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A Novel Amphiphilic Double-[60]Fullerene-Capped Triblock Copolymer

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Introduction

Since its discovery in 1985, [60]fullerene (C_{60}) has been a subject of intense research due to its unique structure, interesting properties, and many potential applications.[1−4] However, poor solubility and processability are among the main obstacles which severely hinder the potential utilization of fullerene-containing materials. C_{60} polymeric materials are generally prepared by incorporating C_{60} into the backbone of polymer chains or by attaching C_{60} onto tailor-made functional polymers.[5−21] Manolova et al.[5] synthesized PEO-C_{60} with an amino-functional PEO precursor. Weis et al.[6] prepared polystyrene-modified C_{60} by reacting C_{60} with polystyrene possessing amino groups. C_{60}-containing polystyrene was also prepared by reacting polystyryl radical with C_{60}.[7,8]

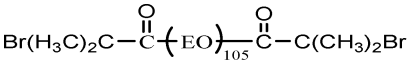
More recently, well-defined C_{60}-containing polymers have been synthesized via atom transfer radical polymerization (ATRP). ATRP[22] is a convenient technique to prepare polymers with low polydispersity and end-capped with functional groups. Typically, the end group is either bromine or chlorine which can be coupled to C_{60} directly[9] or via azido addition.[23,24] Li et al.[9] prepared PSt-C_{60} and PMMA-C_{60}, and Tam et al.[10−12] synthesized PDMAEMA-C_{60}, PtBMA-C_{60}, and PMAA-C_{60} via the ATRP technique. Particular interests are directed toward C_{60}-capped amphiphilic copolymers which self-assembled into various types of aggregates. Song et al.[25] reported the aggregation behavior of single- and double-C_{60}-end-capped poly(ethylene oxide) (PEO) in THF and in aqueous solutions. The structure of the aggregates varies, depending on the type of solvent and the chain length of PEO. The double-C_{60}-end-capped PEO (453 EO units) aggregates into simple spherical micelles in THF, but in aqueous solution, only the network structure was observed. On the other hand, single-C_{60}-capped poly(2-(dimethylamino)ethyl methacrylate)s (C_{60}-*b*-PDMAEMA)s were reported to form simple micelles in aqueous solution from dynamic light scattering studies.[10] However, two decay modes with comparable proportions were detected in the decay time distribution function, indicating a substantial proportion of unimers was in coexistence with micelles in the solution. The micellar size was ∼55 nm. No aggregation number and no static light scattering data were presented.

In this paper, we report the synthesis of a new amphiphilic ABA triblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-*block*-poly(ethylene oxide)-*block*-poly(2-(dimethylamino)ethyl methacrylate) capped with C_{60} at both ends (C_{60}-DMAEMA$_{60}$-*b*-EO$_{105}$-*b*-DMAEMA$_{60}$-C_{60}). The triblock copolymer form simple spherical micelles in aqueous solution, with only one decay mode observed in dynamic light scattering studies.

Experimental Section

Materials. C_{60} (99.5%) was obtained from SES Research. Poly(ethylene glycol) (PEO: M_n 4600, PDI 1.06), 2-bromoisobutyryl bromide (99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%), copper(I) chloride (CuCl, 99.5%), and sodium azide (99%) were purchased from Aldrich. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%) was purchased from Acros.

Synthesis. *Synthesis of Macroinitiator* (**I**). The macroinitiator was prepared according to the method described by Jankova et al.[26] To a 50 mL round-bottomed flask containing THF solution (20 mL), PEO (M_n = 4600, PDI = 1.06) (0.5395 mmol), triethylamine (0.45 mL), and THF solution containing 3.24 mmol of 2-bromoisobutyryl bromide (10 mL) were added dropwise at 0 °C. The mixture was allowed to react at 25 °C overnight. The volume of the solution was then reduced to about 2 mL. **I** was obtained by precipitation into 20-fold ether, followed by filtration, washed by ether, and dried under vacuum overnight. The yield was 2.51 g (93.1 wt %). ^{1}H NMR in $CDCl_3$ (ppm): 4.35 (t) ($-OCH_2C\mathbf{H}_2-OC{=}O$), 3.66 (s) ($(-OC\mathbf{H}_2C\mathbf{H}_2-)_n$), 1.97(s) ($-C\mathbf{H}_3$).



