

Synthesis and Micellization Behavior of Amphiphilic Graft Copolymer with 1-Octene as Hydrophobic Moiety

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ABSTRACT: Two new kinds of amphiphilic copolymers were synthesized in this work. Poly(1-octene-co-acrylic acid) copolymers were prepared through the copolymerization of 1-octene and *tert*-butyl acrylate, and the hydrolysis of *tert*-butyl acrylate units. Poly(1-octene-co-acrylic acid)-*g*-poly(ethylene glycol) copolymers were obtained from the esterification reaction between poly(1-octene-co-acrylic acid) and poly(ethylene glycol) monomethyl ether. They were characterized by means of ¹H-NMR, ¹³C-NMR, GPC, and FTIR.

These amphiphilic copolymers can form stable micelles in aqueous solutions. The critical micelle concentration was determined by fluorescence spectroscopy. The micellar morphology and size distribution were investigated by transmission electron microscopy and dynamic light scattering. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2423–2431, 2010

Key words: amphiphilic copolymer; micellization; copolymerization; micelles

INTRODUCTION

The copolymerization of α -olefins with polar vinyl monomers remains an area of great interest because the incorporation of functional groups can greatly enhance the properties of polyolefins.¹ Since the direct copolymerization of olefins with functional vinyl monomers by Ziegler-Natta or metallocene catalysts suffers significantly from reduced catalyst activity and polymer molecular weight as a result of deactivation effects of the functional groups,² many efforts are devoted to discovering new catalysts that can tolerate polar groups. The development of late transition metal complexes is a promising area of research, since these complexes are typically less oxophilic, and thus more functional-group tolerant than early transition metals. The copolymerization of ethylene and higher α -olefins with acrylates and vinyl ketones using Pd-based diimine catalyst was reported, however, a maximum incorporation of 12% methyl acrylate in the copolymer was achieved.^{3–6} Grubbs has also discovered a catalyst based on neutral nickel compounds which is able to

polymerize functionalized alkenes.⁷ Other late-transition-metal-based complexes are also used as catalysts for the functionalization of polyolefins. Related work in this field is summarized in recently published reviews.^{1,2} Although catalyst systems showing excellent behavior for both olefins and polar monomers have been discovered, the polymerization mechanism is not well-established. Recently, Novak⁸ brought forward that olefins can copolymerize with vinyl monomers via a free radical mechanism in the presence of neutral palladium complexes. Subsequently, the copolymerization of α -olefins with methyl acrylate⁹ and methyl methacrylate¹⁰ under conventional free radical polymerization and atom transfer radical polymerization was reported. In this work, our objective is to synthesize a novel amphiphilic graft copolymer containing polyolefin segments in the hydrophobic part. Poly(1-octene-co-*tert*-butyl acrylate) as the precursor is expected to be prepared through free radical polymerization using AIBN as initiator. Since free radical polymerization has a long history of commercial application and scientific investigation, this process is expected to be easily and efficiently industrialized.

The micellization behaviors of amphiphilic copolymers with hydrophobic and hydrophilic chains have been investigated extensively both in aqueous media and in nonpolar solvents. A well-known and systematically-studied example is poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) system. This work was mainly done by Eisenberg research group. They found that different morphologies, for example, sphere, rod,

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vesicle, large compound micelle, were influenced by many variables, such as the composition of copolymer, copolymer concentration, type of common solvent, and temperature.^{11–15} The precise control of micelle morphology is the key issue in practical application. Studies in this field are of great importance and interests. In contrast, much less attention is paid to the self-assembly of amphiphilic copolymers with polyolefin segments in the hydrophobic part. Chung and coworkers synthesized polyolefin-*b*-poly(ϵ -caprolactone)¹⁶ and poly(α -olefin)-*b*-poly(ethylene oxide)¹⁷ and explored their application as polymeric compatibilizers. Dieter Richter et al. prepared poly[ethylene-*co*-propylene-*b*-(ethylene oxide)] copolymers and preliminarily studied their solubility in water and *n*-decane.¹⁸ These authors focused most of their attention on the synthesis and characterization of amphiphilic copolymers, and very few efforts was given to study on their micellization behaviors.

In our previous work,^{19,20} we have synthesized a new kind of amphiphilic graft copolymers, poly(1-dodecene-*co*-*para*-methylstyrene (*pMS*))-*graft*-poly(ethylene glycol) (PEG) by a different reaction route. A limitation of that route is, the PEG content of the synthesized copolymers are all below 30 wt %. Because of their high content of hydrophobic units, they cannot dissolve in water. Therefore, we studied their micellization behavior in *n*-octane. Meanwhile, our attempt to prepare that kind of amphiphilic copolymers with high PEG content still continues.

