Synthesis and Characterization of an Amphiphilic Graft Copolymer with a Poly(acrylic acid) Backbone and *n*-Octylphenyl Polyoxyethylene Side Chains

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ABSTRACT: A novel, well-defined, amphiphilic graft copolymer was synthesized by the free-radical copolymerization of acrylic acid and an amphiphilic macromonomer, *n*-octylphenyl polyoxyethylene acrylate. This acrylic copolymer was characterized by IR and ^{1}H-NMR. The number-average molecular weight was determined by gel permeation chromatography to be 4.37×10^4 (weight-average molecular weight/number-average molecular weight = 1.23). The graft copolymer exhibited good solubility in water and high surface activity at much lower concentrations. The molecules of the AA–C$_8$PhEO$_{10}$Ac copolymer formed polymolecular micelles at 3.0×10^{-4} g/mL. The aggregation of the copolymer was examined in aqueous solution by measurement of the fluorescence of 2-*p*-toluidinylnaphthalene 6-sulfonate as a fluorescent probe. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3677–3682, 2008

Key words: fluorescence; graft copolymers; macromonomers; micelles; surfaces

INTRODUCTION

The design, synthesis, and characterization of amphiphilic copolymers have become one of the most important research areas in the polymer sciences in recent decades.[1–3] The types, length, and distribution of different parts of amphiphilic molecules determine the structure and, therefore, the properties of assemblies. The hydrophilic and hydrophobic segments serve as attractive building blocks for versatile applications, such as the delivery and release of drugs,[4,5] agrochemistry,[6] personal care,[7] and food products.[8] Notably, amphiphilic graft copolymers modify interfacial properties and dramatically enhance their compatibilities. A few reports have dealt with the synthesis and micellar behavior of amphiphilic graft copolymers with hydrophilic groups and long hydrophobic side chains in aqueous solution. However, few descriptions have been presented for the aggregation of amphiphilic graft copolymers in aqueous solution in detail because of the difficulty of sample separation.[9–13]

Studies of the self-assembly behaviors of block copolymers in water have shown that the critical micelle concentration (cmc) and micelle aggregation number are influenced by the pH value of the solution, ionic strength, preparation conditions, copolymer concentration, molecular weight of the copolymer, and the composition of the copolymer,[14–20] although few studies have focused on the behaviors of amphiphilic graft copolymers in water. Recently, it was revealed that the architecture of the copolymer also plays an important role in the determination of the properties of the micelles. Comblike amphiphilic copolymers with chemically different backbones and side chains have a number of features that make them attractive candidates for diverse applications. Depending on the solubility of the main chain and side chains, two qualitatively different scenarios of aggregation behavior are visible.[21–24]

In this study, a novel amphiphilic graft copolymer poly(acrylic acid) grafted octylphenyl polyoxylethylene ether (AA–C$_8$PhEO$_{10}$Ac) was synthesized by the reaction of *n*-octylphenyl polyoxyethylene acrylate (C$_8$PhEO$_{10}$Ac) and acrylic acid (AA) in aqueous solution. This novel acrylic copolymer with amphiphilic character was easily characterized by IR, ^{1}H-NMR, gel permeation chromatography (GPC), and fluorescence spectroscopy because of the built-in aromatic moiety in its side chain. With the incorporation of poly(oxylethylene alkylphenyl ether) (C$_8$PhEO$_{10}$) in the main poly(acrylic acid) chain, micellar formation of the amphiphilic graft copolymer in water was examined by surface tension measure-

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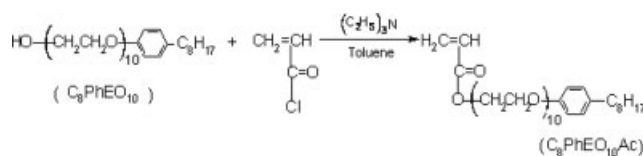
Scheme 1 Synthesis of the macromonomer.

ments and a fluorescence technique with 2-*p*-toluidi-nylnaphthalene 6-sulfonate (TNS) as a probe. The effect of the presence of a long molecular side chain on the solution properties of AA–C$_8$PhEO$_{10}$Ac was examined, and the preliminary findings are reported.

