Synthesis of Poly(di[methylamine]ethyl methacrylate)-*b*-Poly(cyclohexyl methacrylate)-*b*-Poly(di[methylamine]ethyl methacrylate) Amphiphilic Triblock Copolymers by ATRP: Condensed-phase and Solution Properties

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ABSTRACT: The synthesis of amphiphilic triblock copolymers, poly(di[methylamine]ethyl methacrylate)-*b*-poly(cyclohexyl methacrylate)-*b*-poly(di[methylamine]ethyl methacrylate) PDMAE-*b*-PCH-*b*-PDMAE, has been performed by atom transfer radical polymerisation. Those have been obtained in a well-controlled manner in terms of molecular weight and polydispersity index. The triblock copolymer characterisation has been made in condensed state and in solution. The existence of microphase separation has been confirmed by differential scanning calorimetry. However, the domains of both inner and outer blocks seem not to be ordered for one another from small-angle X-ray scattering (SAXS) measurements using synchrotron radiation. The micelle formation in dilute methanol solutions has been confirmed for all triblock copolymers by dynamic light scattering analyses. The size of these micelles has been demonstrated to be dependent on the molecular weight. Similar observations have been made in concentrate methanol solutions by using SAXS experiments, pointed also out that an increment of the intermicelle interactions is produced as the concentration increases. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 85–92, 2008

Keywords: amphiphilic block copolymers; atom transfer radical polymerization; block copolymers; DLS; DSC; micelle formation; microphase separation; SAXS; self-organization

INTRODUCTION

It is well-known that atom transfer radical polymerisation (ATRP) is one of the most successful controlled radical polymerisation developed during recent years.^{1–8} This polymerisation can be initiated with different alkyl halides,^{5,6,9–13} sulfonfyl halides,^{14–17} and N-halides,^{18,19} diverse cat-

alyst/ligand systems,^{20–26} and can be carried out in organic and aqueous media^{5–14,27} as well as in carbon dioxide, ionic liquids, or other solvent of low volatility^{18,28,29} principally for styrene, meth (acrylate), and acrylonitrile monomers. Its success is due to the effective minimization of termination and chain transfer reactions, which allows developing a great variety of molecular architectures and functionalities with controlled molecular weights and low polydispersities.^{30–34} Among these, the block copolymers represent a type of materials with a growing interest because of their peculiarities.

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A block copolymer is a material that can adopt different morphologies, including spherical, cylindrical, and lamellar structures, in solution as well as in solid state. It is well demonstrated that the solution and bulk properties of these materials come together with their chain architecture.³⁵ They present unique properties in solution, their self-assembly capability,^{36–40} and for this particularity they can be applied as nanoreservoirs in controlled drug delivery, gene therapy, bioreactors, diagnostic tools, nonviral gene vectors, and phase transfer catalysis, as templates for the fabrication of nanostructured hybrids and nanoparticles and as reaction media for biocatalyst in liquid phase, and so forth.^{41–48}

Poly(cyclohexyl methacrylate) is a perfect component of coatings with similar thermal, optical, and permeability characteristics to poly(methyl methacrylate).⁴⁹ Its homopolymerization and block copolymerization by controlled radical polymerization have been recently reported.^{50–52} Poly(di[methylamino]ethyl methacrylate), PDMAE, is both thermoresponsive and pH sensitive. This homopolymer is a weak cationic polyelectrolyte, which is soluble in water at acidic or basic pH at ambient temperature. However, the polymer has a very low charge density and solubility at either basic or neutral pH due to hydrogen bonding. Under these conditions, the polymer possesses a LCST or cloud point at 32–52 °C again depending on the molecular weight,^{53–56} which gives to the polymer its pH and thermosensitive properties.

In this article the synthesis of poly(di[methylamine]ethyl methacrylate)-*b*-poly(cyclohexyl methacrylate)-*b*-poly(di[methylamine]ethyl methacrylate) PDMAE-*b*-PCH-*b*-PDMAE amphiphilic triblock copolymers by ATRP is described. The study of these well-controlled copolymers in condensed state is presented in terms of glass transition temperature analysis and morphological examination by small angle X-ray scattering employing synchrotron radiation. In addition, the solution properties in methanol of these amphiphilic copolymers are analysed by dynamic light scattering and also by small angle X-ray scattering measurements.

