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Macromolecules
NOTE

Self-Assembly and Structural Analysis of Multiblock Poly(oxyalkylene) Copolymers

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ABSTRACT: The self-assembled structures of newly synthesized, low molecular weight poly(oxyalkylene) block copolymers in aqueous solution were investigated using scattering methods. Diblock copolymers were synthesized using methoxy poly(ethylene glycol) 1100 as the hydrophilic block and poly(propylene oxide), poly(butene oxide), and poly(hexene oxide) as the hydrophobic moieties. The ratios of hydrophile to hydrophobe were 1:2, 1:1, and 2:1. In the cases of tri- and tetrablock copolymers, the total hydrophile to hydrophobe ratio was kept constant, at 1:1, and the same hydrophilic block was used each time. The ratios of hydrophobic moieties were varied among the tri- and tetrablock copolymers (which contained two and three types of hydrophobic units respectively). These products self-assemble in aqueous solution to give micelles or irregular aggregates with very broad size distributions. Dynamic light scattering and small-angle X-ray scattering were used as tools to determine the size and structure of these self-assembled micelles. It is shown that with very short hydrophobic chain lengths, even at room temperature, well-defined self-assembled structures are formed.

Introduction

Because polyoxyethylenes with hydrophobic end groups show amphiphilic properties, they are in widespread use as nonionic surfactants and emulsifiers.[1,2] The hydrophobic part of such molecules can be alkyl, acyl, or alkyl−aryl groups, but they can also be blocks consisting of propylene oxide (PO) or higher epoxides. The block copolymers of alkylene oxides are amphiphilic in nature. The blocks in such amphiphilic polymers can be arranged in different ways: as AB diblock; or as ABA or BAB triblock copolymers. The most common class of such block copolymers is the poloxamers (EO−PO−EO), which are commercially available under various trade names (Pluronic, Synperonic, Imbentin, etc.).[4−6] There is a wide body of literature about applications of these commercially available block copolymers of ethylene oxide and propylene oxide as surfactants, which has been reviewed comprehensively by Edens and Whitemarsh.[7] While polymers of ethylene oxide (EO) and propylene oxide (PO) can be produced in large quantities,[8,9] this is not the case with the higher epoxides, even though they may be useful as hydrophobic building blocks in amphiphilic molecules.[3,7]

The size and shape of self-assembled amphiphilic block copolymers is tunable through the synthetic chemistry of the constituent molecules.[10] In earlier publications in this series, we reported microwave-assisted anionic ring-opening polymerization of epoxides for the synthesis of amphiphilic block copolymers, and their characterization by using different chromatographic techniques.[11−15] The block copolymers synthesized have various architectures, such as bottlebrushes with hydrophilic handles, hydrophobic brushes with various lengths of pendant groups, and block copolymers with increasing length of pendant groups, which give rise to cone-type structures. The self-assembly and structural analysis of micelles of polyoxalkylene block copolymers has, to date, not been studied thoroughly. There are some reports on the structural analysis of micelles formed by EO−BO block copolymers,[16,17] but there is very little literature on the self-assembly behavior of EO−HO block copolymers or poly(oxyalkylene) multiblock copolymers.

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Experimental Section

Di-, tri-, and tetrablock copolymers were synthesized by microwave-assisted anionic ring-opening polymerization of epoxides using MeO−PEO 1100 as initiator and NaH as co-initiator. The products were characterized by using a combination of different chromatographic techniques. Detailed procedures and methods have been described elsewhere.[11,13−15]

Dynamic Light Scattering (DLS). This technique was used to obtain information about the rough size and size distribution of the different samples and to filter out those that were not suitable for SAXS. The instrumental setup, raw data and the techniques for evaluation are given in the Supporting Information.

Small-Angle X-ray Scattering (SAXS). The amphiphilic block copolymer samples that formed small enough aggregates (< 40 nm) were evaluated with SAXS. The instrumental setup and the procedures for data evaluation are given in the Supporting Information. All scattering patterns were transmission corrected by adjusting the attenuated scattering intensity at $q = 0$ to unity, and correcting for the scattering of the sample cell and the solvent. In order to obtain the scattering patterns on an absolute scale, water was used as a secondary standard.[18] Samples were equilibrated at 25 °C for 10 min before each measurement. The samples were exposed to X-rays at 25 °C for three 10 min periods, and the integrated scattering profiles were averaged. Raw data and evaluation fits can be found in the SI.