EXPERIMENTAL

Materials

Toluene was dried by distillation over CaH$_2$. AA and acryloyl chloride were purified by distillation under reduced pressure. C$_8$PhEO$_{10}$ (Tianjin Fuchen Chemicals, China) and triethylamine (Tianjin Fuchen Chemicals, China) were used as received. Tetrahydrofuran (THF) was dried over CaH$_2$ for several days and distilled from sodium and benzophenone under a N$_2$ atmosphere. We purified copper(I) chloride (Aldrich, LA, USA) (CuCl; Aldrich, 98%) by stirring it overnight over CH$_3$CO$_2$H at room temperature; we then washed the solid with ethanol, diethyl ether, and acetone before drying it at 40°C *in vacuo* for 1 day.

Measurements

Fourier transform infrared spectra were recorded on a Nicolet 670 spectrometer (Madison, WI, USA). The ^{1}H-NMR spectrum of AA–C$_8$PhEO$_{10}$Ac in dimethyl sulfoxide-d_6 was obtained with a Mercury Plus AS400 spectrometer (Palo Alto, CA, USA) at room temperature. GPC measurements were conducted on an Alliance GPCV2000 instrument (Milford, MA, USA) with THF as the eluent (flow rate = 1 mL/min at 35°C), the molecular weights were calibrated against polystyrene standards. The surface tension was determined with a JZ-200 tensiometer (Chengde, China) at 20°C. The fluorescence spectra were performed on a PerkinElmer LS-55B spectrofluorometer (Shelton, CT, USA).
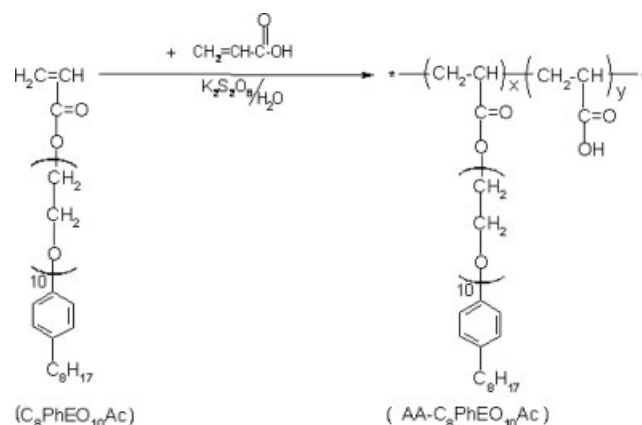
Synthesis of the macromonomer (C$_8$PhEO$_{10}$Ac)

C$_8$PhEO$_{10}$Ac was prepared with C$_8$PhEO$_{10}$ and acryloyl chloride in toluene, as shown in Scheme 1. C$_8$PhEO$_{10}$ (27.5 mmol), triethylamine (49.4 mmol), and toluene (100 mL) were charged into a 250-mL, three-necked, round-bottom flask equipped with a dropping funnel, thermometer, and water condenser. The resulting reaction mixture was cooled in an ice bath, and the temperature was maintained in the

range 0–7°C; then, acryloyl chloride (59 mmol) was added in a dropwise manner. After the completion of the addition, the reaction mixture warmed to room temperature, and continuous stirring was applied for 24 h. After the solvent was removed, the residue was purified by column chromatography with 1 : 1 ethyl acetate/petroleum ether as the eluent.

Polymer synthesis

Copolymerization involving macromonomers is very important for the design of well-defined graft copolymers. Consider a copolymerization between a conventional monomer, A, and a macromonomer, B, to obtain a graft copolymer with A as a backbone or trunk and B as a side chain or branch.[25–28] It is difficult to synthesize graft copolymers with a macromonomer as a backbone and a comonomer as a side chain, and this is probably due to the large steric hindrance of the macromonomers. In this study, the macromonomer C$_8$PhEO$_{10}$Ac contained an acrylate chain end, so it could copolymerize with the AA monomer to produce a graft copolymer with a poly (acrylic acid) backbone and *n*-octylphenyl polyoxyethylene side chains by free-radical polymerization.