EXPERIMENTAL

Materials

Cyclohexyl methacrylate (CH) (>97%, Fluka) was passed through an alumina column prior to use. Di(methylamino)ethyl methacrylate (DMAE)

(Aldrich 98%), was used as received. N,N,N',N',N''-pentamethyldiethylenetriamine, PMDETA, (99%, Aldrich) was used as received. The difunctional initiator 1,2-Bis(bromoisobutyryloxy) ethane, BrIBE, was prepared according to Karanam et al.⁵⁷ Copper(I)bromide, CuBr, (Aldrich 98%) was purified according to the method of Keller and Wycoff.⁵⁸ Toluene (99.5%, Merck) was used as received.

Synthesis of PDMAE-*b*-PCH-*b*-PDMAE Amphiphilic Triblock Copolymers

Polymerisation of CH was carried out using BrIBE as a difunctional initiator in toluene solution 50% v/v at 40 °C. The [Monomer]/[Initiator]/[CuBr]/[Ligand] ratio was 200/1/1/1. Polymerisations were carried out using standard Schlenk technique under an atmosphere of nitrogen. BrIBE, PMDETA, CH, and toluene were placed in a Schlenk tube and the mixture deoxygenated by three freeze–pump–thaw cycles prior to addition of CuBr and three further vacuum–nitrogen cycles carried out. The reaction was immersed in a thermostated oil bath. The polymerisation was stopped at a desired reaction time, isolated by dilution in chloroform and passed through over alumina to remove the catalyst, then rotary-evaporated to eliminate the eluent. The solution was poured into a large excess of methanol, and finally the polymer is dried under vacuum until reaching constant weight. Afterwards, the amphiphilic triblock copolymers were performed by adding the second monomer DMAE in toluene solution (50% v/v) using CuBr and PMDETA as catalyst system in a ratio of 1/1. The [Monomer]/[Macroinitiator] relationship was 550/1. The samples were taken periodically from the mixture at suitable time periods and conversion measured using ¹H-NMR. The reaction mixtures were subsequently diluted with toluene prior to purification by passing through an alumina column. After concentration of the solution under reduced pressure the polymer was precipitated in petroleum ether and volatiles removed in vacuum. The triblock copolymers were labelled with the degree of polymerisation of each block.

Structural Polymer Characterisation

Size exclusion chromatography (SEC) to determine the molecular weight averages and the polydispersity index, PDI, was measured using a modular Polymer Laboratories system equipped with a PL Marathon autoinjector, a PL-gel 5 μm

($50 \times 75 \text{ mm}^2$) guard column, two PL-gel $5 \mu\text{m}$ ($300 \times 7.5 \text{ mm}^2$) mixed-C columns, and a differential refractive index detector, using chloroform/triethylamine 95:5 (v/v) as the eluent with a flow rate of 1.0 mL min^{-1} . Poly(MMA) standards (1.0×10^6 – 200 g mol^{-1}) were used to calibrate the SEC.

$^1\text{H-NMR}$ spectroscopy was used to estimate the monomer conversion. The spectra were recorded on a Bruker DPX300 spectrometer with polymer solutions in chloroform d_4 purchased from Scharlau.

Dynamic Light Scattering

Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer 3000 spectrometer with a 10 mW HeNe laser at $\lambda = 633 \text{ nm}$ with a 7132 correlator operating with 8×8 groups. All measurements were performed at a scattering angle of 90° and at 25°C . The solutions were prepared by dissolving the samples in previously filtered solvent ($0.2 \mu\text{m}$).

Specimen Preparation

Copolymer films were prepared by casting from 8% (w/v) toluene solution for small-angle X-ray scattering (SAXS) measurements in the condensed state. To further promote the formation of equilibrium morphologies, the bulk films were annealed under vacuum at 130°C during 72 h. The films were then cooled slowly to room temperature.

