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Synthesis, Characterization and Modeling of ABC Triblock Terpolymers: The Effect of Block Sequence

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Summary: Four equimolar terpolymers comprising ten units from each of the monomers methoxy hexa(ethylene glycol) methacrylate (HEGMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA) and methyl methacrylate (MMA) were prepared by group transfer polymerization (GTP), and characterized by gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy to confirm size homogeneity and composition. These terpolymers were the three block sequence isomers, ABC, BAC and ACB, as well as the statistical isomer. Aqueous solutions of the terpolymers were characterized by dynamic light scattering and turbidimetry to determine the hydrodynamic sizes and cloud points. The results indicated micelle formation in the triblocks, and absence of micellization with the statistical terpolymer. In general, a strong dependence of the hydrodynamic size and cloud point on polymer architecture was observed. Monte Carlo simulations on non-aggregating isomeric terpolymers of similar structure also showed a strong dependence of the radius of gyration on polymer architecture.

Introduction

ABC triblock terpolymers represent a new class of synthetic polymers, comprising three blocks, each of which consisted of a different type of monomer.[1] Morphology studies of such polymers in the absence of solvent indicated separation into microphases, which, in some cases were simple combinations of the shapes observed in diblocks and ABA triblocks,[2] and in others were new shapes unique to ABC triblock terpolymers.[3-5] The aim in this investigation was the study of ABC triblock terpolymers not in the solid state but in solution, for which there are only a limited number of studies.[6-10] The main focus was to determine the effect of block sequence on the solution properties of two ABC triblock terpolymer systems. First, in an experimental system which forms spherical micelles in water. Second, in a theoretical system with vacuum as the "solvent" where no aggregation takes place among the polymer chains.

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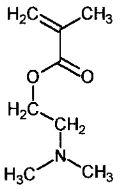
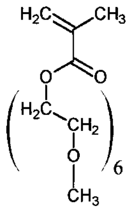
Experimental

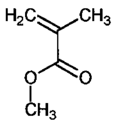
All chemicals were purchased from Aldrich, Germany. The chemical formulas and names of the monomers and initiator employed for the polymer synthesis are shown below:



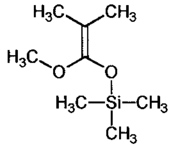
2-(Dimethylamino)
ethyl methacrylate
(DMAEMA)



Methoxy hexa(ethylene
glycol) methacrylate
(HEGMA)



Methyl
methacrylate
(MMA)



1-Methoxy-1-(trimethylsiloxy)-
2-methyl propene
(MTS)

DMAEMA and MMA were passed through basic alumina columns to remove inhibitors and protic impurities, were stirred over calcium hydride and distilled before the polymerization. A 50% v/v HEGMA solution in tetrahydrofuran (THF) was also passed through a basic alumina column, stirred over calcium hydride, and, due to its low volatility, was filtered through a syringe filter directly into the polymerization reactor. The MTS initiator was distilled prior polymerization. The polymerization solvent, THF, was dried by refluxing it over potassium for three days. The polymerization catalyst, tetrabutylammonium bibenzoate (TBABB), was in-house synthesized by the method of Dicker et al.[11] All glassware was dried overnight at 120 °C and assembled hot under dynamic vacuum prior to use. The polymerizations were carried out in 15 mL cylindrical vials fitted with a rubber septum. Catalytic amounts (5-10 mg) of TBABB catalyst were transferred to the reactor, which was immediately purged with dried nitrogen. Freshly distilled THF was transferred directly from the still into the reactor via a syringe. All terpolymers were prepared by group transfer polymerization (GTP).[11,12] The triblock terpolymers were prepared using sequential monomer addition, whereas the three monomers were starve-fed during the synthesis of the statistical terpolymer.

Results and Discussion

Terpolymers Aggregating in Water

Four terpolymers were synthesized using group transfer polymerization (GTP).[11,12] These polymers are based on a hydrophobic monomer, which leads to micellization in water, and on two different hydrophilic monomers that ensure the water-solubility of the polymers. The hydrophobic monomer is MMA, whereas the hydrophilic monomers are the nonionic HEGMA and the ionizable DMAEMA. The theoretical degree of polymerization of each monomer was ten, resulting in an overall degree of polymerization of 30. The three triblock terpolymers, ABC, ACB and BAC, and the statistical terpolymer were synthesized. The structure of these terpolymers, along with their characterization results, are shown in Table 1.

Table 1. Molecular weights, aqueous hydrodynamic sizes and aqueous cloud points of the terpolymers.