Distilled water (125 mL) was added to a 250-mL, three-necked reactor equipped with a magnetic stirrer, thermometer, water condenser, and nitrogen inlet and outlet. The solvent was purged by N$_2$ for 30 min. C$_8$PhEO$_{10}$Ac (3 g) and AA (6 g) were then added, and the solution was further purged for 20 min. The temperature was adjusted to 70°C; the potassium persulfate initiator (0.14 g) was then charged. The reaction was carried out at 70°C under a nitrogen atmosphere for 24 h. Solvent in the reaction mixture was then removed with a rotary evaporator (Shanghai, China). The crude product was purified by ethyl acetate reprecipitation. The purified product was dried in a vacuum oven to remove the trapped solvent at 30°C for 48 h. The reaction process is shown in Scheme 2.
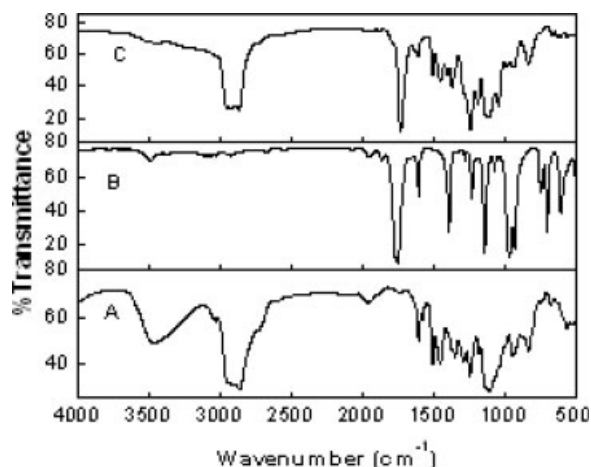

Scheme 2 Synthesis of the graft copolymer.

Figure 1 IR spectra of (A) C_8PhEO_{10}, (B) acryloyl chloride, and (C) the macromonomer.

Measurement of cmc

The cmc values were measured by the method of surface tension (the ring method) with a JZ-200 tensiometer at 20°C.

RESULTS AND DISCUSSION

Characterization of the macromonomer

Figure 1 shows the IR spectra of C_8PhEO_{10}, acryloyl chloride, and the macromonomer. Compared to the IR spectrum of C_8PhEO_{10} [Fig. 1(A)], the spectrum of the macromonomer [Fig. 1(C)] had a new band of the ester group of $C_8PhEO_{10}Ac$ appear at 1736 cm^{-1} ($\nu_{C=O}$) accompanied by the disappearance of the band of the terminal hydroxyl group of C_8PhEO_{10} at 3348 cm^{-1}. The other characteristic peaks of the macromonomer were observed at 1614, 1511, and 1457 cm^{-1} for phenyl group (C=C) stretching vibrations;
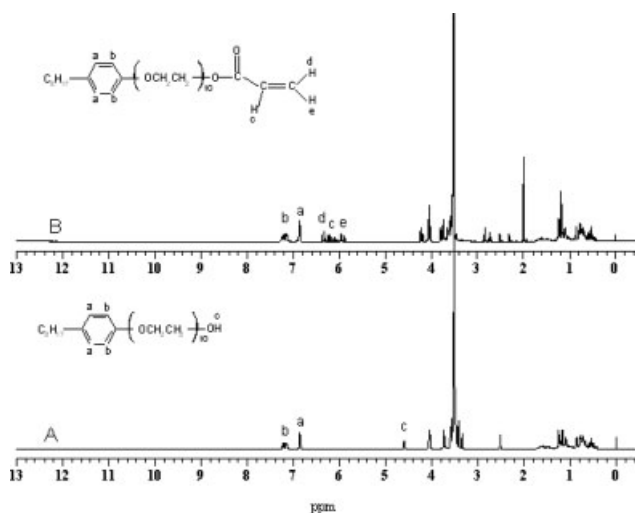
the bands at 1247 and 1105 cm^{-1} were assigned to the symmetric C—O—C stretching modes of the ester group. These results provided direct evidence for complete acylation.