In this article, a new route to synthesize a similar kind of amphiphilic copolymers consisting of hydrophobic 1-octene segments and high content of hydrophilic poly(ethylene glycol) chains is explored. The synthetic procedure includes three steps, (i) the copolymerization of 1-octene and *tert*-butyl acrylate, (ii) the hydrolysis of *t*-butyl acrylate units, (iii) esterification reaction between the hydroxyl of poly(ethylene glycol) monomethyl ether and carboxyl of poly(1-octene-*co*-AA). Interestingly, the intermediate, poly(1-octene-*co*-AA) copolymers, are also amphiphilic. Therefore, the micellization behaviors of both poly(1-octene-*co*-AA) and poly(1-octene-*co*-AA)-*g*-PEG copolymers will be investigated, including CMC determination, micellar morphologies and sizes.

EXPERIMENTAL

Materials

Tert-butyl acrylate (Alfa Aesar, Beijing, China, 99%, *tBA*) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over CaCl₂ and distilled twice over CaH₂ under reduced pressure just before use. 1-octene (Acros, Shanghai, China, 99+%, abbreviated as Oct)

was distilled and stored over molecular sieves. *N,N*-azobisisobutyronitrile (Fluka, Shanghai, China, 98+%, AIBN) was recrystallized twice from ethanol before use. Toluene and tetrahydrofuran (THF) as solvents were distilled over sodium/benzophenone ketyl under dry N₂ atmosphere before use. Trifluoroacetic acid (Alfa Aesar, 99%), *N,N'*-dicyclohexyl carbodiimide (Alfa Aesar, 99%, DCC), 4-dimethylaminopyridine (Alfa Aesar, 99%, DMAP), poly(ethylene glycol) monomethyl ether (Alfa Aesar, PEG, $M_n = 350 \text{ g mol}^{-1}$) and pyrene were used as received. Dialysis tubing (Benzoylated cellulose) (MWCO = 1200) was purchased from Sigma-Aldrich Co. (Shanghai, China).

Measurements

FTIR spectra were performed on a Vector 22 Bruker spectrometer. NMR spectra were recorded on a Varian Mercury 300 Plus (300 MHz) instrument at room temperature. Molecular weight and polydispersity index (PDI) were measured with gel permeation chromatography on a PL-GPC220 at 40°C with THF as eluent with a 1.0 mL min⁻¹ flow rate. Three PLgel (10 μm) mixed B columns (7.5 mm \times 300 mm) were used. The system was calibrated with narrow dispersity polystyrene standards. Fluorescence spectra were recorded at ambient temperature using Perkin Elmer LS55 Luminescence spectrofluorimeter. The excitation wavelength used for emission spectra was 339 nm. The widths of slits were chosen to be 5 nm and 5 nm for excitation and emission, respectively. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1230 electron microscopy operating at an acceleration voltage of 80 kV. A drop of micelle solution was placed onto a 200-mesh copper grid coated with a thin film of carbon. The solvent was evaporated at room temperature under atmospheric pressure for 24 h. After that, the grids were negatively stained by 2 wt % phosphor-tungstic acid. The hydrodynamic diameter and size distribution of micelles were determined by dynamic light scattering using a Brookhaven 90 Plus particle size analyzer. The scattered light of a vertically polarized He-Ne laser (632.8 nm) was measured at an angle of 90° and was collected on an autocorrelator. Each analysis lasted for 3 min and performed at 25°C. Before the light scattering measurements the sample solutions were filtered using Millipore Teflon filter with a pore size of 0.45 μm .

Copolymerization of 1-octene and *tBA*

A typical polymerization was carried out in a 100 mL round-bottom flask connected to a standard Schlenk line and equipped with a magnetic stirrer. The flask was evacuated and filled with nitrogen

three times. Toluene (20 mL), Oct (5.46 g, 48.7 mmol), *t*BA (2.08 g, 16.2 mmol) and AIBN (20 mg, 0.12 mmol) were accurately weighed and transferred to the flask. Then the flask was immersed in a thermostated oil bath maintained at 80°C. The reaction started under N₂ atmosphere and lasted for 19 h. The reaction product was washed by methanol. Since the unreacted *t*-butyl acrylate and trace amount of homo-poly(*t*-butyl acrylate) can dissolve in methanol, they were removed in this treatment. The poly(Oct-*co-t*BA) was precipitated and then dried in vacuum over night.

Hydrolysis of poly(Oct-*co-t*BA)

Poly(Oct-*co-t*BA) (2 g) was dissolved in anhydrous THF (60 mL) and then a fivefold molar excess (with respect to the ester groups in the copolymer) of trifluoroacetic acid (4.35 mL, 58.5 mmol) was added. The mixture was heated to boiling temperature and refluxed for 48 h. Finally, the solvent and CF₃COOH were removed by rotary evaporation. Traces of CF₃COOH in the copolymer were removed by vacuum drying at 40°C overnight.

Polyesterification reaction

Poly(Oct-*co-AA*) (1.8 g, 16.5 mmol AA units) and PEG (5.78 g, 16.5 mmol) were dissolved in 50 mL anhydrous THF in a sealed flask. Then DCC (3.41 g, 16.5 mmol) and DMAP (0.2 g, 1.65 mmol) were added to the solution under stirring. The reaction was continued for 72 h at room temperature. The precipitated DCC urea was removed by filtration. The product was precipitated in *n*-hexane to remove the excess DCC. The crude product was collected and dried under vacuum at 40°C. Unreacted PEG was removed by dialysis method. The crude product was firstly dissolved in THF at 50°C. After cooled to room temperature, the solution was transferred to a dialysis tube (MWCO = 1200) to remove the unreacted PEG. After purification, the solvent was removed by rotary evaporation, and the final product was dried under vacuum overnight.

