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COPOLYMERIZATION OF SODIUM 11-ACRYLAMIDOUNDECANOATE WITH ACRYLAMIDE AND THE SOLUTION PROPERTIES OF THE COPOLYMERS

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ABSTRACT

The radical copolymerization of micelle-forming sodium 11-acrylamidoundecanoate (Na 11-AAU) with acrylamide (AM) has been studied. The copolymer compositions were determined from elemental analyses and ^{13}C NMR. The radical reactivity ratios for Na 11-AAU (M_1) and AM (M_2) were found to be $r_1 = 0.71$ and $r_2 = 0.62$. The molecular weights of the copolymers as determined by light scattering ranged from 0.88 to 1.62×10^6. The presence of AM up to 50 mol% in the feed did not seem to affect the molecular weights of the copolymers. However, the radius of gyration of the copolymers increased slightly with the increase of AM. The viscosities of the copolymer solutions also increased with AM content, but they were sharply reduced by the effect of NaCl or on aging at room temperature.

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INTRODUCTION

Polyelectrolytes are widely used in many industrial applications such as water treatment, soil conditioning, and antistatic treatment of textiles [1–3]. Most of the anionic polyelectrolytes are based on acrylamide due to their utility as water-soluble viscosifiers and displacement fluids in enhanced oil recovery [4, 5]. This has stimulated a great interest in copolymerization of acrylamide and ionic comonomers.

The copolymerizations of acrylamide with short alkyl chain length anionic comonomers have been investigated. These ionic comonomers are potassium or sodium styrenesulfonate [6], sodium 2-acrylamido-2-methylpropanesulfonate, sodium 2-sulfoethyl methacrylate [7, 8], sodium 3-acrylamido-3-methylbutanoate [9, 10], sodium 3-(*N*-propyl) acrylamido-3-methylbutanoate [11, 12], sodium 3-methacrylamido-3-methylbutanoate [13, 14], and sodium acrylate [15]. It was observed that the rate of copolymerization and the solution properties of the resulting copolymers [6] depend on the ionic strength (arising from varying the ionic monomer concentration) and polarity of the solvent. A short alkyl chain length cationic monomer of 2-acrylamido-2-methylpropane-dimethylammonium chloride was also copolymerized with acrylamide [16, 17]. The solution properties of these copolymers have been studied with respect to the composition, the effect of temperature and electrolyte, as well as aging.

We have recently synthesized and polymerized a series of micelle-forming monomers of sodium acrylamidoalkanoates [18, 19]. The copolymerization of long alkyl chain length anionic sodium 11-acrylamidoundecanoate [Na 11-AAU] with acrylamide and the solution properties of the copolymers are discussed in this paper.

EXPERIMENTAL

Materials

Acrylamide from Tokyo Chemical Industry Co. was recrystallized from chloroform. Sodium 11-acrylamidoundecanoate was synthesized as reported previously [18]. Sodium chloride from Merck was used as received. Potassium persulfate from Reachim was recrystallized from water. Water was doubly distilled.

Copolymerization

An aqueous solution of known concentration of Na 11-AAU, AM, and potassium persulfate was prepared in a flask and purged with nitrogen for 15 min. The copolymerization was carried out at 50 ± 0.1°C. A certain amount of the reaction mixture was precipitated at different time intervals in a large quantity of reagent-grade acetone. The copolymer was washed several times with methanol and dried in a vacuum oven at 30°C for 24 h. Its conversion (%) was then calculated.

Elemental Analysis

Elemental analyses for carbon, hydrogen, and nitrogen of the copolymers were obtained by an Elemental Analyser 240C (Perkin-Elmer). The copolymer compositions were calculated based on C/N ratios.

Spectroscopic Measurements

Infrared spectra were recorded by a Perkin-Elmer 1310 spectrophotometer using KBr pellets. Carbon-13 NMR spectra were obtained in D_2O by a Jeol FX90Q Fourier Transform NMR spectrometer. The ^{13}C-NMR spectra of the homopolymer and copolymer were recorded at 22.5 MHz by using a 5% polymer solution (D_2O) in 10mm tubes. The probe temperature was 25°C. A total of 33,000 transients were accumulated.