Typical ^{1}H-NMR spectra of C_8PhEO_{10} and the macromonomer in dimethyl sulfoxide (DMSO) are shown in Figure 2. The ^{1}H-NMR spectrum of C_8PhEO_{10} in Figure 2(A) displays all of the resonance structures corresponding to the aromatic protons (δ = 7.20 and 6.85 ppm), the protons of the ethylene oxide moiety (δ = 3.72 ppm), the protons of —OH (δ = 4.59 ppm), and the —CH$_3$, —CH$_2$, and —CH units (δ = 0.9–1.5 ppm). Figure 2(B) shows the ^{1}H-NMR spectrum of the macromonomer. In comparison with Figure 2(A), the proton peak of —OH (δ = 4.59 ppm) disappeared, and the characteristic proton peaks of CH$_2$=CH— (δ = 6.41, 6.17, 5.87 ppm) of acryloyl group occurred via acylation. These chemical shifts provided additional evidence for successful acylation. The ^{1}H-NMR spectrum corresponded well with the IR spectrum.
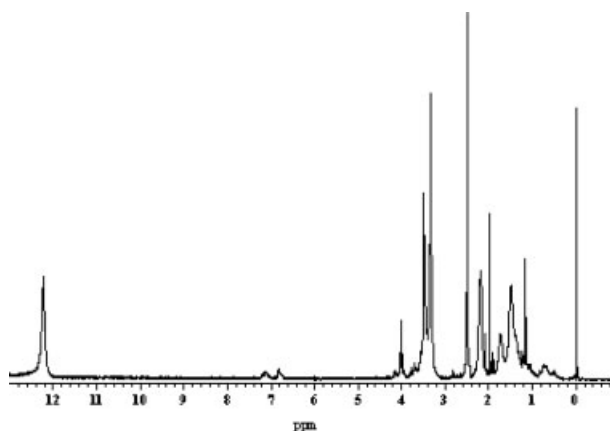

Figure 3 IR spectra of the (A) macromonomer and (B) graft copolymer.

Figure 2 ^{1}H-NMR spectra of (A) C_8PhEO_{10} and (B) the macromonomer in DMSO.

Figure 4 ^{1}H-NMR spectrum of the graft copolymer in DMSO.

| Copolymer | C$_8$PhEO$_{10}$Ac : AA (molar ratio) | | GPC | | C$_8$PhEO$_{10}$Ac (wt %) | Surface tension (mN/m) |
	In the feed	In the copolymer[a]	$M_w \times 10^{-4}$	M_w/M_n		
AA–C$_8$PhEO$_{10}$Ac	1 : 10	1 : 9	5.4	1.23	52.01	39.8

M_n = number-average molecular weight; M_w = weight-average molecular weight.
[a] By ^{1}H-NMR.

Characterization of the graft copolymer

The IR spectrum of the graft copolymer is shown in Figure 3(B). The absorption peaks at 1721 cm^{-1} (C=O) for the carboxyl group; 614, 1511, and 1457 cm^{-1} for the phenyl group (C=C) stretching vibration band; and 1247 and 1105 cm^{-1} doublets were assigned to the symmetric C—O—C stretching modes of the ester group. Compared to the IR spectrum of the macromonomer [Fig. 3(A)], a new stretching vibration band at 3438 cm^{-1} of the hydroxyl group (O—H) appeared, and the out-of-plane bending band at 990 and 945 cm^{-1} for unsaturated hydrocarbons (C—H) disappeared. These provided evidence for the successful copolymerization of AA and C$_8$PhEO$_{10}$Ac.

The ^{1}H-NMR spectra of AA–C$_8$PhEO$_{10}$Ac is shown in Figure 4. Compared to the ^{1}H-NMR spectrum of the macromonomer [Fig. 2(B)], the characteristic proton peaks of CH$_2$=CH— (δ = 6.41, 6.17, and 5.87 ppm) of the acryloyl group disappeared, and a new peak at δ = 12.25 ppm, corresponding to the proton of —COOH, occurred via the copolymerization. These chemical shifts provided additional evidence for the successful copolymerization of AA and C$_8$PhEO$_{10}$Ac.

In addition, the molecular weights estimated from the GPC measurements with polystyrene standards are summarized in Table I. The GPC (Fig. 5) trace of the graft copolymer showed a unimodal shape. This further indicated that the polymerization was completed successfully and that there was no homopolymer in the reaction product.