Preparation of micelles

The modified dialysis method of Zhang and Eisenberg¹¹ was used in this article to prepare micelle solutions. Typically, the amphiphilic graft copolymers were firstly dissolved in THF, a common solvent for both 1-octene segments and PEG chains, to obtain homogeneous solutions. Subsequently, deionized water was added to polymer/THF solutions at a rate of 1 drop every 10s with vigorous stirring. The addition of water was continued until the water content reached 20–30 wt % depending on the composi-

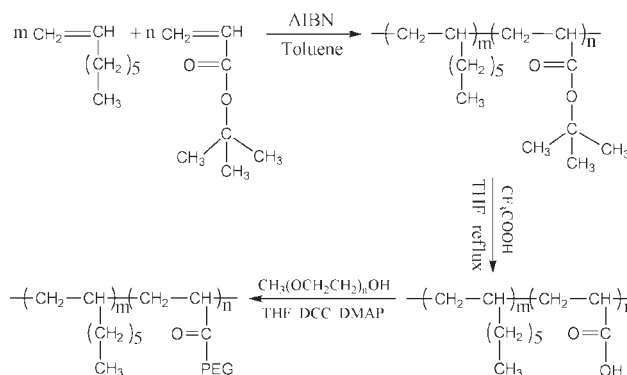


Figure 1 The synthetic process of amphiphilic copolymers.

tion of the graft copolymer. The resulting solutions were transferred to dialysis tubes (MWCO = 1200) and dialyzed against deionized water for 48 h to remove the organic solvent. After dialysis, the solutions were transferred to volumetric flasks, then a certain volume of deionized water was used to wash the dialysis bags and added to the flasks to make the final concentration of micelle solutions at $1 \times 10^{-4} \text{ g mL}^{-1}$.

Determination of critical micelle concentration

Sample solutions for fluorescence investigation were prepared as described previously.²¹ Briefly, a known amount of pyrene in acetone was added to each of a series of empty 10 mL flasks, and the acetone was evaporated under a flow of N₂ gas. A total of 10 mL graft copolymer aqueous solution of various concentration (from $4 \times 10^{-6} \text{ g mL}^{-1}$ to $3 \times 10^{-4} \text{ g mL}^{-1}$) was added to each flask. The final concentration of pyrene was $6 \times 10^{-7} \text{ mol L}^{-1}$, slightly below the saturation concentration of pyrene in water (2–3 μM). The flasks were heated with stirring overnight to equilibrate the pyrene and the micelle, and left to cool to room temperature.

RESULTS AND DISCUSSION

The whole synthetic route by combination of copolymerization, hydrolysis and esterification was illustrated in Figure 1. The detailed studies are discussed below.

Synthesis of poly(Oct-*co-t*BA)

1-Octene cannot homopolymerize via a free radical mechanism due to the fact that α -olefins undergo degradative chain transfer of allylic hydrogens.²² Fortunately, α -olefins does copolymerize with methyl acrylate and methyl methacrylate resulting in greater than 20% incorporation of α -olefins in the copolymers. The present article deals with the

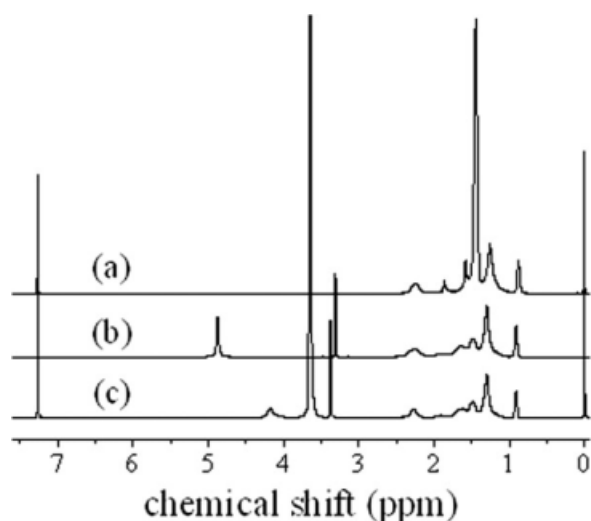


Figure 2 ^1H -NMR spectra of copolymers, (a) poly(Oct-*co*-*t*BA) in CDCl_3 , (b) poly(Oct-*co*-AA) in CD_3OD and (c) poly(Oct-*co*-AA)-*g*-PEG in CDCl_3 .

copolymerization of 1-octene with *t*BA initiated by AIBN. *t*BA is chosen since it can be easily transformed to acrylic acid with CF_3COOH in the following hydrolysis reaction. Figure 2(a) shows the ^1H -NMR spectrum of a typical poly(Oct-*co*-*t*BA) copolymer (copolymer **3a**, Oct% = 25.2%). The strong peak at 1.45 ppm is the characteristic peak of methyl protons of the *t*-butyl groups. The 1-octene content in the copolymer can be determined from the integrated intensity ratio between the peaks at 0.8 ppm (corresponding to the methyl protons of 1-octene units) and the peaks in the region from 2.2 ppm to 2.3 ppm (corresponding to the methine protons of *t*BA units).

