polymerization techniques to produce block copolymers represents a significant scientific challenge due to the synthetic limitations of the various techniques. Hence, even AB block copolymers representative of the simplest polymeric structures derived from such a combination of polymerization techniques usually require a significant synthetic effort. However, this approach provides the opportunity to combine very different types of monomers into one macromolecule. Two very extensively investigated controlled polymerization techniques are metal-mediated controlled free radical methods (e.g., atom transfer radical polymerization, ATRP)[1−4] and living ring-opening polymerization (ROP). Both techniques have been used to prepare a variety of complex polymer structures. Hyperbranched and star-shaped polymers prepared utilizing ROP[5−8] and ATRP,[9−14] respectively, are reported in the literature. A block copolymer comprising a poly(caprolactone) (PCL) and a poly(methyl methacrylate) (PMMA) block prepared by tandem ROP and ATRP has been described.[15] Using a double-headed initiator, both blocks can be grown simultaneously in one pot.[16] More complex molecular architectures such as dendritic starlike block copolymers comprising PCL as the first block and PMMA as the outer block, highly branched block copolymers prepared from ABC/BCD monomers and graft copolymers have been reported recently.[17−19] We now extend the combination of ATRP and ROP techniques to the production of star polymers with alternating PCL and PMMA arms as shown in Figure 1.

Star polymers containing chemically different arms have been designated miktoarm (mixed) star polymers (μ-stars). They reveal interesting properties in the solid state as well as in solution due to their unique architectures.[20−24] One general strategy for the synthesis of miktoarm stars is based on the use of living anionic polymers that are consecutively grafted onto a reactive multifunctional core in a consecutive polymer reaction (core first).[22,23,25,26] Although this synthetically demanding procedure produces well-defined miktoarm stars, the geometric sequence, i.e., topological arrangement, of the arms of the resulting star polymer cannot be controlled. Another approach utilizes the addition of anionically derived living polymers to a small amount of polyfunctional polymerizable core (e.g., divinylbenzene). This leads to the formation of a star molecule with additional anionic sites on the polymerized core. Subsequent addition of another monomer capable of anionic polymerization yields the miktoarm star polymer.[26,27] In this case, neither the exact number of arms nor the precise topological arrangement of the arms can be controlled. Two recent, detailed reviews of miktoarm copolymers have been published by Hadjichristidis.[20,21]

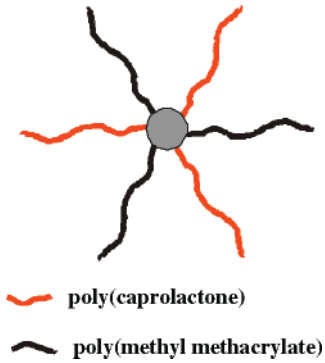

Figure 1. Schematic description of the target structure of a 6-arm star polymer comprised of poly(caprolactone) and poly(methyl methacrylate) in an alternating geometry.

Results and Discussion

In a novel synthetic approach to miktoarm systems, we employ a building block containing initiating sites for both ROP and ATRP. Coupling of this building block to a multifunctional core leads to a multiarm initiator

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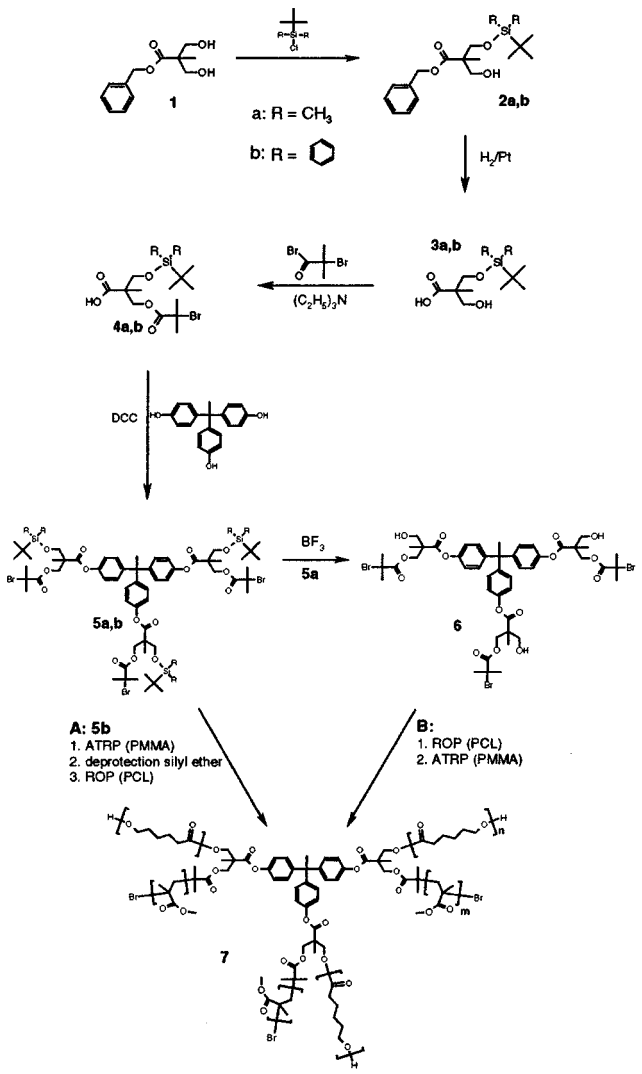
Scheme 1. Synthetic Route to 6-Arm Alternating Arm Initiator and Poly(caprolactone)/ Poly(methyl methacrylate) Block Copolymer



with initiating sites arranged in an alternating fashion for the synthesis of block copolymers containing alternating arms of PMMA and PCL emanating from a core (Figure 1). The alternating arm block copolymers can be prepared in a core-out mode utilizing consecutive ATRP and ROP processes. Although the polymeric arms in each 2-arm initiating fragment are strictly alternating, attachment of these fragments to a multifunctional core leads to an initiator where the registry between fragments can be scrambled by rotation around the C−O single bond connection to the core. However, in the case of the 6-arm derivative, such rotation would always result in at least four alternating arms; thus, the variation in intramolecular topologies is limited. The key to this technique is the initiator molecule, since it determines the structure of the resulting copolymer. This approach provides another level of control to the preparation of miktoarm polymers.