As shown in Figure 6, AA–C$_8$PhEO$_{10}$Ac gave rise to its intrinsic fluorescence because of its built-in phenyl groups in the side chain, which corresponded well with the IR and ^{1}H-NMR spectra for the incorporation of aromatic moieties in the copolymer.

cmc

In this graft copolymer, there was a large pendant hydrophilic spacer group, which was expected to decrease the rigidity of the polymer backbone. The amphiphilic character of AA–C$_8$PhEO$_{10}$Ac is essentially due to the presence of hydrophilic oxyethylene groups and hydrophobic aromatic groups with *n*-octyl chains in the molecule, which provide an opportunity for the formation of micelles in water. The amphiphilic C$_8$PhEO$_{10}$ attached to the poly(acrylic acid) backbone may be responsible for its aggregation and good solubility in water.

The plot of the surface tension versus the logarithm of AA–C$_8$PhEO$_{10}$Ac concentration is shown in Figure 7. The surface tension of AA–C$_8$PhEO$_{10}$Ac reached a first plateau around 5.0 $\times$ 10^{-5} g/mL,
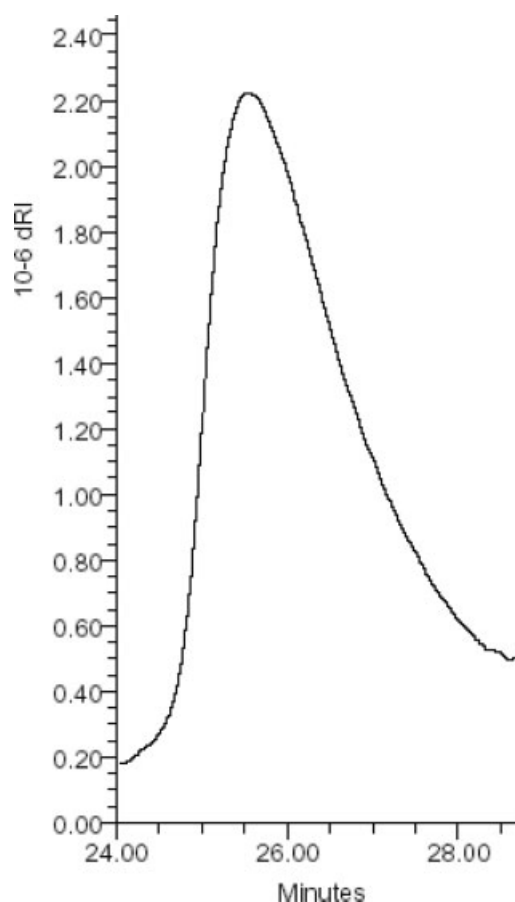

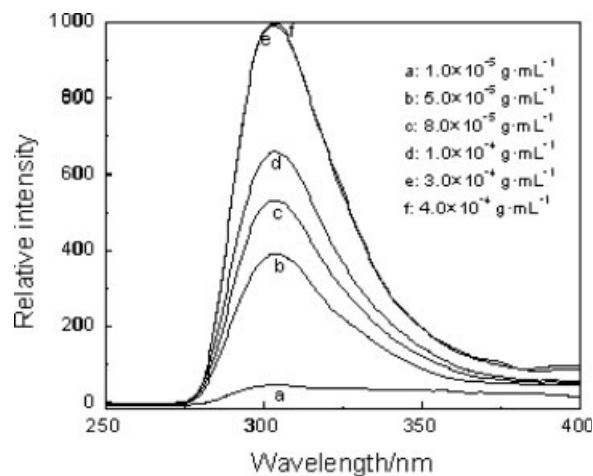**Figure 5** GPC curve of the copolymer. dRI: differential refractive index.

Figure 6 Fluorescence spectra of AA–$C_8PhEO_{10}Ac$ in aqueous solution. The excitation wavelength was 224 nm.

which corresponded to the first cmc. The surface tension continuously decreased with increasing concentration of AA–$C_8PhEO_{10}Ac$ in aqueous solution. Finally, the second cmc, 3.0×10^{-4} g/mL, was obtained.