^{13}C -NMR spectral analysis reveals that the copolymer produced in the copolymerization of 1-octene and *t*BA is a random copolymer with long runs of *t*BA and isolated 1-octene in the backbone. The ^{13}C -NMR spectrum of copolymer **3a** is shown in Figure 3. Two signals are observed for the carbonyl carbon in long *t*BA runs. The peak at 174.1 ppm is assigned to the carbonyl carbon in long *t*BA runs. The peak at 174.5 ppm is assigned to a *t*BA carbonyl carbon adjacent to a 1-octene unit.²³ The presence of this peak also provides evidence that 1-octene is incorporated into the copolymer chains. The chemical shifts at 79.8 and 28.1 ppm are attributed to carbons adjacent to oxygen atoms and methyl carbons of *tert*-butyl groups, respectively. The peaks at 42.4 and 36.3 ppm belong to methine and methylene carbons of *t*BA on the polymer backbone. The peaks for the methine and methylene carbons of 1-octene on the polymer backbone locate at 37.2 and 34.9 ppm. The other six peaks (14.2, 22.9, 26.3, 29.9, 32.1, and 33.8 ppm) are assigned to the carbons in the side group of 1-octene units. The absence of peaks between 38 and 41 ppm

is evidence that octene–octene diads are not present in the copolymer, which indicated that 1-octene presents as nearly isolate unit in the copolymer chains.⁸

The experimental results were summarized in Table I. Several conclusions can be drawn from the results. (1) As the mole percent of 1-octene was increased in the monomer feed, its incorporation was higher in the copolymer (compare entries 1, 2, 3, and 4), since the probability of 1-octene incorporation in the copolymer become larger. At the same time, higher mole percent of 1-octene in the monomer feed resulted in lower molecular weight coupled with lower conversion (compare entries 1, 2, 3, and 4). The phenomena can be explained as follows. Due to composition drift, the fraction of 1-octene in the remaining monomer increases, which leads to a decrease in average propagation rate constant, and a increase in probability of end-capping a 1-octene moiety at the chain end. Thus the propagating chain will be virtually inactive. As a result, the molecular weight and conversion decrease. The tendency for 1-octene to behave as a chain transfer agent under FRP conditions has been reported.¹⁰ (2)

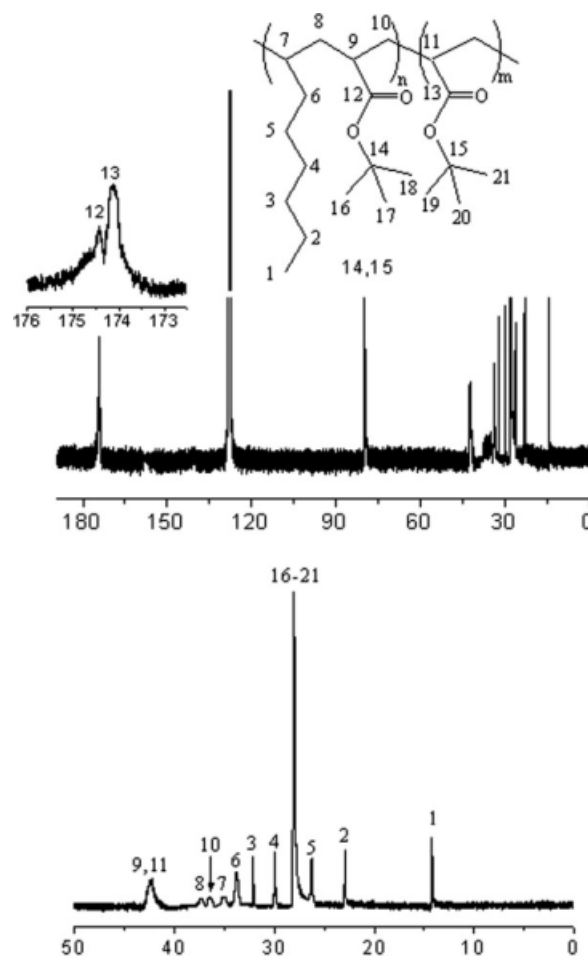


Figure 3 ^{13}C -NMR spectrum of copolymer **3a**.