For the initiator (Scheme 1), we prepared an ABC building block that contains a protected hydroxyl group which after deprotection can initiate ROP, an activated bromide for ATRP and a carboxylic acid group for coupling to a polyhydroxy functionalized core. Starting from the benzyl ester of bis(hydroxymethyl)propionic acid, **1** (bis-MPA), one hydroxy group was selectively

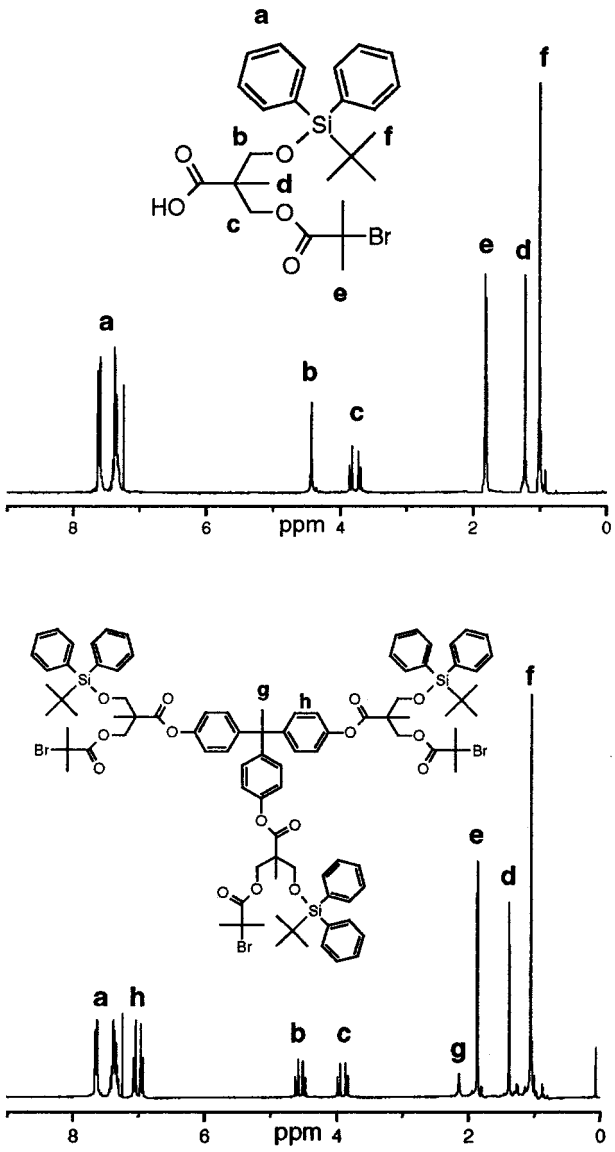


Figure 2. ^{1}H NMR spectra of the alternating arm building block and initiator.

protected as a *tert*-butyldiphenylsilyl ether (**2b**, 88% yield). By palladium-catalyzed hydrogenolysis, the benzyl ester was quantitatively cleaved without effecting the protecting group to yield **3b**. The ATRP initiator functionality was introduced into the building block by subsequent esterfication of the unprotected hydroxy group of **3b** with 2-bromo-2-methylpropionyl bromide. To minimize the formation of mixed anhydrides and thus improve the yield in this step, both components are used in equimolar amounts. After purification by flash chromatography, the ABC building block **4b** was obtained in 80% yield. The sequence of the functionalization reactions was important since the activated bromide is not compatible with hydrogenolysis procedure. The monoprotected 6-arm initiator **5b** was synthesized from the ABC building block **4b** and the hydroxy functionalized core 1,1,1-tris(hydroxyphenylethane) in 83% yield using dicyclohexyl carbodiimide (DCC). All spectrocopic data are in accordance with the proposed structures. Figure 2 shows the respective ^{1}H NMR spectra of the building block **4b** and the protected 6-arm initiator **5b** as representative examples. In addition to the signals of the appended building block, the initiator spectrum shows the signals of the aromatic core

h. The signal of the diaesteriotopic methylene protons **c** appear as an AB quartet centered at 3.8 ppm both in the 2-arm building block and in the 6-arm initiator. The other methylene protons **b** appear as an apparent singlet at 4.2 ppm in the building block and as an AB quartet in the initiator.

The same reaction sequence was accomplished using a *tert*-butyldimethylsilyl protecting group. However, using this protecting group, purification of the initial carboxy-containing building block **3a** resulted in lower isolated yields (ca. 40%). The *tert*-butyldimethylsilyl group is apparently less stable in the presence of the free carboxylic acid group.

To obtain the alternating arm polymer, the polymerization can be performed using either of the two sequences shown in Scheme 1. In A, MMA is first polymerized by ATRP using the silyl ether protected initiator **5b** followed by the deprotection of the silyl ether group in a polymer analogous reaction. This macroinitiator can then be used for the ROP of caprolactone. In sequence B, the silyl ether protecting group is removed first to produce the initiator **6**, and the ROP and ATRP procedures are performed consecutively. Each route offers certain advantages.