Determination of Critical Micelle Concentration (CMC)

The CMC of Na 11-AAU was determined at 30 ± 0.1°C by surface tension measurements by using a torsion balance tensiometer (White Electric Instrument Co.). The concentration at the breakpoint of the plot of surface tension versus log [Na 11-AAU] curve is the CMC. Similarly, the CMCs of the mixed micelles of Na 11-AAU and AM were determined.

Viscosity Measurement

The viscosities of the aqueous copolymer solutions were measured in an Ubbelohde dilution capillary viscometer (Kapenekas Laboratory Services, Akron, Ohio) in a thermostated water bath at 23 ± 0.1°C. Intrinsic viscosities were obtained in the usual way by extrapolation of both the reduced viscosity η_{sp}/c and the inherent viscosity ln η_r/c to infinite dilution according to the Huggins [20] and Kraemer [21] relationships, respectively.

Molecular Weight Determination by Light Scattering

Light-scattering measurements were performed with a Malvern Instruments system 4700C submicron particle analyser. The intensities of the scattered light were measured over a range of angles from 10 to 150° by using vertically polarized light of wavelength 633 nm at 21°C. Aqueous NaCl solution was used as solvent. The concentrations of the copolymer solution ranged from 0.1 to 0.8 g/L. All the copolymer solutions were filtered by 0.22 μm disposable membrane filters (cellulose acetate) before the measurements. The experimental data were analyzed by the Zimm plot method [22].

RESULTS AND DISCUSSION

Mixed Micelles and Copolymerization

The CMC of Na 11-AAU was found to be 2.24×10^{-3} mol/L at 30°C. In the presence of AM, the CMC of Na 11-AAU decreased to 1.86×10^{-3} and 1.41×10^{-3} mol/L as the molar ratio of AM/Na 11-AAU was increased to 1 : 1 and 4 : 1, respectively. It is likely that some of the AM molecules were interdispersed between the ionic head groups of Na 11-AAU at the interfaces of the mixed micelles. Such a molecular arrangement of the mixed micelle would reduce the mutual repulsion between the ionized groups of Na 11-AAU, and thus the CMC would decrease [23]. It has also been reported that AM can act as a cosurfactant in a microemulsion where AM is mostly located at the interfaces of the microemulsion droplets [24]. Besides being present in the mixed micelles, monomer AM also exists in the bulk aqueous phase because of its high solubility in water. Monomers AM and Na 11-AAU in the aqueous phase thus established an equilibrium with those in the mixed micelles.

The copolymerizations of Na 11-AAU and AM at different molar ratios with a total monomer concentration of 0.4 mol/L were carried out at 50°C. Since a water-soluble initiator ($K_2S_2O_8$) was used, the free radicals produced would probably first initiate AM and/or Na 11-AAU and form radical oligomers in the aqueous phase. It is envisaged that the growing oligomers might diffuse into the mixed micelles and proceed with rapid copolymerization in the micellar environment. Figure 1 shows the overall fast copolymerization of Na 11-AAU/AM at different molar ratios. The increase of AM in the feed reduced the rate of copolymerization. Since the molecular weights of the copolymers obtained were over one million, it is believed that the nucleated particles continued to grow as the monomers were supplied from the nonnucleated micelles.

Radical Reactivity Ratios

The feed molar ratios of Na 11-AAU and AM as well as the resultant copolymer compositions were used to calculate the radical reactivity ratios of Na 11-AAU (r_1) and AM (r_2). The compositions of the copolymers can be calculated from both elemental analyses and ^{13}C-NMR measurements. A portion of the ^{13}C-NMR spectra of the Na 11-AAU-AM copolymer is shown in Fig. 2. The peak at 182 ppm became more intense as the percentage of AM in the copolymer increased. The peaks at 182 ppm