Results and Discussion

EO−PO Diblock Copolymers. The EO−PO block copolymers, with various ratios of PO block in comparison to fixed hydrophilic block (MeO−PEO 1100), form bigger aggregates, and their hydrodynamic radii R_h, obtained by DLS

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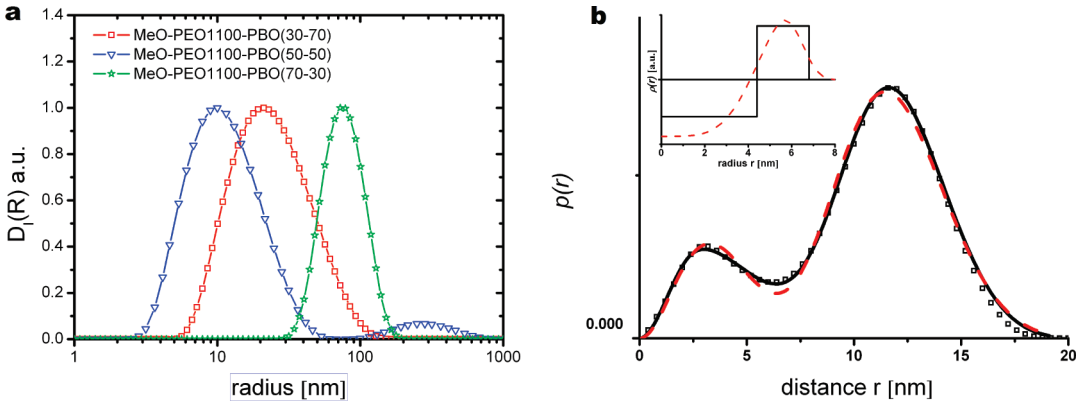

Figure 1. (a) Intensity-weighted size distributions from DLS for the MeO−PEO1100−PBO block copolymers (sample nos. 4, 5, and 6 in Table 1). (b) (□)PDDF of MeO−PEO1100−PBO (50−50) block copolymer from SAXS, the fit corresponding to (−) a two-step core−shell spherical model and (red --) a continuous core−shell model using splines (sample no. 5 in Table 1). Inset: electron-density difference profiles corresponding to the fits.

Table 1. Composition, Hydrodynamic Radius, and Aggregation Number (N_{agg}) of the Block Copolymers

no.	product	composition (wt %)	av no. of units	total length[a] [nm]	R_h [nm]	N_{agg}
1	MeO−$(EO)_{25}$−$(PO)_{44}$	30−70	25−44	29.4	108	
2	MeO−$(EO)_{25}$−$(PO)_{19}$	50−50	25−19	19.4	70	
3	MeO−$(EO)_{25}$−$(PO)_{8}$	70−30	25−8	14.5	90	
4	MeO−$(EO)_{25}$−$(BO)_{35}$	30−70	25−35	26.4	20	
5	MeO−$(EO)_{25}$−$(BO)_{15}$	50−50	25−15	17.6	11	102
6	MeO−$(EO)_{25}$−$(BO)_{7}$	70−30	25−6.5	13.9	73	
7	MeO−$(EO)_{25}$−$(HO)_{25}$	30−70	25−25	22	130 and 19	
8	MeO−$(EO)_{25}$−$(HO)_{11}$	50−50	25−11	15.8	11	178
9	MeO−$(EO)_{25}$−$(HO)_{5}$	70−30	25−4.7	13.1	6	54
10	MeO−$(EO)_{25}$−$(PO)_{10}$−$(BO)_{8}$	50−25−25	25−9.5−7.5	18.2	169	
11	MeO−$(EO)_{25}$−$(PO)_{6}$−$(BO)_{5}$	60−20−20	25−6.3−5	16	249	
12	MeO−PEO1100-$(PO)_{6}$−$(BO)_{5}$−$(HO)_{4}$	50−17−17−17	25−6.3−5−3.6	17.6	11	
13	MeO−PEO1100-$(PO)_{5}$−$(BO)_{5}$−$(HO)_{5}$	50−12−16−22	25−4.8−4.8−4.8	26.8	11	

[a] This is the sum of the averaged bond lenghts of the stretched molecule.

measurements, were 108, 70, and 90 nm, respectively. Therefore, it was not possible to investigate these samples by SAXS with our setup. The reason for the larger size of these structures might be the low hydrophobicity of PO blocks at 25 °C, which are hydrophilic enough to stay in the aqueous phase rather than in the core of the micelle.