For route A, the ATRP of MMA using the protected initiator and CuBr/dinonylbipyridine (dNbipy) as a catalyst is nicely controlled. It provides a well-defined 3-arm star polymer approaching the target molecular weight of 1.0×10^4 g/mol (determined from the ratio of the ^{1}H NMR integrated peak areas of the methyl ester groups of the PMMA relative to the aromatic core signals) with a low polydispersity of 1.18 (determined by size exclusion chromatography (SEC), calibrated to linear polystyrene). The polymer analogous deprotection of the *tert*-butyldiphenylsilyl ether in this macromonomer was achieved without molecular weight degradation using boron trifluoride etherate in chloroform at 60 °C. The progress of this reaction is easily followed by the disappearance of the aromatic proton signals in the ^{1}H NMR spectrum attributed to the protecting group. The desired miktoarm polymer containing alternating arms of PMMA and PCL was obtained from the 3-arm PMMA macroinitiator by the subsequent ROP of ϵ-caprolactone in toluene using stannous octanoate. The molecular weight of the resulting PCL block was about 1.6×10^4 g/mol according to ^{1}H NMR. The polydispersity of the resulting alternating arm block copolymer prepared in this fashion was 1.29 (SEC). In some cases, we noticed the formation of small amounts of PCL homopolymer (SEC and ^{1}H NMR).

For route B, the silyl ether was deprotected prior to the initial polymerization. Deprotection of the *tert*-butyldiphenylsilyl ether protecting group (**5b**) is slow, resulting in low yields (18%), and several byproducts are detected by thin-layer chromatography (TLC). Since the deprotection of this group apparently works well for the macroinitiator (see route A), we attribute the synthetic difficulties to the presence of the reactive bromide group of the ATRP initiator portion of the molecule. Improved yields were obtained using the more reactive *tert*-butyldimethylsilyl ether protecting group (**5a**, 45% yield). In this case, subsequent ROP of ϵ-caprolactone yielded PCL ($M_n = 2.40 \times 10^4$ g/mol), corresponding to a number-average degree of polymerization (DP_n) per arm of 71 as determined by end group analysis using ^{1}H NMR spectroscopy. A polydispersity of 1.33 for the 3-arm PCL was determined by size

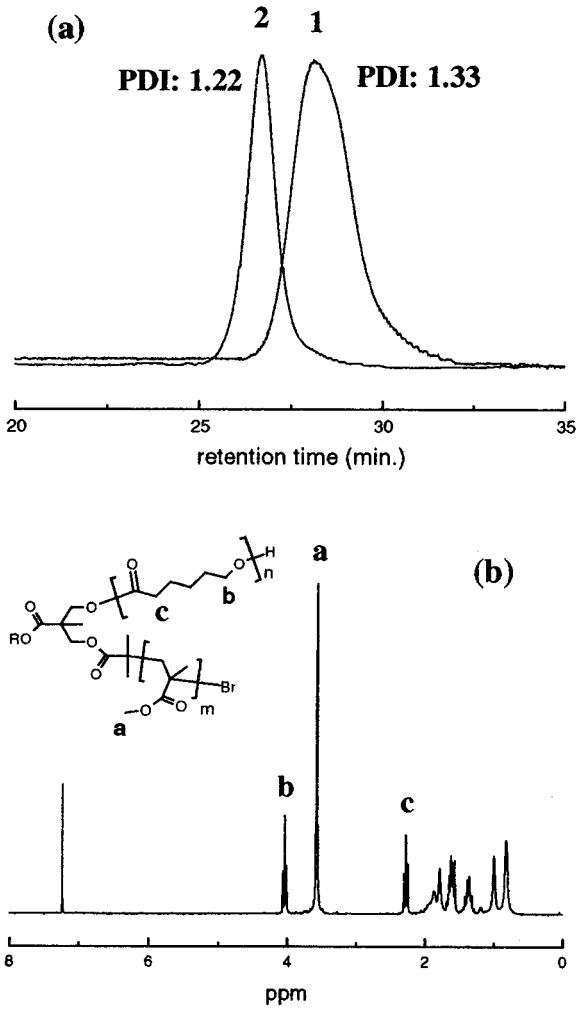


Figure 3. (a) SEC traces of poly(caprolactone) macroinitiator and 6-arm alternating arm poly(caprolactone)/poly(methyl methacrylate) block copolymer (route B; entry B1 in Table 1). (b) ^{1}H NMR spectrum of the respective alternating arm block copolymer.

exclusion chromatography. By using the 3-arm PCL as a macroinitiator for the polymerization of MMA in bulk with CuBr/dNbipy as a catalyst, starlike polymers with perfectly alternating PCL/PMMA arms for each 2-arm fragment could be obtained. In this case, the total number-average molecular weight of the PMMA blocks was 6.0×10^4 g/mol ($DP_n = 200$/arm). Figure 3a shows the GPC traces of both the macroinitiator and the resulting alternating star polymer demonstrating the expected increase in molecular weight caused by the formation of the PMMA blocks. The overall polydispersity index of the resulting alternating arm star polymer is still relatively low (1.22). The ^{1}H NMR spectrum of the alternating arm copolymer is shown in Figure 3b (with the resonances for both polymer blocks assigned).