$$\mathrm{Br(H_3C)_2C-\overset{\overset{\displaystyle O}{\|}}{C}\!\left(EO\right)_{105}\overset{\overset{\displaystyle O}{\|}}{C}-C(CH_3)_2Br}$$

(I)

Synthesis of Br-DMAEMA$_{60}$-b-EO$_{105}$-b-DMAEMA$_{60}$-Br (**II**). A 25 mL Schlenk flask was charged with **I** (0.50 g), DMAEMA (2.246 g), CuCl (20.2 mg), HMTETA (55.5 mL), and methanol (2.0 mL) according to the procedure for the ATRP of DMAEMA reported earlier.[27] Sealed with a rubber septum, the flask was degassed with three freeze−pump−thaw cycles. Then the ligand HMTETA was injected by an argon-purged syringe. The mixture was allowed to react at room temperature for 3.5 h before the reaction was stopped by the addition of 20 mL of THF. The solution was then filtered through a basic alumina column to remove the catalyst. The filtrate was concentrated to ∼2 mL. The triblock polymer **II** was obtained by precipitating the concentrated solution into 20-fold hexane. The product was isolated and dried in a vacuum. The yield was 2.35 g (85.5 wt %); M_n = 23 700 and PDI = 1.20 (from GPC). ^{1}H NMR in $CDCl_3$ (ppm): 4.05 (s,b) ($-COOC\mathbf{H}_2$-$CH_2N\langle$), 3.66 (s) ($(-OC\mathbf{H}_2C\mathbf{H}_2-)_n$), 2.60 (s,b) ($\rangle NC\mathbf{H}_2-$), 2.40 (s) ($\rangle NC\mathbf{H}_3$), 1.80−2.0 (m) ($-C\mathbf{H}_2CCH_3$), and 0.8−1.1 (m) ($-CH_2CC\mathbf{H}_3$).

Synthesis of N$_3$-DMAEMA$_{60}$-b-EO$_{105}$-b-DMAEMA$_{60}$-N$_3$ (**III**). **II** (1.85 g) was placed in a 50 mL round-bottomed flask, and 5 mL of DMF solution containing 14.0 mg of NaN_3 was added. The solution was allowed to react with stirring at 25 °C overnight. The solvent was then removed almost completely under reduced pressure, and the residue was redissolved in 10 mL of THF. The solution was filtered, and the filtrate was concentrated to ∼2 mL. The concentrated solution was added to 20-fold hexane for precipitation. The precipitate was filtered,

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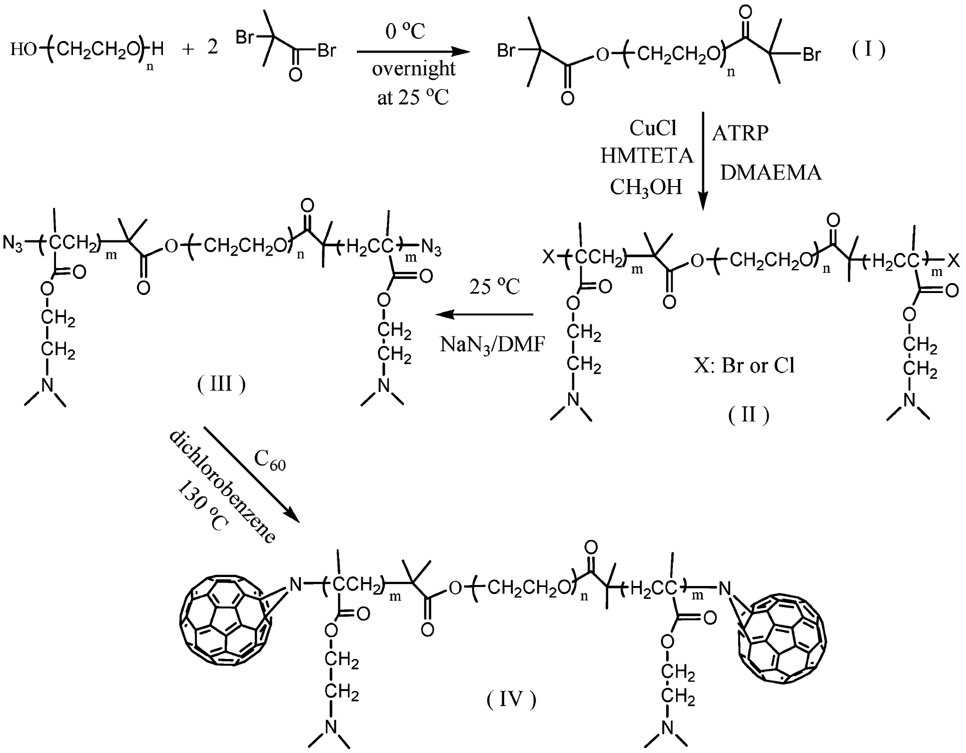
Scheme 1. Synthetic Route of C_{60}-DMAEMA$_{60}$-*b*-EO$_{105}$-*b*-DMAEMA$_{60}$-C_{60}