TABLE I
Free Radical Polymerization of 1-Octene and *t*BA Initiated by AIBN at 80°C

Entry	Oct	Oct/ <i>t</i> BA	Time	AIBN	Conversion	Oct%	$M_n \times 10^3$	PDI
	mol	mol/mol	h	mol mL ⁻¹	%	mol%	g mol ⁻¹	
1	0.03313	1/1	19	4.06×10^{-3}	45.0	13.6	14.1	2.4
2	0.04358	2/1	19	4.06×10^{-3}	33.9	19.8	9.7	2.6
3	0.04868	3/1	19	4.06×10^{-3}	28.6	25.2	7.5	2.2
4	0.05174	4/1	39	4.06×10^{-3}	17.3	27.1	4.3	2.2
5	0.04868	3/1	4	4.06×10^{-3}	18.5	24.21	5.6	2.2
6	0.04868	3/1	10	4.06×10^{-3}	25.7	24.15	6.4	2.3
7	0.04868	3/1	14	4.06×10^{-3}	26.9	24.7	6.8	2.5
8	0.04868	3/1	19	3.04×10^{-3}	24.9	23.8	8.3	1.9
9	0.04868	3/1	19	2.03×10^{-3}	27.7	24.1	9.0	2.2

Oct, 1-octene.

Comparing entries 5, 6, 7 and 3, it is seen that longer reaction time leads to higher MW and higher conversion, while the 1-octene contents in copolymers slightly increase. (3) The molecular weight values increase as the amount of AIBN decreases (compare entries 3, 8 and 9), while there are small changes in the 1-octene contents of the copolymers.

In all, the molecular weight values and 1-octene contents of copolymers can be regulated by feed ratio, reaction time and the amount of AIBN. In this study, our objective is to obtain copolymers with high molecular weight and high 1-octene content, so copolymers **3a**, **8a**, and **9a** obtained from entry 3, 8, and 9 were selected to undergo the following reactions.

Hydrolysis of poly(Oct-*co-t*BA)

The hydrolysis procedure of poly(Oct-*co-t*BA) copolymers with CF₃COOH is very simple and effective. Figure 2(b) shows the ¹H-NMR spectrum of a typical poly(Oct-*co-AA*) copolymer. The disappear-

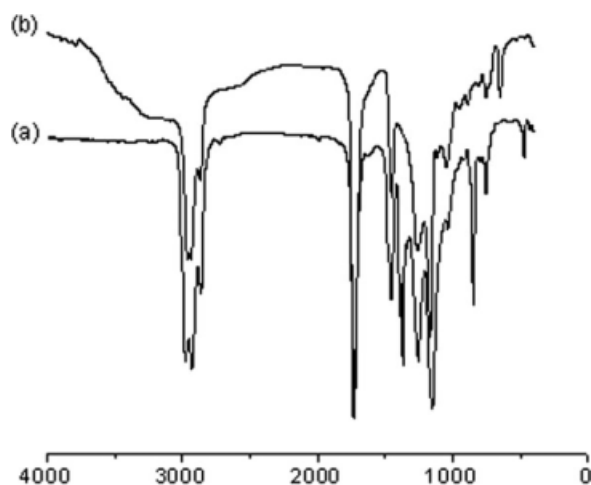


Figure 4 FTIR spectra of (a) poly(Oct-*co-t*BA) and (b) poly(Oct-*co-AA*).

ance of the characteristic strong peak at 1.45 ppm corresponding to the methyl protons of *t*-butyl group demonstrates the successful hydrolysis. FTIR spectra of poly(Oct-*co-t*BA) (a) and poly(Oct-*co-AA*) (b) are shown in Figure 4. A broad peak between 3600 cm⁻¹ and 3100 cm⁻¹ assignable to the hydroxyl of the carboxyl appeared in (b). Furthermore, the stretching vibration peak of the *t*-butyl groups at 1400–1350 cm⁻¹ disappeared after hydrolysis, indicating the completeness of hydrolysis. Both ¹H-NMR and FTIR assured the complete hydrolysis and the formation of AA units. Poly(Oct-*co-AA*) copolymers **3b**, **8b**, and **9b** were prepared from poly(Oct-*co-t*BA) copolymers **3a**, **8a**, and **9a**. The characteristic data of the three hydrolyzed products are listed in Table II.

Synthesis of the poly(Oct-*co-AA*)-*g*-PEG

The amphiphilic graft copolymer was synthesized by esterification reaction between the hydroxyl group of PEG and carboxyl of poly(Oct-*co-AA*) in the presence of a condensation reagent DCC and a catalyst DMAP. Figure 2(c) shows the ¹H-NMR of a typical amphiphilic graft copolymer. Compared with Figure 2(b), three new peaks attributable to protons of PEG chains appeared. The peak at 3.3 ppm represents —O—CH₃ protons while those at 3.5–3.6 ppm arise from —O—CH₂—CH₂—O— protons. Chemical shifts at 4.2 ppm correspond to methylene protons

TABLE II
The Characteristic Data of Copolymers Poly(Oct-*co-AA*) **3b**, **8b**, and **9b**

Copolymer	Oct%	M_n (g mol ⁻¹)	PDI	CMC (g mL ⁻¹)	Mean diameter ^a (nm)
3b	25.2	5.4×10^3	2.0	2.4×10^{-4}	84.6
8b	23.8	6.1×10^3	1.7	2.1×10^{-4}	81.3
9b	24.1	6.6×10^3	2.1	2.0×10^{-4}	92.3

^a Number-average mean diameters by DLS.