Utilizing the PCL functionalized macroinitiator for the ATRP of *tert*-butyl acrylate and subsequent cleavage of the *tert*-butyl ester yields alternating arm amphiphilic block copolymers containing three PCL and three poly(acrylic acid) arms. Figure 4 shows the SEC traces of the PCL macroinitiator (1) and two PCL/PtBA copolymers with varying molecular weights (see Table 1). The signals of the *tert*-butyl ester group can be assigned in the ^{1}H NMR spectrum of the block copolymer (**a** in Figure 5a), confirming the incorporation of the PtBA blocks in the miktoarm star polymer. Although this

Table 1. Characteristics of 6-Arm Alternating Arm Star Polymers[a]

		block 1	block 2	block copolymer	
route	polymer	$M_n \times 10^{-4}$ [b] g/mol (M_w/M_n)[b]	$M_n \times 10^{-4}$ [b] g/mol	$M_n \times 10^{-4}$ [d] g/mol (M_w/M_n)[c]	av DP_n/arm block 1/block 2
A1	PMMA/PCL	1.40 (1.18)[c]	1.60	3.00 (1.29)[c]	46/48
B1	PCL/PMMA	2.40 (1.33)	6.00	8.40 (1.22)	71/200
B2	PCL/PtBA (PAA)	2.40 (1.33)	3.20 (PtBA) 1.80 (PAA)	5.60 (1.23)	71/84
B3	PCL/PtBA (PAA)	2.40 (1.33)	6.80 (PtBA) 3.90 (PAA)	9.20 (1.08)	71/180

[a] PtBA = poly(*tert*-butyl acrylate); PAA = poly(acrylic acid); PCL = poly(caprolactone); PMMA = poly(methyl methacrylate). Polymer molecular weights describe the 3-arm sums. The core molecular weight is not included in the table. [b] M_n for PCL blocks were determined from the ratio of integrated peak areas of initiator peaks around 7 ppm and the methylene group around 4 ppm in the ^{1}H NMR spectrum. M_n of the PMMA blocks were determined accordingly from the methyl ester peak around 3.5 ppm. M_n of the PtBA blocks were determined from the *tert*-butyl ester peak around 1.4 ppm relative to the PCL block. [c] Derived from size exclusion chromatography (SEC) calibrated with polystyrene. [d] Represents the sum of values of the single blocks determined by ^{1}H NMR.

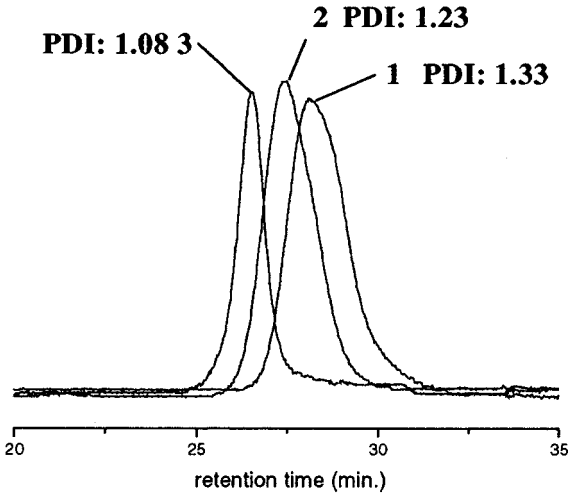


Figure 4. SEC traces of poly(caprolactone) macroinitiator and 6-arm alternating arm poly(caprolactone)/poly(*tert*-butyl acrylate) block copolymer with varying molecular weights (route B; entry B2 and B3 in Table 1).

signal is overlays the PCL signal, comparison with the integrated peak areas of the PCL macroinitiator allows the molecular weight of the PtBA blocks to be calculated (see Table 1).The PtBA blocks were subsequently deprotected by treatment of the *tert*-butyl ester with trifluoroacetic acid (TFA). This reaction was followed by the disappearance of signal **a** in the ^{1}H NMR spectrum (Figure 5). The resulting miktoarm star polymer contains three PCL arms and three PAA arms. As shown in Table 1, the average block length ratio PCL/PAA calculated from the degree of polymerization (DP_n) is about 1:1 and 1:2, respectively, for the two polymers. Because of the unique alternating arrangement of the components in these block copolymers and the intrinsic solubility differences between the respective polymer arms, we are currently investigating the solution properties of these systems and their tendency to form (unimolecular) micelles. The morphology of the heteroarm block copolymers was investigated by dynamic mechanical analysis (DMA), transmission electron microscopy (TEM), and calorimetry measurements. Figure 6 shows the dynamic mechanical spectra of copolymer B1 (Table 1). There are clearly two transitions, consistent with the T_g's of the respective blocks and a microphase-separated structure. The first transition is nearly identical to that of poly(ϵ-caprolactone) (∼−60 °C), while the second transition is comparable to that