washed by hexane, and dried under vacuum at 25 °C. The yield was 1.54 g (83.2 wt %). The ^{1}H NMR spectrum in $CDCl_3$ was almost identical to that of **II**.

Synthesis of C_{60}-DMAEMA$_{60}$-b-EO$_{105}$-b-DMAEMA$_{60}$-C_{60} (**IV**). A 50 mL round-bottomed flask equipped with a spiral condenser was charged with **III** (1.22 g), C_{60} (109.8 mg), and 1,2-dichlorobenzene (10 mL). The flask was immersed in an oil bath maintained at 130 °C under an argon atmosphere. After refluxing for 48 h, the solvent was removed by rotary evaporation. THF (5 mL) was then added, and the excess C_{60}, which was not soluble, was separated by centrifugation. The supernatant was withdrawn and precipitated into 20-fold hexane. The brownish product **IV** was filtered, washed, and dried in a vacuum at 60 °C. The yield was 1.17 g (88.0 wt %); $M_n = 25\,800$ and PDI = 1.28 (from GPC). The ^{1}H NMR spectrum in $CDCl_3$ was almost identical to that of **II**.

Results and Discussion

Synthesis of C_{60}-DMAEMA$_{60}$-*b*-EO$_{105}$-*b*-DMAEMA$_{60}$-C_{60}. The synthetic route for the C_{60}-containing triblock polymer is shown in Scheme 1. The triblock polymer **II** was first synthesized via ATRP using macroinitiator **I**. The GPC curves show smooth increment of molar mass with reaction time (Figure S1, Supporting Information). The reaction reached 85.5 wt % conversion after 3.5 h, at which point $M_n = 23\,700$ and PDI = 1.20. After cycloaddition to C_{60}, a slight broadening of the GPC curve was observed. The PDI value also increased slightly to 1.28. A similar phenomenon was observed in the synthesis of PSt-C_{60}.[23] The ^{1}H NMR spectrum of **IV** is shown in Figure 1. The M_n value of PEO was calculated from the proton peak intensity ratio of $-C\mathbf{H}_2C\mathbf{H}_2O-$ to that of $Br(C\mathbf{H}_3)_2COO-$ in **I**. On the basis of the M_n value of PEO, the M_n values of **II** and **IV** were similarly calculated from the peak intensity ratio of PEO to $\rangle NC\mathbf{H}_2-$ of DMAEMA. The M_n values obtained from GPC agreed reasonably well with those from NMR analysis (Table 1). In the conversion reaction from **II** to **III**, 50 mol % excess of NaN_3 was used in order to drive the reaction to almost full completion. The clear IR absorption band at 2030 cm^{-1} of the azide group of **III** disappeared after cycloaddition to C_{60} (Figure S2, Supporting Information). To maximize azido-addition to C_{60}, 50 mol % C_{60} in excess was employed. Prato et al. have shown that even with an equimolar of C_{60}, multiaddition to C_{60} was not observed.[13] Compared to the aqueous solution of **II**, which was transparent up to wavelength ~320 nm, the absorption of **IV** was found extending to longer wavelength with clear absorption maxima, occurring at 330 nm in THF solution and 340 nm in aqueous solutions (Figure S3, Supporting Information). The results strongly suggest that monocycloaddition of C_{60} had occurred, as C_{60} in cyclohexane and hexane solutions,[10,17] PEO-C_{60}[17] in THF and PSt-C_{60}[23] in CH_2Cl_2 also showing similar absorption properties with maxima at ~330 nm. The linking of C_{60} to the polymer chain was further confirmed by the similarity of the GPC traces recorded using RI and UV detectors at λ 330 nm (Figure S4), a wavelength where C_{60} has an absorption maximum[10,17] and the polymer does not absorb.