EO−BO Diblock Copolymers. Three different types of diblocks of EO−BO class were investigated in this study. These block copolymers differ from each other in the length of their hydrophobic blocks. The intensity-weighted size distributions of EO−BO block copolymers are depicted in Figure 1a.

The diblock with the highest wt % of butene oxide (sample 4 in Table 1) showed a rather broad size distribution. SAXS yielded a PDDF but it was not possible to deconvolute it. There is no signature for the formation of well-defined micelles.

The second diblock of this class had the same wt % of hydrophilic and hydrophobic blocks. In this case, the DLS and SAXS data were in good agreement. Furthermore, we were able to deconvolute the PDDF with the assumption of micelles of spherical symmetry (Figure 1b).

The third diblock, with the lowest amount of butylene oxide, again gave no micellar structures. The measured R_h was about 73 nm (Figure 1a).

EO−HO Diblock Copolymers. As is stated above, the hydrophilic block was always MeO−$(EO)_{25}$, while the hydrophobic block (PHO) makes up 30, 50, and 70% of the weight of diblock copolymers in this class. All three samples formed micellar structures (Figure 2) and, in two cases, they were small enough to be investigated with SAXS. The EO−HO block copolymer with the highest content of PHO had a hydrodynamic radius that was bigger than the stretched length of the polymer chain. It is possible that this sample formed small vesicles or cylindrical (elongated) micelles. These types of structures were not investigated further. The EO−HO diblock with 50 wt % for both blocks formed micelles with a hydrodynamic radius of 11 nm. The PDDF shows the characteristics of an inhomogeneous micelle (Figure 2b). Furthermore, the PDDF was deconvoluted and revealed a very good fit for a two-step density spherical model (inset in Figure 2b).

The third EO−HO block copolymer, with 30 wt % of HO, showed similar behavior, the only difference being (as expected) the smaller hydrophobic core (see Supporting Information).

Triblock Copolymers (EO−PO−BO). None of the triblocks, which were mostly intermediates for the tetrablocks, showed any kind of well-determined micellar aggregate small enough to be investigated with SAXS. The hydrodynamic radii of two triblocks in the study were 169 and 249 nm (Figure 3a). Surprisingly, some of the tetrablocks formed micellar structures, whereas the triblocks did not. This was particularly unexpected because the MeO−$(EO)_{25}$−$(HO)_5$ diblock had a hydrophobic-block length similar to that of the triblocks.

Tetrablocks (EO−PO−BO−HO). Two poly(oxyalkylene) tetrablocks with different individual hydrophobic block lengths were investigated. DLS results show nearly the same size distribution for the two, with a radius of about 10 nm (Figure 3).

The evaluation of SAXS data with IFT and the so-obtained PDDF functions show that the micelles are inhomogeneous, and that the sample with the higher hexene oxide content (Figure 3b) has a larger electron-density difference than the tetrablock with less hexene oxide (Figure 4). It was not possible to deconvolute the PDDFs, which indicates that the micelles are not spherical. Neither a prolate nor an oblate rotational ellipsoid could be fitted to the data. Therefore, it can