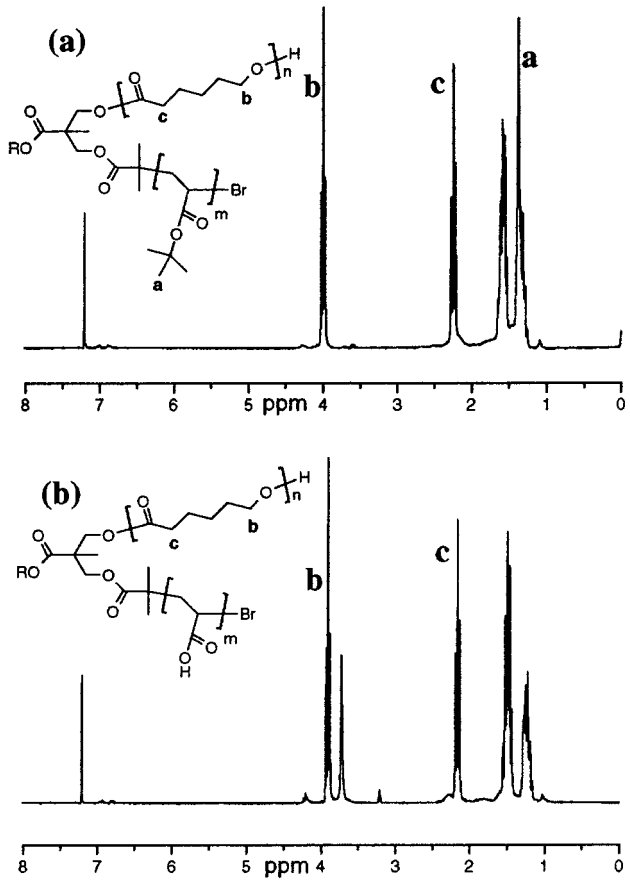


Figure 5. ^{1}H NMR spectrum of the 6-arm poly(caprolactone)/poly(*tert*-butyl acrylate) (a) and poly(caprolactone)/poly(acrylic acid) alternating arm block copolymer (b) (entry B2 in Table 1).

of poly(methyl methacrylate) (∼95−100 °C). There is a small shoulder on the damping peak associated with the PMMA (50 °C, tan δ), which presumably arises from the melting of the PCL block. Consistent with these data, the calorimetry measurement showed two T_g's (−58 and 95 °C) and a melting transition at 52 °C. The TEM micrograph (Figure 7) of this symmetrically substituted heteroarm block copolymer clearly shows the formation of a microphase structure with a lamellar morphology. This morphology is expected for an A_nB_n star block copolymer since such structures follow the predictions for the linear block copolymers.[28]

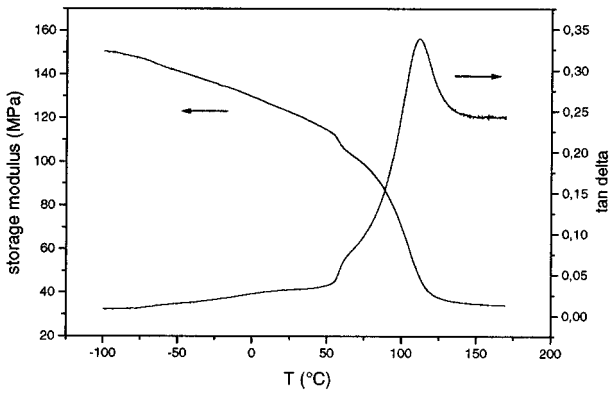


Figure 6. Dynamic mechanical analysis (DMA) of poly(caprolactone)/poly(methyl methacrylate) block copolymer (entry B1 in Table 1).

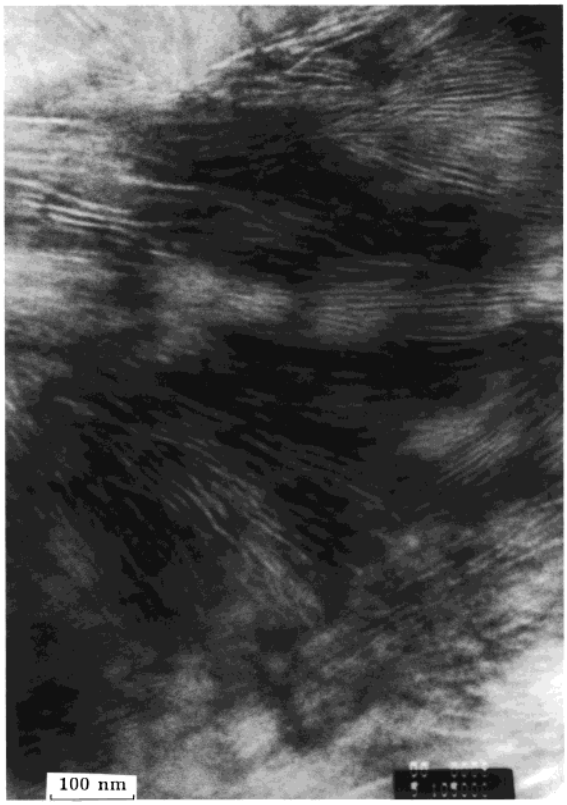


Figure 7. Transmission electron micrograph of poly(caprolactone)/poly(methyl methacrylate) block copolymer (entry B1 in Table 1).

Conclusions

In conclusion, we have described the rational design of a unique multiarm initiator containing initiating sites for both ROP and ATRP within the same molecule. The versatility of the initiator was proven by the synthesis of miktoarm star polymers in a core-out approach. Because of the unique and well-defined architecture of the polymers, the possibility of intramolecular segregation is very limited. Therefore, we are currently investigating properties such as the micromorphology as a function of architecture and arm length ratio of these materials. In an extension of this work, we will synthesize initiators with a larger number of arms and study the extension of the polymerization to different monomers. The incorporation of more hydrophilic monomers such as acrylic acid derivatives should yield micellar structures.

Experimental Section

All chemicals were purchased from Aldrich Chemical Co. and used without any further purification unless otherwise noted. Methyl methacrylate and *tert*-butyl acrylate were distilled from CaH_2 under reduced pressure. ϵ-Caprolactone was distilled under reduced pressure. Toluene was freshly distilled from potassium. Compound **1** and dNbipy were synthesized according to literature procedures.[2,29]

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM 250 (250 MHz) spectrometer, with the solvent signal as an internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ at 62.5 MHz on a Bruker AM 250 spectrometer with the carbon signal serving as internal standard. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica gel used for flash chromatography was Merck Kieselgel 60 (230−400 mesh). Size exclusion chromatography was carried out at room temperature on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5 μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6 Å) were used with THF as eluant at a flow rate of 1 mL/min. The IR spectra were recorded on a Nicolet Magna 550 instrument.