TGA Analysis. In the decomposition thermograms (obtained under a nitrogen atmosphere) of poly(DMAEMA)$_{125}$, which was synthesized via ATRP as previously described,[27] **II** and **IV** exhibited a distinct decomposition step which occurred at around 350 °C. At this temperature, PEO had not yet decomposed (Figure S5, Supporting Information). On the basis of the percent weight change, the first decomposition steps of b−d have been identified to be due to losses of $-CH_2CH_2N(CH_3)_2$ fragments. The percent weight loss agrees reasonably well with the calculated values based on the molecular formulas of the three polymers (Table 2). At temperature ~460 °C, PEO decomposed completely, but residue masses were observed for all the three polymers studied. The residues are attributed to

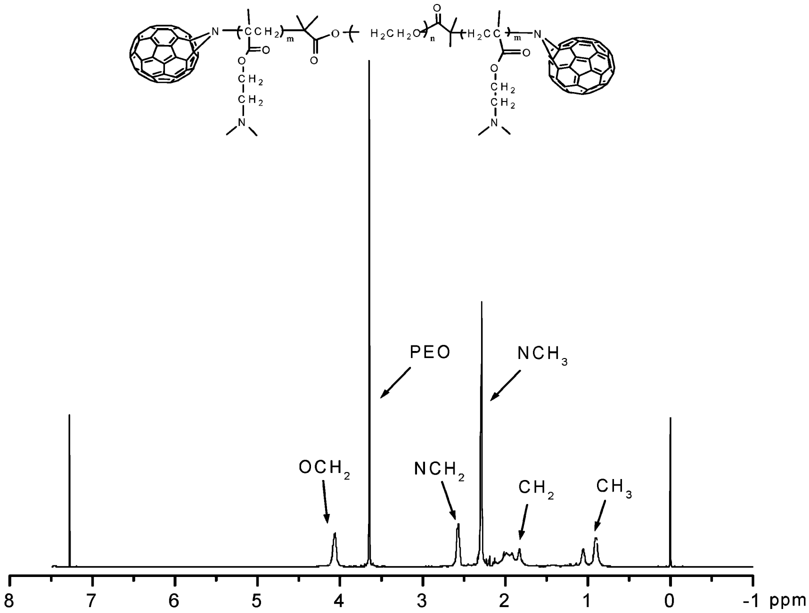
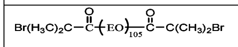


Figure 1. ^{1}H NMR spectrum of **IV** in $CDCl_3$.

Table 1. M_n and PDI Values of the Macroinitiator and Triblock Copolymers II and IV

	M_n (GPC)	M_n (NMR)	PDI
 $Br(H_3C)_2C-\overset{O}{\overset{\|}{C}}-(EO)_{105}-\overset{O}{\overset{\|}{C}}-C(CH_3)_2Br$	6000	4760	1.06
Br-DMAEMA$_{60}$-*b*-EO$_{105}$-*b*-DMAEMA$_{60}$-Br(II)	23700	23300	1.19
C_{60}-DMAEMA$_{60}$-*b*-EO$_{105}$-*b*-DMAEMA$_{60}$-C_{60}(IV)	25300	22800 (excluding C_{60})	1.28

the formation of cross-linked materials which were thermally stable at this temperature range. As C_{60} is thermally stable up to 600 °C,[17] the percent weight of C_{60} in **IV** can be calculated by subtracting the residue mass of **II** from the mass remaining at the corresponding second inflection point **IV** at 471.4 °C. The procedure is based on the assumption that, other than C_{60}, the residue masses of **II** and **IV** are the same as they have identical chemical compositions. The percent weight of C_{60} thus obtained was 5.37, agreeing reasonably well with the calculated value of 5.69% weight based on the chemical formula of **IV**.

