Notes

Synthesis of Amphiphilic (ABC)$_n$ Multiarm Star Triblock Terpolymers

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Introduction

Linear ABC triblock terpolymers represent a relatively new class of polymeric materials with an increasing interest for their properties in the bulk[1−6] and in solution.[7−18] The three chemically different components of these materials, each placed in a separate block, can confer to the terpolymer three different functions. Another similar, but more novel, and equally interesting class of polymeric materials is that of ABC heteroarm[19] or miktoarm[20] star terpolymers, bearing three arms, each of which is a different homopolymer.

The purpose of this investigation was to further extend the synthetic work on three-component polymers and prepare a new structure of star terpolymers whose arms are not different homopolymers but ABC triblock terpolymers. A combination of two hydrophilic and one hydrophobic monomers was chosen, leading to water-soluble, amphiphilic materials.

Experimental Section

The synthesis was performed using sequential group transfer polymerization (GTP)[21−24] of the three monomers and the cross-linker according to published procedures.[11,25] Details for the polymer synthesis and characterization are provided in the Supporting Information. Methoxy hexa(ethylene glycol) methacrylate (HEGMA, nonionic) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, positively ionizable) were the two hydrophilic monomers employed, while methyl methacrylate (MMA) was the hydrophobic monomer used. Ethylene glycol dimethacrylate (EGDMA) served as the cross-linker. Gel permeation chromatography (GPC) was performed on a Polymer Laboratories system using tetrahydrofuran (THF) as the mobile phase to determine the molecular weights (MWs) of the terpolymers relative to linear polyMMA standards. Static light scattering (SLS) on terpolymer solutions in THF was carried out using a thermally regulated (0.1 °C) spectrogoniometer, model SEM RD from Sematech, to determine the absolute MWs of the star terpolymers. Aqueous salt-free terpolymer solutions (1% w/w) were characterized in terms of their cloud points and effective p*K*s, using turbidimetry and hydrogen ion titration, respectively.

Results and Discussion

Polymer Synthesis. The synthetic procedure for the preparation of the ABC star terpolymer with structure DMAEMA$_{10}$-*b*-HEGMA$_{10}$-*b*-MMA$_{10}$-*star* is presented schematically in Figure 1a.

The synthesis involved sequential monomer and cross-linker additions. The first step in Figure 1a resulted in the preparation of linear DMAEMA$_{10}$ homopolymer, active at one end, indicated by asterisks. The second step led to the synthesis of the DMAEMA$_{10}$-*b*-HEGMA$_{10}$ linear diblock copolymer with again one active end. The third step was the addition of MMA, which resulted in the formation of the linear ABC triblock terpolymer DMAEMA$_{10}$-*b*-HEGMA$_{10}$-*b*-MMA$_{10}$. The synthesis was completed by the addition of the EGDMA cross-linker, which effected the interconnection of several terpolymers at their active end, leading to the formation of star ABC triblock terpolymers. The number of arms at the cross-links was not six, as indicated in the figure, but higher, as this will be determined below. Two other star triblock terpolymers, block sequence isomers of this star, were synthesized by altering the order of monomer addition, while the star terpolymer isomer with statistical arms was prepared by simultaneously copolymerizing all three monomers. The four linear analogues to these stars were synthesized using the same procedure as that for the stars, but omitting the last, cross-linker addition, step. Figure 1b shows schematically all eight terpolymers synthesized.

Terpolymer Molecular Weights. *GPC MWs.* All of the linear and star ABC triblock and statistical terpolymers as well as their homopolymer, diblock, and triblock terpolymer precursors were characterized by GPC in terms of their molecular weight distributions (MWDs), from which the apparent number-average MWs (M_n) and polydispersities (M_w/M_n) were calculated. These results are shown in Table 1 along with the theoretical degrees of polymerization (subscripts in the polymer formula column) and the theoretical MWs. For the linear terpolymers and their precursors, the polydispersities were relatively small (<1.15 in most cases), but the M_ns were consistently slightly higher than the theoretically predicted, indicating some initiator deactivation as well as differences between the synthesized polymers and the PMMA standards used for the MW calibration.