Initiators. 2a,b: A round-bottom flask was charged with **1** (20.0 g, 89.6 mmol), triethylamine (9.06 g, 12.6 mL, 89.5 mmol), and 40 mL of dichloromethane. The mixture became homogeneous upon stirring. The silyl chloride (89.5 mmol) was slowly added to the solution. The reaction mixture was allowed to stir at room temperature overnight. After filtration of the precipitated triethylamine salt, the product was purified by flash chromatography on silica gel using hexane/ethyl acetate (9:1). **2a**: Viscous liquid (84%). ^{1}H NMR: δ 0.05 (s, 6H, Si−CH_3), 0.91 (s, 9H, Si−C−CH_3), 1.11 (s, 3H, −C−CH_3), 3.62−3.95 (2 AB quartet, 4H, −CH_2−), 5.17 (s, 2H, Ph−CH_2), 7.3 (s, 5H, ArH). ^{13}C NMR: δ −5.68 (CH_3)$_2$Si−, 17.27 CH_3−C(CH_2O−)$_2$, 18.14 (CH_3)$_3$*C*−, 25.75 (CH_3)$_3$C−, 49.82 CH_3−*C*(CH_2O−)$_2$, 66.34 (−*C*H_2O−), 66.48 (−*C*H_2O−), 66.85 (−*C*H_2O−) 127.89 (aromatics), 128.16 (aromatics), 128.55 (aromatics), 135.92 (aromatics), 175.25 (ester carbonyl). IR (cm^{-1}): 3200−3600, 2800−3100, 1732, 1085, 812. **2b**: Viscous liquid (88%). ^{1}H NMR: δ 1.03 (s, 9H, Si−C−CH_3), 1.18 (s, 3H, −C−CH_3), 3.62−4.03 (2 AB quartet, 4H, −CH_2−), 5.14 (AB quartet, 2H, Ph−CH_2), 7.29−7.64 (m, 15H, ArH). ^{13}C NMR: δ 17.28 CH_3−C(CH_2O−)$_2$, 19.28 (CH_3)$_3$*C*−, 26.76 (*C*H_3)$_3$C−, 50.22 CH_3−*C*(CH_2O−)$_2$, 66.18 (−*C*H_2O−), 66.49 (−*C*H_2O−), 67.14 (−*C*H_2O−), 127.75 (aromatics), 127.79 (aromatics), 128.18 (aromatics), 128.60 (aromatics), 129.79 (aromatics), 132.91 (aromatics), 135.62 (aromatics), 135.79 (aromatics), 175.35 (ester carbonyl). IR (cm^{-1}): 3200−3600, 2800−3100, 1724, 1114, 710.

3a,b: Compound **2a,b** (58.10 mmol) was dissolved in 200 mL of ethyl acetate, and 2 g of 10% Pd on activated carbon was added. The mixture was placed in a hydrogenator and was allowed to react under 30 psi of $H_{2\ (gas)}$ overnight. The product could be isolated by filtration of the solution and subsequent evaporation of the solvent. **3a**: Viscous liquid (98%). ^{1}H NMR: δ 0.06 (s, 6H, Si−CH_3), 0.88 (s, 9H, Si−C−CH_3), 1.11 (s, 3H, −C−CH_3), 3.65−3.85 (2 AB quartet, 4H, −CH_2−). ^{13}C NMR: δ −5.69 (CH_3)$_2$Si−, 17.38 (CH_3−C(CH_2O−)$_2$, 18.12 (CH_3)$_3$*C*−, 25.71 (CH_3)$_3$C−, 49.25 CH_3−*C*(CH_2O−)$_2$, 66.26 (−*C*H_2O−), 66.86 (−*C*H_2O−), 179.98 (acid carbonyl). IR (cm^{-1}): 2800−3600, 1756, 1722, 1084, 812. **3b**: Viscous liquid (97%). ^{1}H NMR: d 1.03 (s, 9H, Si−C−CH_3), 1.16 (s, 3H, −C−CH_3), 3.66−3.91 (2 AB quartets, 4H, −CH_2−), 7.31−7.66 (m, 10H, ArH). ^{13}C NMR: δ 17.29 CH_3−C(CH_2O−)$_2$, 19.26 (CH_3)$_3$*C*−, 26.78 (*C*H_3)$_3$C−, 49.68 CH_3−*C*(CH_2O−)$_2$, 65.86 (−CH_2O−), 67.01 (−CH_2O−), 127.81 (aromatics), 129.93 (aromatics), 132.61 (aromatics), 132.74 (aromatics), 135.63 (aromatics), 179.79 (acid carbonyl). IR (cm^{-1}): 2800−3600, 1744, 1713, 1108, 710.