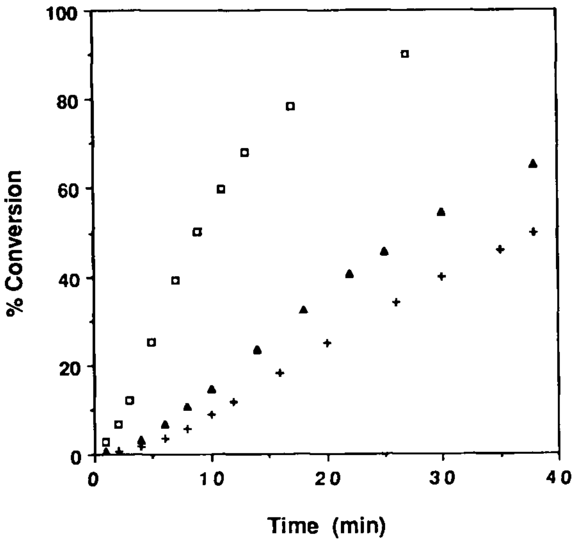

FIG. 1. Copolymerization of Na 11-AAU and AM at different molar ratios at 50°C. Total monomer concentration = 0.4 mol/L, [$K_2S_2O_8$] = 5 × 10^{-4} mol/L. Na 11-AAU : AM feed ratio: (□) 7 : 3; (▲) 1 : 1; (+) 3 : 7.

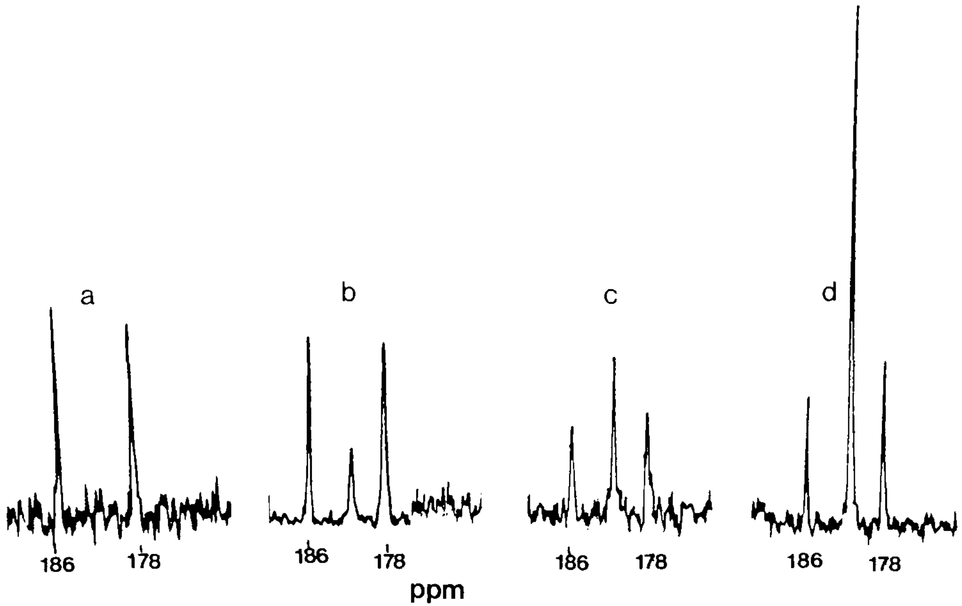

FIG. 2. The ^{13}C-NMR spectra for homopolymer and copolymer of Na 11-AAU with different feed ratios in the region of 178 to 186 ppm. Na 11-AAU : AM feed ratio: a = 1 : 0, b = 7 : 3, c = 1 : 1, d = 3 : 7.

(—CONH$_2$) and 178 ppm (—COO) were integrated in order to obtain the molar ratios of AM and Na 11-AAU in the copolymer. Some of these results are listed in Table 1. It is noted that the values calculated from ^{13}C NMR are slightly different from those obtained from elemental analyses. Such a discrepancy was also observed by other workers [9, 11, 16]. The common practice of calculating the compositions of the copolymers by elemental analyses [9, 11, 16] was thus used in this study.

A Fineman-Ross [25] plot, shown in Fig. 3, was employed for the determination of the radical reactivity ratios at low copolymer conversion. The radical reactivity ratios for Na 11-AAU (M_1) and AM (M_2) were found to be $r_1 = 0.71 \pm 0.05$, $r_2 = 0.62 \pm 0.06$, and $r_1r_2 = 0.44$ according to

$$f/F - f = r_2 - r_1(f^2/F)$$

where $F = d[M_1]/d[M_2]$, $f = [M_1]/[M_2]$.