Lower Critical Solution Temperature (LCST). Poly(DMAEMA) is a thermal sensitive polymer which exhibits LCST (at ~45 °C)[10] in unbuffered distilled water. The C_{60}-capped triblock copolymer **IV** also showed the thermal chain-to-globule transition phenomenon. The plot of percent transmittance measured at $\lambda = 750$ nm as a function temperature for a 4.0 mg mL^{-1} solution of **IV** is shown in Figure 2. The LCST obtained from the first derivative of the plot is 56.0 °C, which is considerably higher than that of poly(DMAEMA)$_{125}$. Evidently, the presence of PEO block and the effect of micellization, the incorporation of C_{60}, had caused the **IV** to shift to a higher value. It could also be caused by the differences in the concentration of DMAEMA units in the two polymers. It is known that the LCST of pH-sensitive poly(DMAEMA) is dependent on the concentration and molecular weight.[28] Interestingly, without the PEO block, poly(DMAEMA) (molar mass of 18 000) coupled with C_{60} at one end was found to have a LCST value almost identical to that without the C_{60}.[10]

Surface Tension Measurements. The triblock copolymer **IV** readily forms micelles in aqueous solution. The critical micelle concentration (cmc) was determined from the plot of surface tension against concentration of **IV** (Figure S6, Supporting Information), yielding cmc $= 2.1 \times 10^{-3}$ g dm^{-3} and $\gamma_{cmc} = 53$ mN m^{-1}.

Dynamic Light Scattering. From dynamic light scattering (DLS), the translational diffusion coefficients, D, can be determined. If the Stokes−Einstein equation is used, the apparent hydrodynamic radius, R_h, can be calculated using the following equation:

$$R_h = \frac{kT}{6\pi\eta D}$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

The relaxation time distribution function of **IV** in aqueous solution at different scattering angles showed that only one decay mode was observed in the decay time distribution (Figure S7, Supporting Information). The peak relaxation time shifted to lower value with increasing angle, suggesting that only one type of particle was present. The relaxation rate Γ is linearly related to the square of the scattering vector (q^2) (Figure S8, Supporting Information), confirming that the decay mode is due to the translational diffusion of the scattering object. The relaxation time distribution was found to be only slightly dependent on the concentration, implying that **IV** aggregated according to the closed-model association mechanism, which predicts a near-concentration-independent R_h. The intercept of the plot of D vs the concentration of **IV** yields $D_0 = 2.23 \times 10^{-12}$ m^2 s^{-1} (Figure S9, Supporting Information). The hydrodynamic radius R_h of the micelles calculated from the Stokes−Einstein equation is 109 nm. Thus, R_g/R_h is 1.03, indicating a core−shell structure of **IV**.

Static Light Scattering (SLS). From the static light scattering experiments, the weight-average molecular weight (M_w), the second virial coefficient (A_2), and the z-average radius of gyration (R_g) could be obtained using the Zimm plot relationship (see Supporting Information).

Table 2. Percent Weight Remaining of TGA of Three Polymers

polymers	*T* at 1st inflection point (°C)	wt % remaining	*T* at 2nd inflection point (°C)	wt % remaining	wt % of C_{60}
PDMAEMA	351.1	53.01 (54.20)[a]	475.3	6.13	
II	345.5	62.23 (63.09)[a]	465.7	4.64	
IV	351.1	64.25 (65.15)[a]	471.4	10.72	5.37 (5.69)[b]

[a] Calculated based on loss of $-CH_2CH_2N(CH_3)_2$. [b] Calculated based on the chemical formula of **IV**.