The linear precursors of the star terpolymers had similar apparent M_ns and polydispersities to those of the linear terpolymers listed in the first part of the table. The apparent M_ns of the star tepolymers were around 100 000 g mol^{-1}, which was an underestimation of their absolute MWs due to their more compact nature than the linear calibration MW standards. Their MWDs were

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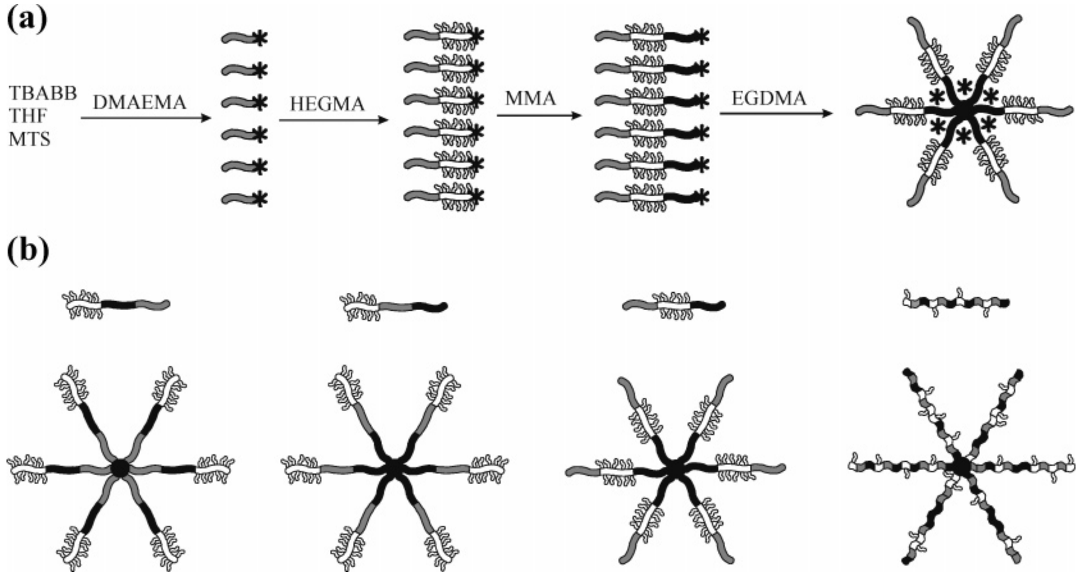

Figure 1. (a) Schematic representation of the synthetic procedure followed for the preparation of the DMAEMA$_{10}$-*b*-HEGMA$_{10}$-*b*-MMA$_{10}$-*star* triblock terpolymer. The DMAEMA units are shown in gray, the HEGMA units in white, and the MMA units in black. The "*" symbols indicate the "living" sites of the polymerization. The number of arms at the cross-links is not six, as indicated in the figure, but higher than 40. (b) Schematic representation of the eight terpolymers synthesized in this study.