Figure 4 shows that the copolymer composition varied as a function of feed composition of Na 11-AAU and AM. In this diagram, time of conversion is not considered. Figure 4 implies that the results strictly refer to instantaneous compositions. Since both r_1 and r_2 were less than unity

TABLE 1. The Compositions of the Copolymers at Different Feed Molar Ratios of Na 11-AAU (M_1) and AM (M_2)

Sample no.	Feed molar ratio $M_1 : M_2$	Copolymer conversion, %	Copolymer composition C, wt%	N, wt%	M_1,[a] mol%	M_1,[b] mol%
CopA20	4 : 1	9.0	51.79	5.24	77.20	74.36
CopA25	3 : 1	4.9	51.87	5.57	72.10	71.46
CopA33	2 : 1	7.8	51.89	6.23	62.40	60.10
CopA50	1 : 1	8.1	51.95	6.97	53.20	50.08
CopA66	1 : 2	5.6	49.55	8.50	34.57	32.27

[a] Calculated from elemental analyses.

[b] Calculated from ^{13}C NMR.

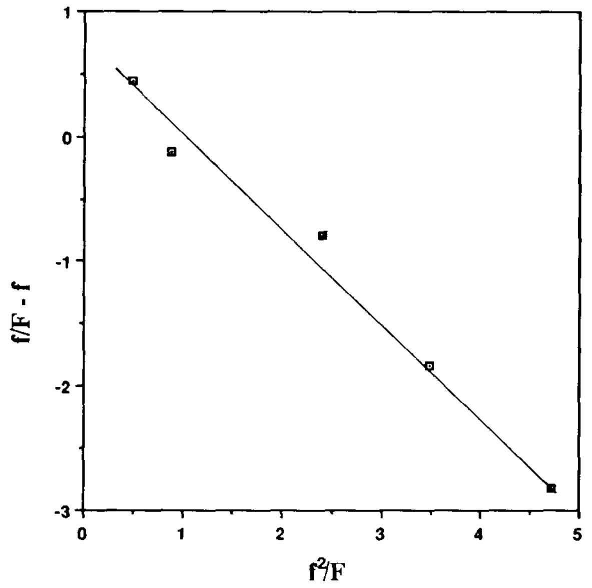

FIG. 3. The Fineman-Ross plot for the determination of radical reactivity ratios in the copolymerization of Na 11-AAU (M_1) and AM (M_2).

and $r_1r_2 = 0.44$, the copolymerization would favor the short sequence of Na 11-AAU and AM. The azeotropic point of copolymerization was at about 60 mol% Na 11-AAU.

Molecular Weights and Radii of Gyration of the Copolymers

All the copolymers prepared exhibited only one glass transition temperature (T_g). The molecular weights of these copolymers were found to be around 1–2 million as determined by light scattering. Since the copolymers are polyelectrolytes, their aqueous solutions are not suitable for light-scattering measurements. However, upon addition of 0.1 or 0.3 mol/L NaCl to the aqueous copolymer solutions, the molecular weights of the copolymers could be determined satisfactorily by light-scattering measurements. The effect of the monomer feed composition on the molecular weights of the copolymers is shown in Table 2. The molecular weights were found to be around 1.5 million, and they remained about the same up to 50 mol% of AM in the monomer feed. They