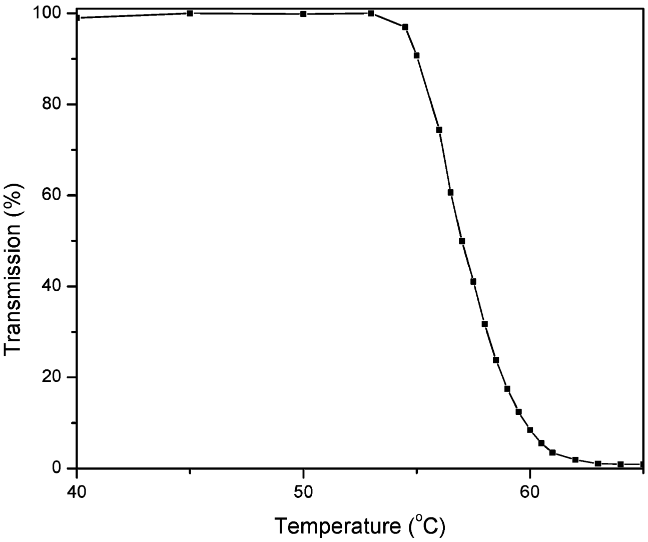
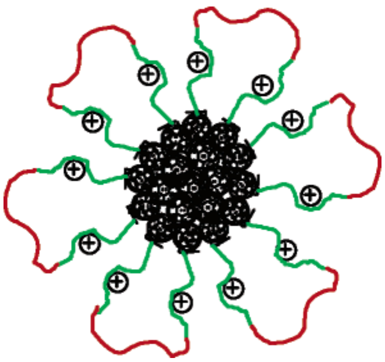


Figure 2. Plot of percent transmittance as a function of temperature of 4 mg mL^{-1} aqueous solution of **IV**. The reference solution is **IV** with same concentration at 25 °C.

Scheme 2. Micellar Structure of IV in Aqueous Solution



For the aqueous solution of **IV**, d*n*/d*C* = 0.1782 mL g^{-1}. From the Zimm plot, $M_w = 7.6 \times 10^5$ g mol^{-1}, $A_2 = 3.0 \times 10^{-4}$ cm^3 mol g^{-2}, and $R_g = 112$ nm were obtained (Figure S10, Supporting Information). From M_w, the aggregation number was calculated to be ~30. The small aggregate number of 30 suggests that the double-end-capped-C_{60} triblock polymer **IV** forms micellar aggregates, induced by the hydrophobic C_{60} at the two chain ends. As PEO at the center block is hydrophilic and poly(DMAEMA) is partially protonated under the experiment conditions, the aggregates of **IV** are proposed to have a micellar structure as depicted in Scheme 2. The relatively large R_h value suggests that the corona is highly stretched caused by the positively charged DMAEMA segments. AFM micrograph confirms the radius of the micelle particles to be ~100 nm (Figure S11), agreeing well with that determined from the laser light scattering studies. The TEM image reveals that indeed the micelles have small core with diameter of ~15 nm (Figure S12). The results demonstrated for the first time that well-defined core−shell micelles from a double-C_{60}-end-capped block copolymer could be obtained in aqueous solution.

Conclusion

A well-defined water-soluble ABA triblock polymer, (Br)Cl-DMAEMA$_{60}$-*b*-EO$_{105}$-*b*-DMAEMA$_{60}$-Cl(Br), was successfully synthesized via ATRP. C_{60} was successfully incorporated at both ends of the polymer chain via azido cycloaddition. TGA and spectrophotometric analysis confirmed monoaddition to C_{60} had occurred. In aqueous solution, **IV** aggregates to form flower micelles. The low cmc value of 2.1 mg dm^{-3} suggests that the micelles could potentially be used as carriers for drug/gene delivery application. The formation of micelles was supported by surface tension, static light scattering, and AFM studies.

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Supporting Information Available: Experimental details, Zimm plot relationship, and Figures S1−S12. This material is available free of charge via the Internet at http://pubs.acs.org.

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