Table 1. Molecular Weight Analysis of the Linear and Star Terpolymers

no.	polymer formula[a]	theor MW[b]	GPC results M_n	GPC results M_w/M_n	SLS results M_w	SLS results N_w[c]
1	H_{10}	3740	4980	1.11		
	H_{10}-*b*-D_{10}	5310	6340	1.10		
	H_{10}-*b*-D_{10}-*b*-M_{10} *linear*	6310	7760	1.11		
2	H_{10}	3740	4810	1.12		
	H_{10}-*b*-M_{10}	4740	5820	1.10		
	H_{10}-*b*-M_{10}-*b*-D_{10} *linear*	6310	7270	1.13		
3	D_{10}	1670	1540	1.30		
	D_{10}-*b*-H_{10}	5310	6090	1.11		
	D_{10}-*b*-H_{10}-*b*-M_{10} *linear*	6310	7060	1.11		
4	(H-*co*-D-*co*-M)$_{10}$ *linear*	6310	7810	1.14		
5	H_{10}	3740	4665	1.12		
	H_{10}-*b*-D_{10}	5310	5280	1.12		
	H_{10}-*b*-D_{10}-*b*-M_{10}	6310	6600	1.13		
	H_{10}-*b*-D_{10}-*b*-M_{10}-*star*		92240	1.23	300 000	40
6	H_{10}	3740	4160	1.13		
	H_{10}-*b*-M_{10}	4740	5110	1.12		
	H_{10}-*b*-M_{10}-*b*-D_{10}	6310	6920	1.13		
	H_{10}-*b*-M_{10}-*b*-D_{10}-*star*		101380	1.28	570 000	73
7	D_{10}	1670	1280	1.34		
	D_{10}-*b*-H_{10}	5310	3130	1.12		
	D_{10}-*b*-H_{10}-*b*-M_{10}	6310	6800	1.12		
	D_{10}-*b*-H_{10}-*b*-M_{10}-*star*		78590	1.17	506 000	66
8	(H-*co*-D-*co*-M)$_{10}$	6310	7690	1.18		
	(H-*co*-D-*co*-M)$_{10}$-*star*		88200	1.20	625 000	72

[a] H = HEGMA, D = DMAEMA, M = MMA. [b] Contribution of 100 g mol^{-1} from the initiator fragment included. [c] Weight-average number of arms calculated from the ratio of the M_w of the star terpolymer measured using SLS divided by the M_n of linear arm measured using GPC. In the calculation, the contribution of the cross-linker units in the core and the percentage of the unattached arms were taken into account.

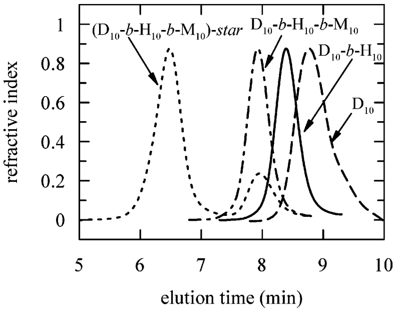

Figure 2. GPC chromatograms of DMAEMA$_{10}$-*b*-HEGMA$_{10}$-*b*-MMA$_{10}$-*star* and its three linear precursors. D, H, and M are further abbreviations for the DMAEMA, HEGMA, and MMA units, respectively.

broader than those of the linear precursors, but their polydispersities always remained lower than 1.3.

Figure 2 shows the GPC chromatograms of the DMAEMA$_{10}$-*b*-HEGMA$_{10}$-*b*-MMA$_{10}$-*star* terpolymer and its three linear precursors. The chromatograms of the linear precursors exhibited monomodal MW distribution. The MWs shifted to higher values with each monomer addition, indicating incorporation of the added monomer into the polymer. The chromatogram of the star terpolymer exhibited a bimodal distribution, in which the lower MW peak coincided with the peak of the linear precursor, indicating incomplete incorporation of all the linear chains into the star terpolymer. The GPC chromatograms of the other three star terpolymers were similar to that shown in Figure 2, also exhibiting bimodal distributions. The percentage of unattached linear terpolymer relative to the overall polymer sample was estimated from the areas under the peaks in GPC and was found to be between ~18 and 22%. In contrast, the GPC chromatograms of the linear triblock terpolymers exhibited monomodal distribution, indicating that the triblock terpolymer was the only polymer present since there was an absence of peaks corresponding to linear homopolymers and diblock copolymers. For comparison, star polymers of MMA with EGDMA cores synthesized by "living" anionic polymerization contained between 10 and 45 wt % unattached arms.[26]

SLS MWs. The absolute M_ws of the four star terpolymers were measured by SLS in THF. The SLS M_ws were found to be several times higher than the corresponding GPC values due to the compact nature of the star architecture. In particular, the absolute M_ws of the star terpolymers ranged between 300 000 and 625 000 g mol^{-1} and are also listed in Table 1. The weight-average number of arms of the star terpolymers, N_w, was estimated from their absolute M_ws and the GPC M_ns of their arms. More specifically, it was calculated as the