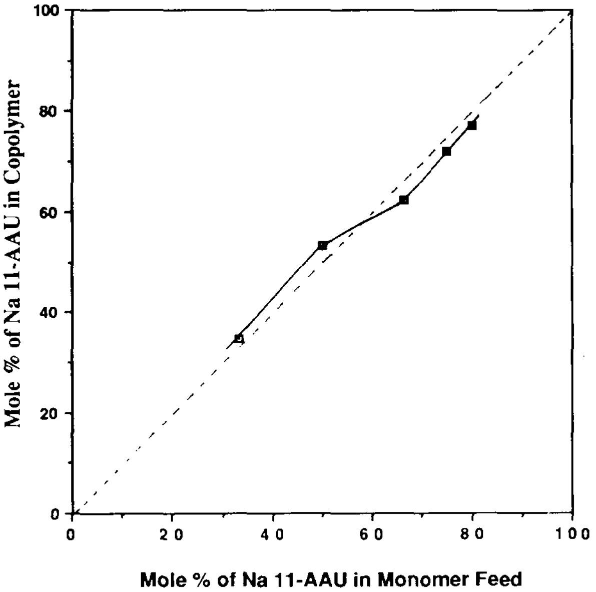

FIG. 4. Copolymer composition as a function of feed composition for the copolymerization of Na 11-AAU with AM. The dashed line represents ideal random copolymerization.

then decreased significantly to $\bar{M}_w = 0.88 \times 10^6$ when the AM in the monomer feed was increased to 70 mol%.

Table 2 also shows that both $<s^2>^{1/2}$ and A_2 increased with an increasing percentage of AM up to 50 mol% in the monomer feed. Since the copolymers consisted of long side chain Na 11-AAU and short side chain AM, the average spacing distance between long side chains with terminal carboxyl groups would increase with an increasing percentage of AM in the copolymer. From this it follows that the long side chains of the copolymers were increasingly expanded, resulting in higher radii of gyration. The increase of A_2 shows that the interaction between copolymer and solvent molecules increased in parallel with an increase of AM in the copolymer.

Both $<s^2>^{1/2}$ and A_2 for CopB50 decreased with increasing ionic strength of the solvent. In the presence of NaCl, certain fractions of the counterions (Na^+) remained associated with each polyion. This effectively reduced the charges on the polyion and hence the reduction of the macro-

TABLE 2. Molecular Weights, Radii of Gyration, and Second Virial Coefficients of Na 11-AAU-AM Copolymers

Sample No.	Feed composition, mol %		$\bar{M}_w \times 10^{-6}$	$A_2 \times 10^3$	$<s^2>^{1/2}$, nm	[NaCl], mol/L
	Na 11-AAU	AM				
A[a]	100	0	1.33	0.141	43.8	0.3
CopB30	70	30	1.62	0.102	45.7	0.3
CopB50	50	50	1.52	0.166	58.9	0.3
CopB50	50	50	1.66	0.712	75.5	0.1
CopB70	30	70	0.88	0.336	58.9	0.3

[a] Poly(Na 11-AAU) homopolymer.

molecular dimension. A similar effect has been observed in other polyelectrolyte systems [26].

Solution Properties of the Copolymers

The copolymers were readily soluble in water. They needed a longer time for dissolution at higher AM content. Their reduced viscosities (η_{sp}/c) increased with the AM content and were very much higher than those of the respective homopolymers (Fig. 5). This is consistent with the results for the radius of gyration which increased with AM content in the copolymers. Table 3 shows the intrinsic viscosities ($[\eta]_0$) of these copolymers dissolved in water and in NaCl solutions. Poly(Na 11-AAU) and polyacrylamide prepared under the same conditions are also included for comparison. The intrinsic viscosities for the copolymers in water were extremely high, i.e., they varied from 81 to 224 dL/g as the AM in the feed was increased from 30 to 70 mol%. But they decreased sharply to as low as 1.35 and 3.65 dL/g by the effect of 0.3 mol/L NaCl. Similarly, the intrinsic viscosity of poly(Na 11-AAU) dissolved in 0.3 mol/L NaCl also reduced from 58 to 0.75 dL/g. On the contrary, the intrinsic viscosity of the noncharged polyacrylamide solution showed a slight increase with the addition of NaCl.