TABLE III
The Characterization Data of Amphiphilic Graft Copolymers

Copolymer	AA/PEG (mol/mol)	Graft efficiency (%)	PEG (wt %)	M_n (g mol^{-1})	PDI	CMC (g mL^{-1})	Mean diameter ^a (nm)
3c	1/1	67.1	79.3	12.6×10^3	2.0	5.2×10^{-5}	80.1
8c	1/0.8	46.3	68.1	11.0×10^3	1.8	4.9×10^{-5}	71.9
9c	1/0.6	35.5	59.4	12.3×10^3	2.1	4.1×10^{-5}	73.3

^a Number-average mean diameters by DLS.

adjacent to the ester groups. ¹H-NMR spectra proved the successful synthesis of poly(Oct-co-AA)-g-PEG. Here the graft efficiency is defined as the ratio of grafted PEG chains to the total AA units in the ungrafted copolymer. PEG content of the graft copolymer can be regulated by varying the molar ratio of AA units and PEG. The characteristic data of the three graft copolymers **3c**, **8c**, and **9c** (prepared from hydrolysis products **3b**, **8b**, and **9b**) are shown in Table III.

Micellization behavior of poly(Oct-co-AA) copolymers

The hydrolyzed products, poly(Oct-co-AA) copolymers, are amphiphilic, so their micellization behaviors in aqueous solution were explored in this article. Their CMC values were determined by fluorescence technique using pyrene as probe.^{21,24–26} This method is based on the sensitivity of pyrene to the changes in the vicinal polarity of microenvironment. In the aqueous micelle solutions, pyrene is preferentially solubilized into the hydrophobic regions of these aggregates. As a result, the values of I_1/I_3 (I_1 : the fluorescent intensity of the first peak; I_3 : the fluorescent intensity of the third peak) in the emission spectra changed sharply with increasing concentrations. We plotted fluorescence peak intensity ratios (I_1/I_3) versus the logarithm of concentrations to determine CMC as the onset of micellization. As shown in Figure 5, plots of I_1/I_3 vs. $\log C$ of three copolymers **3b**, **8b**, and **9b** are

almost flat at low concentrations, and then a significant decrease in I_1/I_3 values, observed at higher concentrations, suggesting transfer of pyrene to a more hydrophobic microenvironment. The CMC value is taken as the intersection of the tangent to the curve at the inflection with the nearly horizontal tangent through the points at low concentrations. The CMC values of three copolymers in aqueous solutions are listed in Table II. Comparing the CMC values of copolymer **3b** with that of copolymers **8b** and **9b**, it can be found that, with similar AA content, the CMC values are close to each other, however, they slowly decrease with the increasing molecular weight.

The morphology of micelles formed by copolymers **3b**, **8b**, and **9b** are illustrated in Figure 6(a) (copolymers **3b**), (b) (copolymers **8b**), and (c) (copolymers **9b**). It can be seen that the micelles adopted a spherical shape. Their size distribution obtained from DLS measurements are given in Figure 6(d) (copolymers **3b**), (e) (copolymers **8b**), and (f) (copolymers **9b**). Both TEM and DLS measurements demonstrate that the particle sizes are quite polydisperse, with diameters varied from tens of nanometers to above a hundred of nanometers. The polydispersity of micelle sizes is probably due to the broad molecular weight distribution and composition distribution of the amphiphilic copolymers. The mean diameters of micelles formed by copolymers **3b**, **8b**, and **9b** in sequence are 84.6 nm, 81.3 nm and 92.3 nm, respectively.

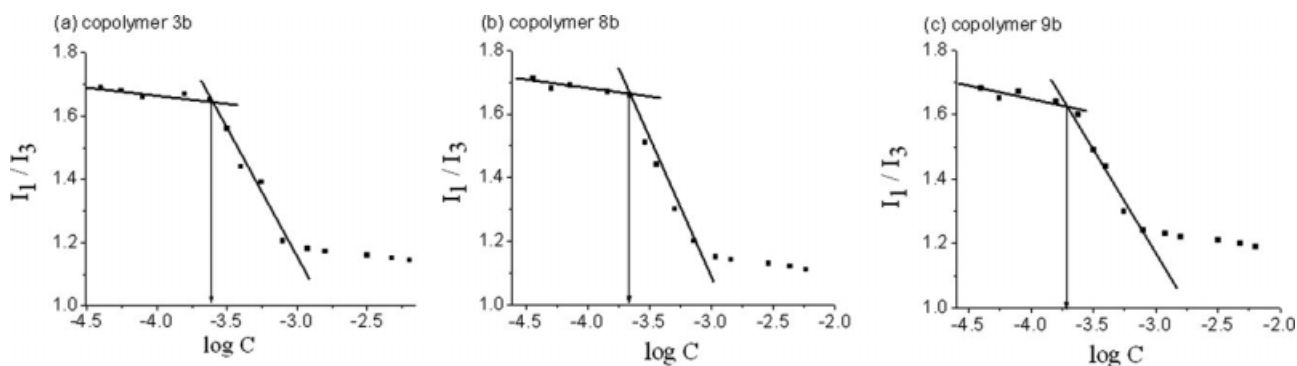


Figure 5 Plots of I_1/I_3 vs. $\log C$ of three copolymers **3b** (a), **8b** (b), and **9b** (c).