Micelle behavior of AA–$C_8PhEO_{10}Ac$

To detect the special microheterogeneity of AA–$C_8PhEO_{10}Ac$ in aqueous solution, TNS was used as a fluorescent probe because the fluorescence of TNS is quite sensitive to the polarity of the microenvironment in which TNS is located, and it, thus, reflects changes in the structure of aggregates. TNS preferably lies inside the microenvironment and strongly emits if micelles are formed in aqueous solution.
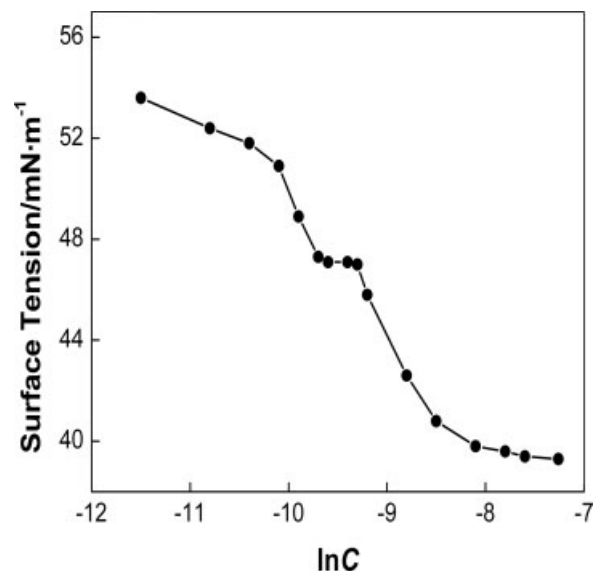

Figure 7 Plot of the surface tension versus the logarithm of the AA–$C_8PhEO_{10}Ac$ concentration (ln C).
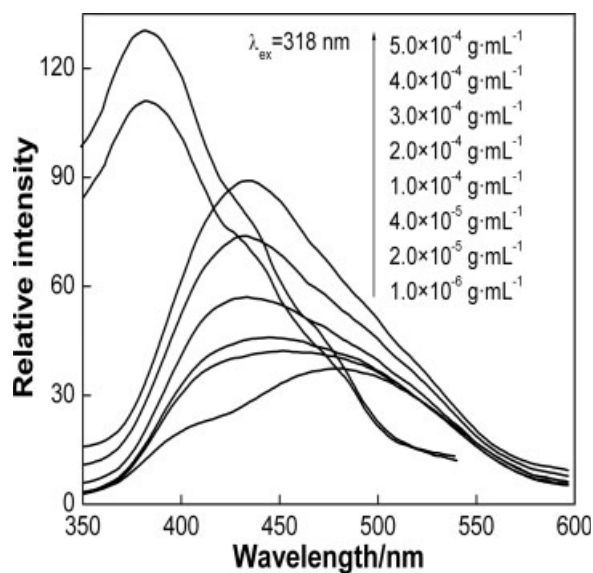

Figure 8 Fluorescence spectra of TNS in the presence of AA–$C_8PhEO_{10}Ac$. The excitation wavelength (λ_{ex}) was 318 nm.

The emission spectra of TNS in the presence of AA–$C_8PhEO_{10}Ac$ at various concentrations in aqueous solution are shown in Figure 8. In all cases, the concentration of TNS was kept at 5×10^{-5} M, and excitation wavelength was kept at 318 nm. The scanning rate was 100 nm/min, and the slit opening was 5 nm. Figure 8 shows the fluorescence maximum of the TNS blueshifts from 482 nm in water to 432 nm in the presence of 5.0×10^{-5} g/mL AA–C_8-$PhEO_{10}Ac$. This critical value was in good agreement with the first cmc obtained by surface tension measurements. Thereafter, the fluorescence intensity of TNS began to rapidly increase with increasing concentration of AA–$C_8PhEO_{10}Ac$. The fluorescence maximum of TNS exhibited the greatest hypsochromic shift (wavelength change = 100 nm) above 3.0×10^{-4} g/mL. Notably, the second critical value was also consistent with the second cmc obtained. These data clearly revealed that the interiors of the second micellar aggregates were relatively nonpolar.

CONCLUSIONS

In this study, a novel amphiphilic graft copolymer of poly(acrylic acid) as the main chain and n-octyl-phenyl polyoxyethylene as the side chains was successfully synthesized by free-radical copolymerization. The amphiphilic graft copolymer could form stable micelles in aqueous solution, the first cmc was 5.0×10^{-5} g/mL, and polymolecular micelles were formed at a concentration of 3.0×10^{-4} g/mL. Our attention is now focused on the self-assembly of this

amphiphilic graft copolymer in aqueous solution and organic solvents. The results will be published in a subsequent article.

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