Glass Transition Temperatures

Differential scanning calorimetry (DSC) measurements were performed in a Perkin Elmer DSC/TA7DX, PC series with an intracooler for low temperatures. The temperature scale was calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples ($\sim 20 \text{ mg}$) weighed were scanned at 10°C/min under dry nitrogen ($20 \text{ cm}^3/\text{min}$). The first heating scan was performed after decreasing the temperature from room temperature to -45°C , then the sample was heated up to 130°C . Consecutively to the heating process, the sample was cooled down at the same rate and after that a new successive heating run was performed.

The actual value for the glass transition temperature, T_g , was estimated as the temperature at the midpoint of the line drawn between the temperature of intersection of the initial tangent

with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The quoted value is the average of several measurements on each sample.

X-Ray Scattering Measurements

The synchrotron studies were performed in the soft-condensed matter beamline A2 at HASYLAB (Hamburg, Germany), working at a wavelength of 0.150 nm . The experimental setup includes a heating chamber specimen holder, a MARCCD detector for acquiring two-dimensional SAXS patterns (sample-to-detector distance being 260 cm) and a linear detector for 1D WAXS measurements (distance 21 cm). All experiments comprise the heating of initially amorphous sample from 30 up to 185°C followed by a cooling and a later a heating run at 10°C/min . The acquiring data was done in frames of 30 s .

In solution, the conditions during the experiment are ensured by sealing the specimen between polyimide films “Kapton” and O-rings rubber seals inside typical screwed rectangular cell compartments designed for measurements of liquids. The experiment is checked by observation of constant intensity over the experiment and presence of liquid in the cell after the experiment ends, which indicates that the solution does not leak off the cell during the run.

RESULTS

The CH macroinitiator was prepared by ATRP using BrIBE as difunctional initiator in toluene solution 50% v/v at 40°C and with a $[\text{Monomer}]/[\text{Initiator}]/[\text{CuBr}]/[\text{Ligand}]$ ratio of $200/1/1/1$. These experimental conditions were chosen since polymers with a well-controlled structure were achieved in a previous work.⁵⁰ The synthesised macroinitiator has a $M_n = 16300$ and $M_w/M_n = 1.13$ (49.1% conversion).

The amphiphilic block copolymers with different outer lengths were prepared in 50% v/v toluene solution at 40°C , using a halide exchange macroinitiator/catalyst system ($[\text{DMAE}]:[\text{Br-PCH-Br}]:[\text{CuCl}]:[\text{PMDETA}] = 550:1:1:1$). Figure 1(a) displays the linear dependence of $\ln [M]_0/[M]$ with time for the reaction, which indicates a constant concentration of growing polymer radicals. The apparent propagation constant, k_p^{app} , is

Figure 1. (a) First-order kinetic plot for ATRP of DMAE using Br-PCH-Br as macroinitiator in 50% v/v toluene solutions at 40 °C. [DMAE]:[Br-PCH-Br]:[CuCl]:[PMDETA] = 550:1:1:1; (b) dependence of block copolymer number average molecular weight, M_n , determined by SEC on monomer conversion; (c) dependence of block copolymer polydispersities, M_w/M_n , on monomer conversion.

obtained from the slope, this being $6.38 \times 10^{-5} \text{ s}^{-1}$. This value is analogous to those obtained in other polymerisations.^{52,59,60} The M_n s increase linearly with conversion [Fig. 1(b)] and they are very similar to those ones theoretically predicted.

In addition, the PDIs remain narrow during the copolymerisation [Fig. 1(c)]. The amphiphilic triblock copolymer characteristics are collected in Table 1.

Condensed State Properties of the Triblock Copolymers

It is well-established that determination of the glass transition temperatures provides information about the processes of phase segregation in block copolymers. The thermal characterisation of the amphiphilic triblock copolymers was performed by DSC. The T_g s of the PDMAE-*b*-PCH-*b*-PDMAE amphiphilic triblock copolymers are also reported in the Table 1. The T_g of PCH macroinitiator was calculated for comparative purposes, acquiring a value of 92.0 °C. Besides, a PDMAE homopolymer with similar characteristics was measured ($M_n = 12,100$ and $M_w/M_n = 1.16$) reaching a T_g of 15.3 °C. This value is very similar those of 10.6 or 19 °C found in the literature for PDMAEMA polymerised by conventional radical polymerisation.^{61,62} The differences could be probably ascribed to the lower molecular weight, since it is well-established that glass transition temperature increases as molecular weight does up to reaching a constant value.⁶³