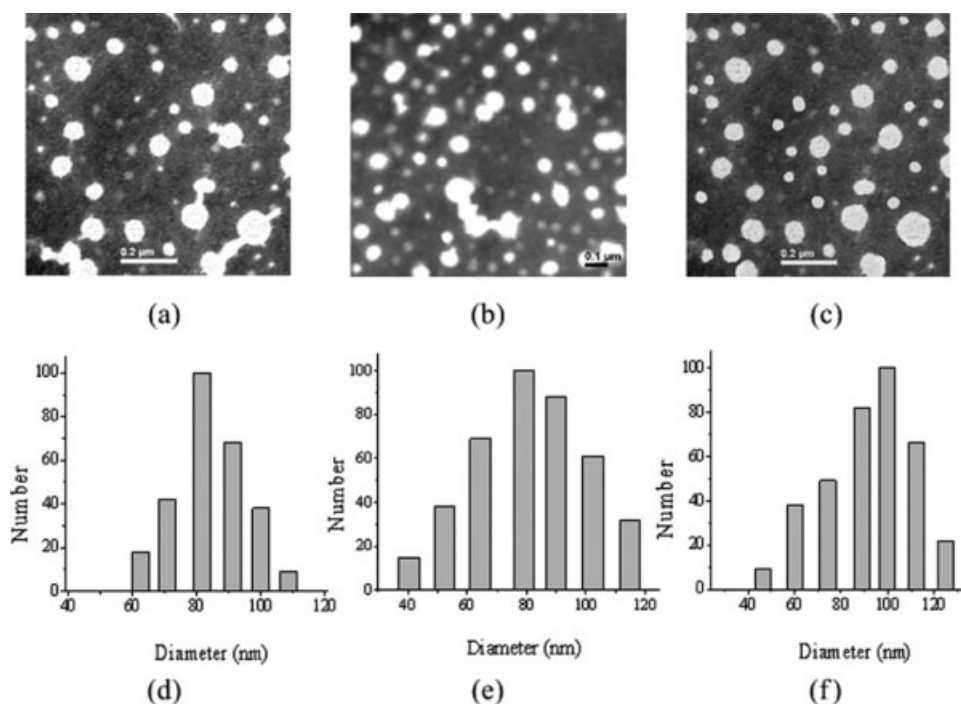


Figure 6 The TEM images of (a) copolymer **3b**, (b) copolymer **8b**, and (c) copolymer **9b**, and DLS of (d) copolymer **3b**, (e) copolymer **8b** and (f) copolymer **9b**.

Micellization behavior of poly(Oct-co-AA)-g-PEG copolymers

With high PEG content, amphiphilic poly(Oct-co-AA)-g-PEG copolymers can be easily dissolved in water, and cannot be dissolved in *n*-octane, so their micellization behaviors in aqueous solution are investigated in this article.

The CMC values of the graft copolymers **3c**, **8c**, and **9c** in aqueous solutions were also obtained from the fluorescent probe studies using pyrene as probe. The plots of I_1/I_3 vs. $\log C$ of the three copolymers are shown in Figure 7. The CMC values of the three copolymers are listed in Table III.

Further information about the micellization behaviors of the three copolymers in water was given by

TEM and DLS measurements. As we all know, in aqueous solution, hydrophobic poly(1-octene) segments tend to form the core, while the hydrophilic PEG chains form the corona. It can be seen from Figure 8(a) (copolymers **3c**), (b) (copolymers **8c**), and (c) (copolymers **9c**), the three copolymers can self-assemble into spherical micelles in water. The size distribution of micelles is estimated by DLS, as illustrated in Figure 8(d) (copolymers **3c**), (e) (copolymers **8c**) and (f) (copolymers **9c**). The mean diameters of micelles formed by three copolymers are listed in Table III. Both TEM and DLS measurements demonstrate the broad size distribution of micelles. The polydispersity of micelle sizes is probably due to the broad molecular weight distribution and

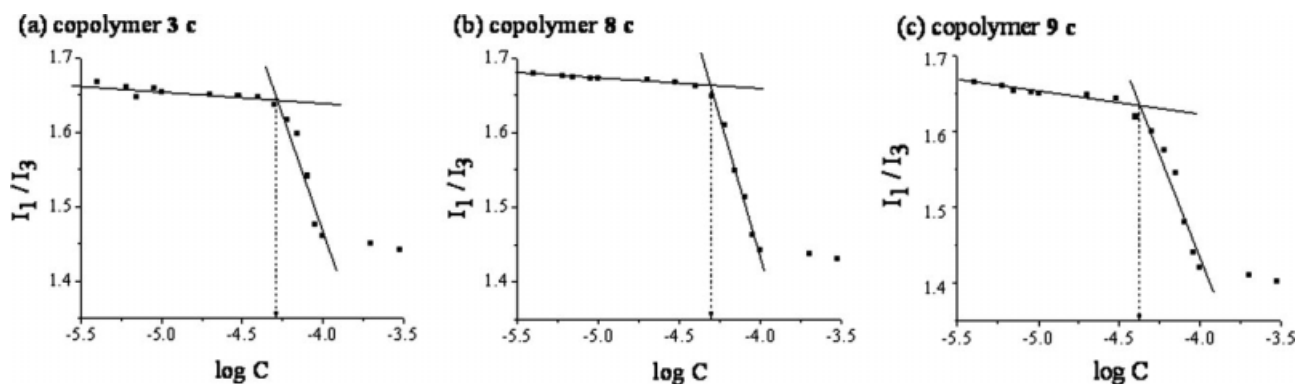


Figure 7 Plots of I_1/I_3 vs. $\log C$ of three copolymers **3c** (a), **8c** (b), and **9c** (c).