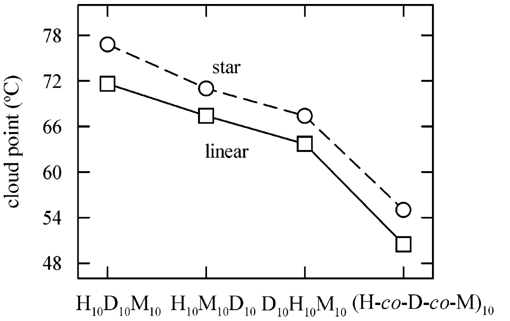

Figure 3. Dependence of the cloud points of the linear and star terpolymers on their monomer distribution.

ratio of these two MWs, after subtraction of the cross-linker weight from the weight of the star terpolymer. This is also displayed in Table 1, and it varied between 40 and 73. These values are in good agreement with the values of 20,[27] 30,[25] 50,[28] 15−40,[29] and 20−100[30] reported in the literature for the number of arms of "arm-first" star polymers with EGDMA cores, also prepared by GTP.

Aqueous Solution Properties. Preliminary aqueous solution characterization of all eight terpolymers was performed to determine the cloud points and effective p*K*s of the DMAEMA units in the terpolymers.

Cloud Points. The cloud points of the linear and star terpolymers are plotted in Figure 3. The cloud points of the star terpolymers were higher than those of their linear counterparts by 5 °C, indicating that the star terpolymers in aqueous solution were more stable than their linear counterparts. This is consistent with the relatively large number of arms of the star terpolymers, effecting a better steric stabilization[31] and a smaller unfavorable contact between the hydrophobic MMA units and water.

The cloud points of the linear terpolymers ranged between 51 and 72 °C. The lowest cloud point was that of the statistical linear terpolymer whose MMA hydrophobic units are randomly distributed along the polymer chain. This monomer distribution excludes both the possibility for intermolecular aggregation, i.e., micellization, and the possibility for intramolecular aggregation of the MMA units, i.e., formation of unimolecular micelles. Thus, the MMA units in this linear terpolymer are minimally protected from water, resulting in the lowest cloud point. The three linear triblock terpolymers exhibited cloud points which were by 13−21 °C higher than those of their statistical counterpart, suggesting possible micellization of the triblocks. The cloud points of the three linear triblocks spanned a range of 8 °C, indicating a pronounced effect of block sequence on their colloidal stability and reflecting differences in their conformation or/and aggregation in aqueous solution.

The cloud points of the star terpolymers ranged between 55 and 77 °C and presented the same order as the corresponding linear terpolymers. The statistical star terpolymer, (HEGMA-*co*-DMAEMA-*co*-MMA)$_{10}$-*star*, presented the lowest cloud point among the star terpolymers because the MMA hydrophobic units are minimally protected from water. The cloud points of the three star triblocks spanned a range from 67 to 77 °C, indicating again the importance of block sequence on this property and suggesting different chain conformation and intra- or intermolecular aggregation in aqueous solution.

Effective pKs and Water Solubility. The effective p*K*s of the DMAEMA units in all the terpolymers ranged between 6.1 and 6.9, which were near the reported effective p*K* value of the DMAEMA homopolymer of around 7.[32] All terpolymer solutions remained optically clear during their titrations between pH 2 and 12 (at room temperature), indicating the increased hydrophilicity of these materials.

Conclusions

In this study, novel multiarm star-shaped ABC triblock terpolymers of the $(ABC)_n$ type and their linear counterparts were synthesized by group transfer polymerization (GTP). The synthetic strategy was that of the "arm-first" method using a bis-unsaturated monomer as cross-linking reagent. The synthetic method allowed the preparation of four equimolar isomeric terpolymers: the statistical and three block sequence isomers for which the position of the different blocks was chosen at will. All the star terpolymers were soluble in water, exhibiting cloud points from 55 to 77 °C. The linear terpolymers were also water-soluble but presented lower cloud points (51−72 °C) than the corresponding stars.