The thermograms of the PDMAE-*b*-PCH-*b*-PDMAE triblock copolymers as well as their corresponding homopolymers are represented in the Figure 2. It is possible to appreciate that only a glass transition temperature is observed, which corresponds to the PDMAE outer blocks. In this case, the DSC is not enough sensitive to distinguish the PCH glass transition temperature, T_{g1} , probably due to its relatively short length. However, the T_g existence of PDMAE blocks, T_{g2} , at close values to that obtained in a PDMAE homopolymer seems to indicate that phase separation takes place. The T_g of the PDMAE segments in the copolymers is moved slightly toward higher values. One of the reasons for this feature could be ascribed to the fact that phase separation between inner and outer blocks is not actually complete. A shift to lower temperatures is observed as length of the outer blocks increases, indicating better domain segregation. The existing microdomains can be randomly distributed or, in other cases, may form a regular arrangements and periodic structures that usually generate profiles in the small angle X-ray region. Therefore, the SAXS profiles analysis allows, if electron density contrast between blocks is high enough,

Table 1. Characteristics of PDMAE-*b*-PCH-*b*-PDMAE Amphiphilic Triblock Copolymers Synthesised by ATRP

Copolymers	Conv (%)	M_n	M_w/M_n	d_H	T_{g1} (°C)	T_{g2} (°C)
PDMAE ₄₂ - <i>b</i> -PCH ₉₇ - <i>b</i> -PDMAE ₄₂	19.4	29500	1.11	30.5	—	30.9
PDMAE ₁₁₄ - <i>b</i> -PCH ₉₇ - <i>b</i> -PDMAE ₁₁₄	30.2	52100	1.19	32.5	—	24.1
PDMAE ₁₂₁ - <i>b</i> -PCH ₉₇ - <i>b</i> -PDMAE ₁₂₁	41.8	54300	1.15	29.4	—	25.8
PDMAE ₁₃₇ - <i>b</i> -PCH ₉₇ - <i>b</i> -PDMAE ₁₃₇	58.1	59300	1.29	31.7	—	28.0
PDMAE ₁₈₂ - <i>b</i> -PCH ₉₇ - <i>b</i> -PDMAE ₁₈₂	69.8	73700	1.32	40.5	—	26.2
PDMAE ₂₁₂ - <i>b</i> -PCH ₉₇ - <i>b</i> -PDMAE ₂₁₂	81.0	83000	1.27	41.2	—	22.2

identifying the morphology developed. However, the films in solid state of these amphiphilic block copolymers do not exhibit any first-order peak in their SAXS profiles. This feature might be associated with a significant diffuseness of the phase boundaries due to a partial mixing of the incompatible chains at the interfaces, probably hindering a stronger phase separation between them at those critical regions. This larger interfacial thickness can be responsible of the lack of reflections.^{64,65} In addition, there is other important aspect that can reduce the ordering capability at large scale in these copolymers together with the just mentioned diffuseness of the phase boundaries. This is the polydispersity (see Table 1), although the values reached are quite low, they are higher than those that can be obtained through living anionic polymerisation. Therefore, differences in the macrochain length make difficult the development of ordered arrangements and longer annealing at temperature higher than glass transition temperature of the rigid block are often necessary to promote ordering, this being

even impossible sometimes.⁶⁵ However, the amphiphilic nature of these copolymers makes the existence of self-assembly more interesting in solution than in condensed matter.

Solution Properties of the Triblock Copolymers

The self-assembly capability of these amphiphilic block copolymers was studied in solution, using methanol as selective solvent good for the outer blocks and nonsolvent for the inner block since the copolymers are insoluble in water. The formation of micelles was examined in dilute solution by DLS using both Contin analysis or/and Cumulant method for data fitting. Hydrodynamic diameter was calculated according to the Stokes–Einstein equation $d_{H,app} = kT/3\pi\eta D_{app}$, where D_{app} is the apparent diffusion coefficient, η is the viscosity of the solution, T is the temperature, and k is the Boltzmann constant. DLS analysis of all triblock copolymer solutions in methanol at a copolymer concentration of 1 g L⁻¹ showed the presence of micellar aggregates with diameters ranging from 25 to 40 nm. As can be seen in Figure 3, the

Figure 2. DSC curves of PDMAE-*b*-PCH-*b*-PDMAE triblock copolymers and the corresponding homopolymers. **Figure 3.** Intensity fraction versus apparent hydrodynamic diameters for PDMAE-*b*-PCH-*b*-PDMAE triblock copolymers in methanol solution, 1 g L⁻¹.