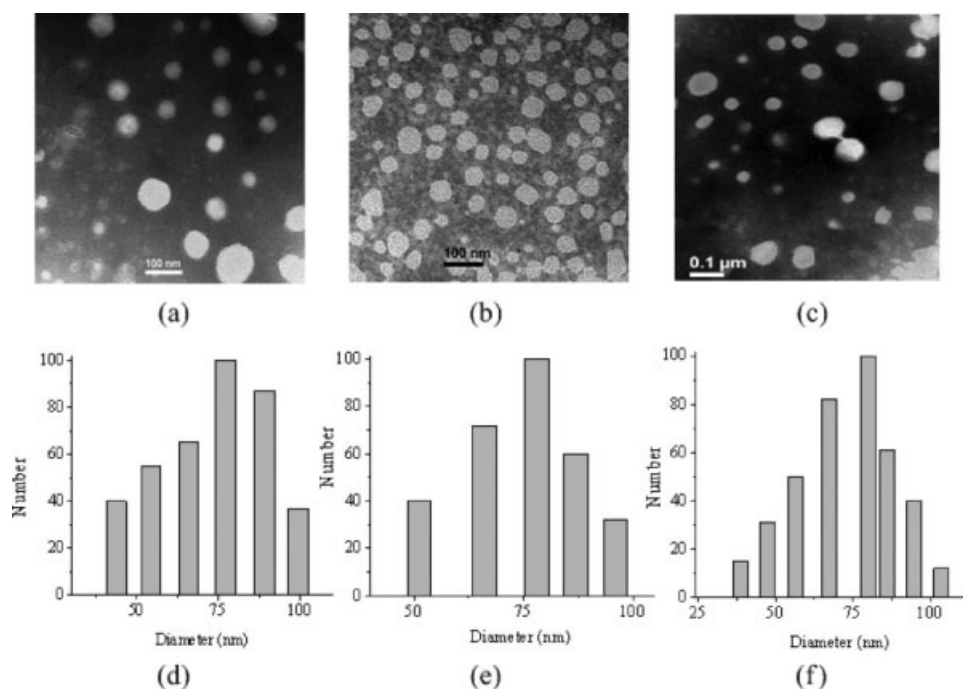


Figure 8 The TEM images of (a) copolymer **3c**, (b) copolymer **8c** and (c) copolymer **9c**, and DLS of (d) copolymer **3c**, (e) copolymer **8c** and (f) copolymer **9c**.

composition distribution of the amphiphilic graft copolymers.

Drawing a comparison between the micellization behaviors of the two kinds of amphiphilic copolymers in this article, it is discovered that, all of them can dissolve in water and have low CMC values of about 10^{-5} g mL $^{-1}$, and they can form spherical micelles in aqueous solution. However, the self-assembly behaviors of poly(1-octene-*co*-AA)-*g*-PEG copolymers differ sharply from the previously prepared poly(1-dodecene-*co*-*p*MS)-*g*-PEG copolymers because of their different PEG content.²⁰ Poly(1-dodecene-*co*-*p*MS)-*g*-PEG, with PEG content below 30 wt %, cannot dissolve in water, but they can self-assemble into spherical reverse micelles in *n*-octane and toluene. Meanwhile, their CMC values of about 1×10^{-4} g mL $^{-1}$ were determined in *n*-octane.

CONCLUSION

In this article, two series of amphiphilic copolymers with 1-octene as hydrophobic segments are synthesized. Poly(1-octene-*co*-acrylic acid) copolymers were prepared through the free radical copolymerization of 1-octene and *tert*-butyl acrylate, and hydrolysis of the *tert*-butyl acrylate units. Poly(1-octene-*co*-acrylic acid)-*g*-PEG copolymers were obtained from the esterification reaction between poly(1-octene-*co*-acrylic acid) and poly(ethylene glycol) monomethyl ether. This method can be extended to realize the functionalization of other long chain α -olefin polymers. Because of

the amphiphilic nature of the two kinds of copolymers, they can spontaneously self-assemble into stable micelles in water. Fluorescence studies show that they have low CMC values of about 10^{-5} g mL $^{-1}$. TEM images demonstrate the micelles all adopt a spherical shape and keep the same morphology with different content of hydrophilic chains. DLS measurements show the broad size distribution of micelles, and their mean diameters are in the range of 70–100 nm. These findings enriched the self-assembly studies of amphiphilic copolymers.

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