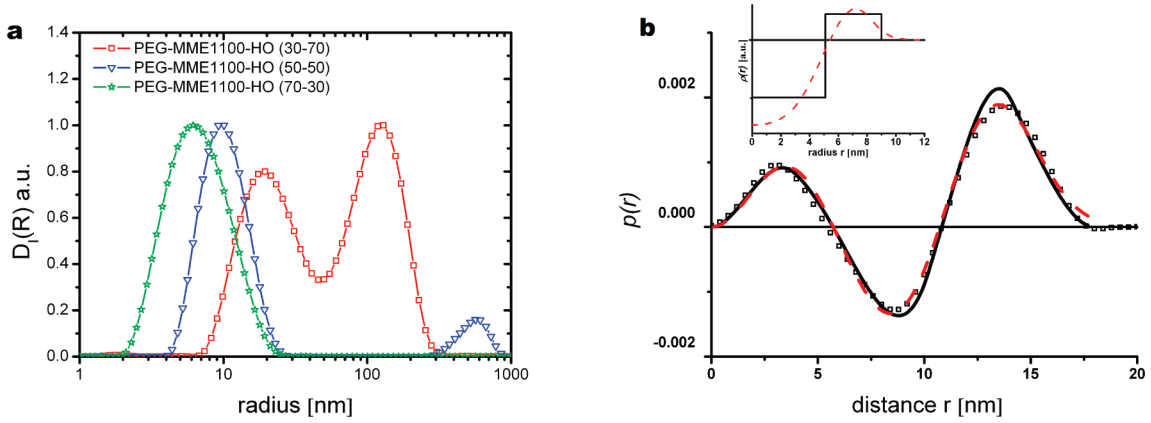

Figure 2. (a) Intensity-weighted size distributions from DLS for the MeO−PEO1100−PHO block copolymers (samples 7, 8, and 9 in Table 1). (b) (□) PDDF of MeO−PEO1100−PHO (50−50) block copolymer from SAXS, the fit corresponding to (−) a two-step core−shell spherical model and (red --) a continuous core−shell model using splines (sample no. 8 in Table 1). Inset: electron-density difference profiles corresponding to the fits.

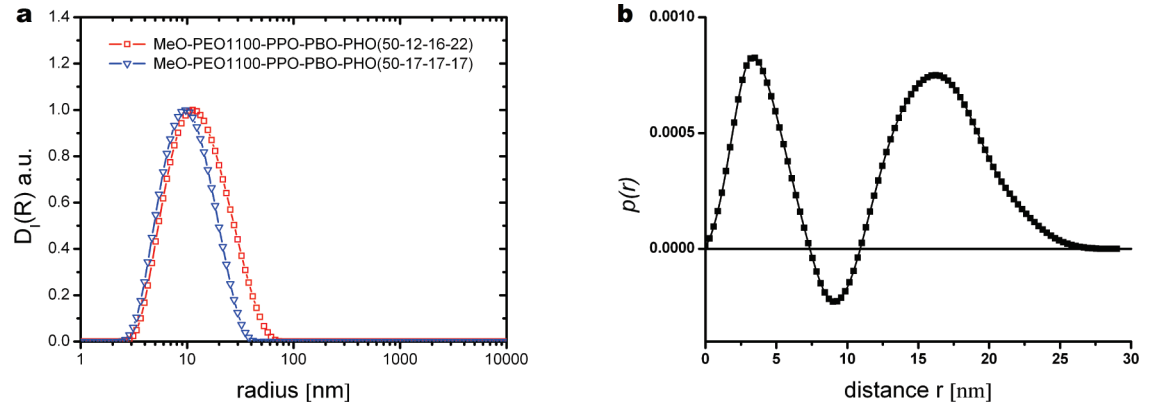

Figure 3. (a) Intensity-weighted size distributions for the MeO−PEO1100−PPO−PBO−PHO block copolymers (DLS; samples 12 and 13 in Table 1). (b) (■) PDDF for the MeO−PEO1100−PPO−PBO−PHO (50−12−16−22) block copolymer (SAXS, sample no. 12 in Table 1).

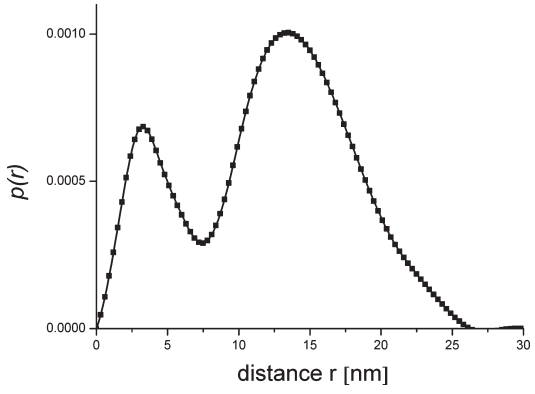

Figure 4. (■) PDDF for the MeO−PEO1100−PPO−PBO−PHO (50−17−17−17) block copolymer (sample no. 13 in Table 1).

be concluded that the micelles are still globular but do not have a well-defined size and shape.