4a,b: A round-bottom flask was charged with **3a,b** (47.20 mmol), 200 mL of dry dichloromethane, and triethylamine (9.55 g, 94.4 mmol). 2-Bromo-2-methylpropionyl bromide (10.85 g, 47.20 mmol) was added dropwise to this solution at 0 °C

under argon atmosphere. The resulting suspension was stirred for another 2 h and then filtered to remove the precipitated triethylamine salt. For **4b**, the crude product was purified by flash chromatography on silica gel (dichloromethane/methanol 9:1). For **4a,b**, the crude product was extracted several times with $NaHCO_3$ solution. **4a**: Viscous liquid (45%). ^{1}H NMR: δ 0.01 (s, 6H, Si−CH_3), 0.88 (s, 9H, Si−C−CH_3), 1.16 (s, 3H, −C−CH_3), 1.81 (d, 6H, −C(Br)−CH_3), 3.69−3.86 (s, 2H, −CH_2−O−C(O)−), 4.36 (AB quartet, 2H, −CH_2−O−Si)). ^{13}C NMR: δ −5.64 (CH_3)$_2$Si−, 17.25 CH_3−C(CH_2O−)$_2$, 18.15 (CH_3)$_3C$−, 25.71 (CH_3)$_3$C−, 30.64 (CH_3)$_2$CBr−, 48.34 CH_3−C(CH_2O−)$_2$, 55.49 (CH_3)$_2C$Br−, 64.88 (−CH$_2$O−), 66.37 (−CH_2O), 171.15 (acid carbonyl), 179.19 (ester carbonyl). IR (cm^{-1}): 2800−3500, 1745, 1714, 1080, 818. **4b**: Viscous liquid (62%). ^{1}H NMR: δ 1.00 (s, 9H, Si−C−CH_3), 1.15 (s, 3H, −C−CH_3), 1.81 (d, 6H, −C(Br)−CH_3) 3.69−3.86 (s, 2H, −CH_2−O−C(O)−), 4.43 (AB quartet, 2H, −CH_2−O−Si), 7.32−7.63 (m, 10H, ArH). ^{13}C NMR: δ 17.45 CH_3−C(CH_2O−)$_2$, 19.31 (CH_3)$_3C$−, 25.71 (CH_3)$_3$C−, 30.68 (CH_3)$_2$CBr, 48.81 CH_3−C(CH_2O−)$_2$, 55.49 (CH_3)$_2C$Br−, 65.47 (−CH$_2$O−), 66.49 (−CH$_2$O−), 127.57 (aromatics), 129.79 (aromatics), 132.93 (aromatics), 135.61 (aromatics), 171.34 (acid carbonyl), 172.63 (ester carbonyl). IR (cm^{-1}): 2800−3600, 1740, 1703, 1103, 710.

5a,b: 1,1,1-Tris(*p*-hydroxyphenylethane) (734 mg, 2.4 mmol) together with **4a,b** (8 mmol) was dissolved in ca. 10 mL of dichloromethane. Then 4-(dimethylamino)pyridinum 4-toluenesulfonate (DPTS, 0.3 g, 1 mmol) and dicyclohexyl carbodiimide (DCC, 2 g, 9 mmol) were added in that order, and the solution was stirred at room temperature overnight. The solution was filtered to remove the urea byproduct and the product purified by flash chromatography on silica gel (hexane/ethyl acetate 4:1). **5a**: white solid (80%). ^{1}H NMR: δ 0.04 (s, 18H, Si−CH_3), 0.88 (s, 27H, Si−C−CH_3), 1.28 (s, 9H, −C−CH_3), 1.84 (s, 18H, −C(Br)−CH_3), 2.12 (s, 3H, Ar_3−C−CH_3), 3.74−3.93 (AB quartet, 6H, −CH_2−O−C(O)−), 4.39−4.49 (AB quartet, 6H, −CH_2−O−Si), 6.92−7.08 (dd, 12 H, core ArH). ^{13}C NMR: δ −5.61 (CH_3)$_2$Si−, 17.35 CH_3−C(CH_2O−)$_2$, 18.18 (CH_3)$_3C$−, 25.78 (CH_3)$_3$C−, 30.84 (CH_3)$_2$CBr−, 49.02 CH_3−C(CH_2O−)$_2$, 51.66 (Ar_3−C−CH_3), 55.44 (CH_3)$_2C$Br−, 65.10 (−CH_2O−), 66.66 (−CH_2O−), 120.84 (aromatics), 129.66 (aromatics), 146.16 (aromatics), 148.88 (aromatics), 171.17 (ester carbonyl), 172.33 (ester carbonyl). IR (cm^{-1}): 2550−3050, 1745, 1175, 1102, 818. **5b**: white solid (83%). ^{1}H NMR: δ 1.00 (s, 27H, Si−C−CH_3), 1.31 (s, 9H, −C−CH_3), 1.80 (d, 18H, −C(Br)−CH_3), 2.08 (s, 3H, Ar_3−C−CH_3), 3.76−3.92 (AB quartet, 6H, −CH_2−O−C(O)−), 4.41−4.56 (AB quartet, 6H, −CH_2−O−Si), 6.87−7.01 (dd, 12 H, core ArH), 7.25−7.60 (m, 30H, ArH−Si). ^{13}C NMR ($CDCl_3$): δ 17.46 CH_3−C(CH_2O−)$_2$, 19.35 (CH_3)$_3C$−, 26.86 (CH_3)$_3$C−, 30.76 (CH_3)$_2$CBr−, 49.28 CH_3−C(CH_2O−)$_2$, 51.67 (Ar_3−C−CH_3), 55.46 (CH_3)$_2C$Br−, 65.86 (−CH$_2$O−), 66.71 (−CH$_2$O−), 120.82 (aromatics), 127.78 (aromatics), 129.65 (aromatics), 129.84 (aromatics), 132.90 (aromatics), 135.64 (aromatics), 146.16 (aromatics), 148.89 (aromatics), 171.18 (ester carbonyl), 172.13 (ester carbonyl). IR (cm^{-1}): 2857−3069, 1740, 1175, 1113, 710.