Figure 4. SAXS profiles at different concentrations of triblock copolymers in methanol solutions: (a) PDMAE₄₂-*b*-PCH₉₇-*b*-PDMAE₄₂, (b) PDMAE₁₂₁-*b*-PCH₉₇-*b*-PDMAE₁₂₁, and (c) PDMAE₂₁₂-*b*-PCH₉₇-*b*-PDMAE₂₁₂.

diameters of the micelles are slightly dependent upon the length of the hydrophilic outer blocks. The size of the micelles in methanol is also reported in Table 1.

In addition, the system was studied at high concentrated solutions by small angle X-ray scattering using synchrotron radiation. The studies were performed with different concentrations ranging from 10 to 90 g L⁻¹. Figure 4 shows the SAXS profiles typical for micelle solutions for the copolymer with the smallest PDMAE₄₂-*b*-PCH₉₇-*b*-PDMAE₄₂, [Fig. 4(a)], intermediate PDMAE₁₂₁-*b*-PCH₉₇-*b*-PDMAE₁₂₁, [Fig. 4(b)], and the highest molecular weight PDMAE₂₁₂-*b*-PCH₉₇-*b*-PDMAE₂₁₂, [Fig. 4(c)]. It can be seen in the SAXS profiles that the overall scattering intensity increases as the copolymer concentration does independently of outer block PDMAE length due to the growing number of micelles in the scattering volume as well as the first order becomes noticeable. This peak is related to the interparticle interactions and gets more pronounced at higher concentration. Moreover, it is shifted to higher values of *q* with increasing concentration since the distance between particles becomes smaller and a shoulder starts to appear overlapped to the main peak. Therefore, it seems that the short-range interdomain order grows with concentration and long-range order becomes evident.

On the other hand the effect of the length within the outer PDMAE blocks at a given concentration is represented in Figure 5. It shows that the first order peak is shifted to lower-*q* values with raising the PDMAE molecular weight within the blocks, in agreement with the previous

observations.⁶⁶ In general terms, the small angle scattering intensity *I*(*q*) of a solution of micelles can be written as the product of the number density of particles, the intraparticle form factor *F*(*q*) and the interparticle structural factor *S*(*q*). In very dilute solution, only the form factor need to be considered and the profile can be modelled to provide information on micelle size and shape. However, the micellar interactions must be taken into account for higher concentrations through the structural factor, giving information of the micellar radius and the micellar volume fraction.⁴⁷ There are complicated models in the literature to fit the experimental data, being the simplest one,

Figure 5. SAXS profiles of PDMAE-*b*-PCH-*b*-PDMAE triblock copolymers at a given concentration in a methanol solution (60 g L⁻¹).

the hard sphere model.⁶⁷ Hence, in a further work, the entire analysis of micelle formation with concentration and temperature will be performed by SAXS.

In summary, well-controlled amphiphilic triblock copolymers, PDMAE-*b*-PCH-*b*-PDMAE, have been synthesised by atom transfer radical polymerization. The existence of microphase separation of amphiphilic triblock copolymers has been confirmed by DSC. SAXS studies using synchrotron radiation of block copolymers in condensed state have demonstrated that none ordered morphology is developed under the annealing experimental conditions imposed probably due to diffuseness of the phase boundaries and polydispersity (see Table 1). On the other hand, dynamic light scattering analyses have confirmed the micelle formation for all triblock copolymers in dilute methanol solutions. The size of these micelles has been confirmed to be dependent on the outer PDMAE molecular weight. Also the micelle formation in concentrate methanol solutions has been confirmed by SAXS experiments using synchrotron radiation, observing a clear increment of the intermicelle interactions as the concentration increases.

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