Conclusions

We have shown that poly(oxyalkylene) block copolymers form micellar structures. Block copolymers consisting of higher alkylene oxides form stable micelles even with smaller hydrophobic block lengths. The samples for which the electron-density profiles were calculated show the characteristics of inhomogeneous micelles with a core consisting of closely packed hydrophobic groups of either PHO or PBO and a water-swollen corona consisting of the PEO block. The electron-density profiles depicted show in almost all cases that the PEO corona had a thickness of 2.5−3.0 nm, but in order to get more accurate information about the density and thickness of the corona SANS measurements with contrast variation and further model fitting as shown by Petersen et al.[20] would have to be done. The reason for the appearance of the larger and polydisperse aggregates that we found for all the MeO−PEO1100−PPO diblocks is most probably the temperature at which they were investigated. In the case of the MeO−PEO1100−PBO block copolymers the large aggregates were found only for the sample with the shortest hydrophobic chain length. Here, the relatively low temperature, as well as the short chain length of the hydrophobic part, might be the reason why well-defined self-assembled structures were not formed. The triblock copolymers generally showed the presence of very large undefined aggregates, which again can be attributed to the relatively short hydrophobic chain length, as well as the polydispersity of the block copolymers themselves, which prevents the formation of well-defined micelles at this temperature. For block copolymers it has previously been shown[19] that at temperatures that are too low to trigger the formation of micelles, large aggregates are present in solution alongside the block copolymer molecules. These aggregates are dissolved upon formation of micelles at higher temperature, as can be seen in Figure 1 in ref 19. The multiblock copolymers consisting of the four different blocks with increasing hydrophobicity did form self-assembled structures, but these were not as well-defined as those arising from the diblocks. This could be due either to the high polydispersity of multiblock copolymers arising from the four-step synthesis or to the short length of hydrophobic blocks at the given temperature.

Our results show that the formation of well-defined self-assembled structures can be achieved with very short chain lengths, even at relatively low temperatures, when more hydrophobic polymer blocks such as PBO and PHO are used for the synthesis of nonionic block copolymers.

Supporting Information Available: Text discussing the dynamic light scattering, the small-angle X-ray scattering, the determination of aggregation numbers, and the SAXS data evaluation and figures showing DLS and SAXS for the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bailey, F. E.; Koleske, J. V.; In *Polymerization of 1,2-Epoxides*; Marcel Dekker: New York, 1991; p 35.
(2) Quirk, R. P.; Ge, Q.; *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.* **2000**, *41*, 1221−1222.
(3) Allgaier, J.; Willbold, S.; Chang, T. *Macromolecules* **2007**, *40*, 518–525.
(4) Trathnigg, B. *Polymer* **2005**, *46*, 9211–9223.
(5) Alexandridis, P.; Alan Hatton, T. *Colloids Surf., A* **1995**, *96*, 1–46.
(6) Perreur, C.; Habas, J.-P.; Lapp, A.; Peyrelasse, J. *Polymer* **2006**, *47*, 841–848.
(7) Edens, M. W.; Whitmarsh, R. H.; In *Developments in Block Copolymer Science and Technology*; Wiley: Chichester, West Sussex, England, 2004; pp 325−340.
(8) Altinok, H.; Yu, G. E.; Nixon, S. K.; Gorry, P. A.; Attwood, D.; Booth, C. *Langmuir* **1997**, *13*, 5837–5848.
(9) Kelarakis, A.; Yang, Z.; Pousia, E.; Nixon, S. K.; Price, C.; Booth, C.; Hamley, I. W.; Castelletto, V.; Fundin, J. *Langmuir* **2001**, *17*, 8085–8091.
(10) Darling, S. B. *Prog. Polym. Sci.* **2007**, *32*, 1152–1204.
(11) Malik, M. I.; Trathnigg, B.; Kappe, C. O. *Macromol. Chem. Phys.* **2007**, *208*, 2510–2524.
(12) Malik, M. I.; Trathnigg, B.; Kappe, C. O. *Eur. Polym. J.* **2008**, *44*, 144–154.
(13) Malik, M. I.; Trathnigg, B.; Kappe, C. O. *Eur. Polym. J.* **2009**, *45*, 899–910.
(14) Malik, M. I.; Trathnigg, B.; Kappe, C. O. *J Chromatogr A* **2009**, *1216*, 1167–1173.
(15) Malik, M. I.; Ahmed, H.; Trathnigg, B. *Anal Bioanal Chem* **2009**, *393*, 1797–1804.
(16) Bedells, A. D.; Arafeh, R. M.; Yang, Z.; Heatly, F.; Attwood, D.; Padget, J. C.; Price, C.; Booth, C. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1235–1242.
(17) Tanodekaew, S.; Deng, N.-J.; Smith, S.; Yang, Y. W.; Attwood, D.; Booth, C. *J. Phys. Chem.* **1993**, *97*, 11847–11852.
(18) Orthaber, D.; Bergmann, A.; Glatter, O. *J. Appl. Crystallogr.* **2000**, *33*, 218.
(19) Brown, W.; Schillen, K.; Hvidt, S. *J. Phys. Chem.* **1992**, *96*, 6038–6044.
(20) Petersen, J. S.; Svaneborg, C.; Almdal, K.; Hamley, I. W.; Young, R. N. *Macromolecules* **2002**, *36*, 416–433.