No.	**Polymer Chemical Formula**	**Theor. MWs**	**GPC Chromat.**		**Hydr. Diam. (nm)**	**Cloud Points (°C)**
			M_n	**M_w/M_n**		
1	$DMAEMA_{10}$-*b*-$HEGMA_{10}$-*b*-MMA_{10}	6170	11500	1.18	11.0	80.0
2	$HEGMA_{10}$-*b*-MMA_{10}-*b*-$DMAEMA_{10}$	6170	13050	1.09	6.4	80.7
3	$HEGMA_{10}$-*b*-$DMAEMA_{10}$-*b*-MMA_{10}	6170	9300	1.09	12.0	89.5
4	$HEGMA_{10}$-*co*-$DMAEMA_{10}$-*co*-MMA_{10}	6170	13250	1.08	4.5	57.2

The composition of the terpolymers was confirmed by proton nuclear magnetic resonance (^1H NMR) spectroscopy in $CDCl_3$. The molecular weights and their distributions were characterized by gel permeation chromatography (GPC) in THF and the results are also shown in Table 1. The polydispersity indices (M_w/M_n) were satisfactorily low (< 1.2) and number average molecular weights (M_ns) were almost double their theoretical value due to partial initiator deactivation.

Aqueous solutions of the terpolymers were characterized by dynamic light scattering and turbidimetry for the determination of the hydrodynamic diameters and the cloud points, respectively, which are also given in Table 1. The values of the hydrodynamic diameters of the triblock copolymers imply formation of spherical micelles. The micelle size of the triblock with an MMA midblock was almost one half of those of the two other triblocks with MMA endblocks. The statistical terpolymer did not form micelles in water. The cloud points of the triblocks are also affected by their structure. The statistical terpolymer, that does not form micelles, has the lowest cloud point because all the MMA units in this polymer contact water, in contrast to the triblocks where the MMA units are protected in the micellar core. The highest cloud point is observed with polymer 3 where both the hydrophobic MMA units and the marginally hydrophilic DMAEMA units (aqueous DMAEMA homopolymer solutions precipitate above 40 °C) are located in the core of the micelle, in contrast to the micelles of the other two triblocks that have DMAEMA units exposed in the micellar corona.

Non-Aggregating Terpolymers

The behavior of the terpolymers in non-selective solvents was studied using Monte Carlo simulation. To this end, the terpolymers were considered to consist of freely-jointed bonds of length *l*. At the ends of each bond there is a sphere. The three types of repeat units, A, B and C, are represented with spheres of different diameters, *l*/4, *l*/2 and *l*, respectively. The bonds can go through the spheres, but the spheres cannot overlap. Figure 1 represents the four equimolar isomeric terpolymers, the three ABC triblocks and the alternating terpolymer.

The Monte Carlo simulations start with the polymers being at fully extended configuration (as in Figure 1) and evolve with the use of the pivot algorithm.[13-16] With this method, a monomer unit (sphere) in the polymer chain is chosen at random as the pivot point, which divides the polymer in two sections. The smaller section is then rotated by a random angle, thus giving a new trial configuration. If this leads to an overlap between spheres, this configuration is rejected and the previous is retained. If not, it is accepted. This procedure is repeated 10^6 times, and the properties of the polymers are calculated.

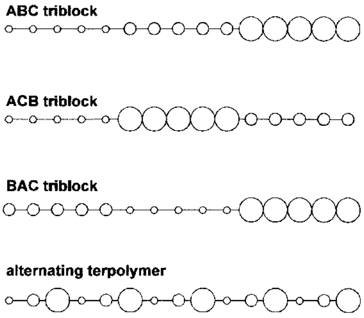


Figure 1. Representation of the four equimolar isomeric terpolymers with overall degree of polymerization 15.

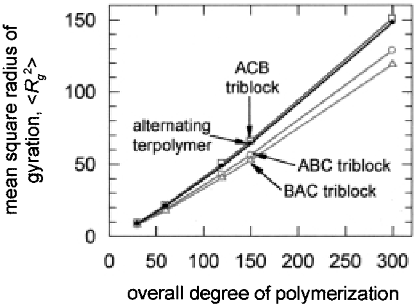


Figure 2. Dependence of the mean square radius of gyration on the overall degree of polymerization and the terpolymer structure.

Figure 2 presents the dependence of the mean square radius of gyration, $<R_g^2>$, on the overall degree of polymerization of isomeric triblocks with different architectures, ABC, ACB and BAC, as well as the alternating terpolymer. In all cases, $<R_g^2>$ increases almost linearly with the degree of polymerization. From the triblocks, the one with the bulkiest monomer as the midblock, i.e. ACB, exhibits the greatest $<R_g^2>$ because this midblock, which is the most rigid from the three, separates away the two endblocks, thus leading to large polymer dimensions. The opposite is true with BAC triblock terpolymer which exhibits the smallest $<R_g^2>$. It is noteworthy that the alternating terpolymer also exhibits a large value for $<R_g^2>$, similar to that of the ACB triblock.

The $<R_g^2>$s were also calculated for triblocks of different compositions with overall degree of polymerization 120. The polymer architecture effect on $<R_g^2>$ was found to be qualitatively the same as that mentioned above, and was maximized for equimolar terpolymers.

Conclusions

The block sequence in ABC triblock terpolymers emerges as a new design parameter for tayloring polymer properties. In the present work it appears that the block sequence affects the solution behavior of ABC triblock terpolymers both in aggregating and in non-aggregating systems.

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