6: Compound **5a** (1.0 g, 0.7 mmol) was dissolved in ca. 5 mL of chloroform, and boron trifluoride etherate (1 M in THF, 0.2 g, 1.4 mmol) was added under argon atmosphere. After stirring 2 h at room temperature, the reaction mixture was consecutively extracted with 2 N HCl solution, 2 N $NaHCO_3$ solution, and water. After drying with $MgSO_4$ the solvent was evaporated: white solid (60%). ^{1}H NMR: δ 1.37 (s, 9H, −C−CH_3), 1.90 (s, 18H, −C(Br)−CH_3), 2.14 (s, 3H, Ar_3−C−CH_3), 3.79−3.89 (AB quartet, 6H, −CH_2−OH), 4.40−4.56 (AB quartet, 6H, −CH_2−O−C(O)−), 6.96−7.06 (dd, 12 H, core ArH). ^{13}C NMR: δ 17.45 CH_3−C(CH_2O−)$_2$, 30.72 (CH_3)$_2$CBr−, 48.87 CH_3−C(CH_2O−)$_2$, 51.67 (Ar_3C−CH_3), 55.33 (CH_3)$_2C$Br−, 65.07 (−CH_2O−), 67.13 (−CH_2O−), 120.84 (aromatics), 129.89 (aromatics), 146.30 (aromatics), 148.71 (aromatics), 171.58 (ester carbonyl), 172.77 (ester carbonyl). IR (cm^{-1}): 2800−3050, 3200−3700, 1740, 1180.

Polymers. ATRP of MMA was carried out in bulk under argon with freshly distilled monomer. In a typical procedure, the respective (macro) initiator, catalyst (CuBr), and the ligand 4,4′-di(5-nonyl)-2,2′-bipyridine (molar ratio 1:3:3) were first weighed into a flame-dried round-bottom flask equipped with a three-way stopcock. Several cycles involving evacuation and subsequent purging with argon were conducted to remove most of the dissolved oxygen. Finally, the purified and degassed MMA was added (monomer/initiator ratio was calculated based on the desired molecular weight). After the (macro) initiator was completely dissolved, the mixture was heated to 95 °C until the contents of the flask solidified. The polymer was purified by precipitation into methanol. Polymerization of *tert*-butyl acrylate (tBA) was carried out similarly using toluene as the solvent (monomer/toluene 1:1). After 1−3 h, the reaction solution was diluted with THF and filtered through a plugged column of neutral aluminum oxide. The polymer was then recovered by evaporation of the solvent. After characterization, a polymer analogous deprotection of the polyacrylate block was performed using trifluoroacetic acid in methylene chloride.

ROP was performed according to a literature procedure.[8]

Preparation of 3-Arm Macroinitiator from Caprolactone (B1, Table 1). Into a flask equipped with a three-way stopcock was placed 0.227 g (0.210 mmol) of the initiator **6**, 5 mg (0.0125 mmol) of stannous octanoate, and 4.5 g (39.5 mmol) of ϵ-caprolactone. The contents of the flask were heated to 55 °C and degassed using a vacuum−argon cycle. The reaction was heated to 110 °C in an oil bath for 20 h. After dilution with 5 mL of THF, the polymer was precipitated into methanol, filtered, and dried overnight in a vacuum oven: 4.0 g (85%), M_n 2.4 × 10^4 (determined by ^{1} H NMR, molecular weight measured by NMR does not include the core, 1100 g/mol), PDI 1.33. This material was used to prepare the various miktoarm block copolymers using ATRP procedures. ^{1}H NMR: δ 1.23 (singlet, CH_3−C(CH_2O−)$_2$, core), 1.29−1.39 (multiplet, −CH_2−CH_2−CH_2−), 1.57−1.69 (multiplet, −$CH_2$$CH_2$−O−), 2.0 (singlet, Ar_3C−CH_3), 2.28 (triplet, CO−CH_2−), 3.63 (multiplet, CH_2OH, end group), 4.04 (triplet, CH_2OCO), 4.27−4.5 (multiplet, CH_3−C(CH_2O−)$_2$, core), 6.90−7.15 multiplet, aromatics, core).

Preparation of 3-Arm Macroinitiator from MMA (A1, Table 1). Into a round-bottom flask equipped with a three-way stopcock was placed 0.5 g (0.29 mmol) of the initiator **5b**, 0.13 g (0.91 mmol) of CuBr, and 0.35 g (0.85 mmol) of dNbipy. Three cycles of vacuum−argon purging were conducted to remove most of the oxygen. Then 4.3 g (43.0 mmol) of degassed MMA was added and the flask heated to 90 °C after the components had dissolved. After 2 h, the reaction mixture solidified. The contents of the flask were dissolved in methylene chloride and precipitated into methanol. Yield: 4.1 g (85%), M_n 1.4 × 10^4 (measured by ^{1}H NMR, molecular weight does not include the core), PDI 1.18. ^{1}H NMR: δ 1.70−2.08 (complex multiplet, PMMA,and core), 3.30 (multiplet, −CH_2O−Si, core), 3.57 (singlet, −CO_2CH_3), 3.74 (singlet, −CBr(CH_3)−CO_2CH_3, end group), 4.80 (multiplet, CH_3−C(CH_2OCOC-(CH_3)$_2$−PMMA), core), 6.83−7.12 (multiplet, aromatics, core), 7.28−7.68 (multiplet, Ph_2Si−).

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