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Supporting Information Available: Details of the polymer synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Leibler, L.; Fredrickson, G. H. *Chem. Br.* **1995**, 42−45.
(2) Lohse, D. J.; Hadjichristidis, N. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 171−176.
(3) Kudose, I.; Kotaka, T. *Macromolecules* **1984**, *17*, 2325−2332.
(4) Mogi, Y.; Mori, K.; Matsushita, Y.; Noda, I. *Macromolecules* **1992**, *25*, 5412−5415.
(5) Auschra, C.; Stadler, R. *Macromolecules* **1993**, *26*, 2171−2174.
(6) Gido, S. P.; Schwark, D. W.; Thomas, E. L.; Gonçalves, M. C. *Macromolecules* **1993**, *26*, 2636−2640.
(7) Patrickios, C. S.; Hertler, W. R.; Abbott, N. L.; Hatton, T. A. *Macromolecules* **1994**, *27*, 930−937.
(8) Chen, W.-Y.; Alexandridis, P.; Su, C.-K.; Patrickios, C. S.; Hertler, W. R.; Hatton, T. A. *Macromolecules* **1995**, *28*, 8604−8611.
(9) Patrickios, C. S.; Forder, C.; Armes, S. P.; Billingham, N. C. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1181−1195.
(10) Patrickios, C. S.; Lowe, A. B.; Armes, S. P.; Billingham, N. C. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 617−631.
(11) Triftaridou, A. I.; Vamvakaki, M.; Patrickios, C. S. *Polymer* **2002**, *43,* 2921−2926.
(12) Giebeler, E.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 3815−3825.
(13) Kříž, J.; Pleštil, J.; Tuzar, Z.; Pospšíl, H.; Doskočilová, D. *Macromolecules* **1998**, *31*, 41−51.
(14) Yu, G.; Eisenberg, A. *Macromolecules* **1998**, *31*, 5546−5549.
(15) Liu, F.; Eisenberg, A. *J. Am. Chem. Soc.* **2003**, *125*, 15059−15064.
(16) Tsitsilianis, C.; Sfika, V. *Macromol. Rapid Commun.* **2001**, *22*, 647−651.
(17) Sfika, V.; Tsitsilianis, C.; Kiriy, A.; Gorodyska, G.; Stamm, M. *Macromolecules* **2004**, *37*, 9551−9560.
(18) Liu, S.; Weaver, J. V. M.; Tang, Y.; Billingham, N. C.; Armes, S. P.; Tribe, K. *Macromolecules* **2002**, *35*, 6121−6131.
(19) Tsitsilianis, C.; Voulgaris, D. *Macromol. Chem. Phys.* **1997**, *198*, 997−1007.

(20) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747−3792 and references therein.
(21) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473−1488.
(22) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706−5708.
(23) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034−4041.
(24) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2855−2860.
(25) Vamvakaki, M.; Patrickios, C. S. *Chem. Mater.* **2002**, *14*, 1630−1638.
(26) Efstratiadis, V.; Tselikas, G.; Hadjichristidis, N. *Polym. Int.* **1994**, *33*, 171−179.
(27) Haddleton, D. M.; Crossman, M. C. *Macromol. Chem. Phys.* **1997**, *198,* 871−881.
(28) Vamvakaki, M.; Hadjiyannakou, S. C.; Loizidou, E.; Patrickios, C. S.; Armes, S. P.; Billingham, N. C. *Chem. Mater.* **2001**, *13*, 4738−4744.
(29) Simms, J. A. *Rubber Chem. Technol.* **1991**, *64*, 139−151.
(30) Lang, P.; Burchard, W.; Wolfe, M. S.; Spinelli, H. J.; Page, L. *Macromolecules* **1991**, *24*, 1306−1314.
(31) Hunter, R. J. *Foundations of Colloid Science*, 1st ed.; Oxford University Press: New York, 1989; Vol. I, Chapter 8, pp 451−493.
(32) Simmons, M. R.; Patrickios, C. S. *Macromolecules* **1998**, *31*, 9075−9077.

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