The solution behaviors of poly(Na 11-AAU) and its copolymers with

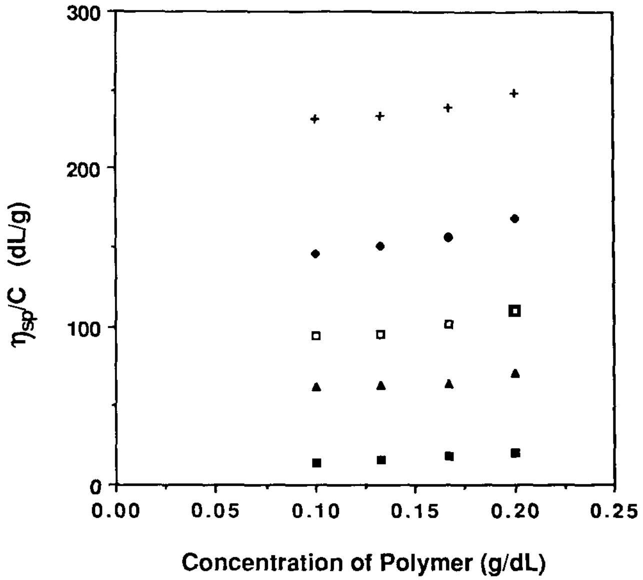

FIG. 5. Reduced viscosities of homopolymers and copolymers of Na 11-AAU and AM as a function of concentration. (▲) Poly(Na 11-AAU); (□) CopB30; (♦) CopB50; (+) CopB70; (■) polyacrylamide.

acrylamide are similar to those of typical polyelectrolytes. The hydrodynamic volume of a charged polymer decreases with an increase in the ionic strength of the polymer solution. The decrease in viscosity with increasing salt concentration is due to increased shielding of the ionized groups in the presence of excess counterions. This results in less expansion of the polymer chains owing to the diminishing effect of charge repulsion between the ionized groups.

The reduced viscosity (η_{sp}/c) of each aqueous copolymer solution decreased drastically during the first few weeks of aging at 23°C, as shown in Fig. 6. They then gradually reduced to their respective minimum viscosity. On the other hand, polyacrylamide was very stable while poly(Na 11-AAU) was sensitive to aging. The reduced viscosities for the copolymers with 30 and 70 mol% AM in the feed decreased by about 45% after 40 days of aging. But the copolymer with equimolar Na 11-AAU and AM (CopB50) suffered a severe loss of its viscosity by nearly 90%. This may be attributed to changes in inter- and intrachain hydrogen bonding via the carboxyl and amino groups of the copolymer. The variation of the

TABLE 3. The Intrinsic Viscosities of the Homopolymers and the Copolymers of Na 11-AAU and AM Dissolved in Water and in NaCl Solutions

Sample No.	Feed composition, mol%		$[\eta]_0$ in water, dL/g	$[\eta]_0$ in NaCl, dL/g	
	Na 11-AAU	AM		0.1 mol/L NaCl	0.3 mol/L NaCl
Poly(Na 11-AAU)	100	0	58	1.36	0.75
CopB30	70	30	81	2.28	1.35
CopB50	50	50	123	3.82	2.10
CopB70	30	70	224	6.30	3.65
Polyacrylamide	0	100	9	9.60	10.75

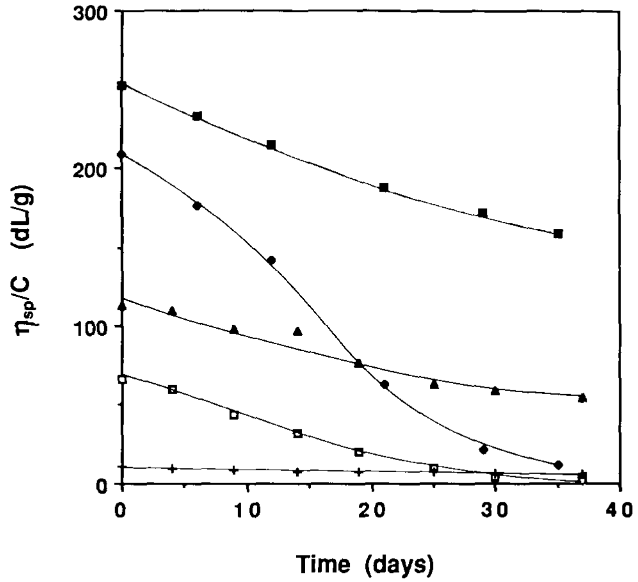

FIG. 6. Aging of homopolymer and copolymer of Na 11-AAU and AM at a polymer concentration of 0.3 g/dL and 23°C. (□) Poly(Na 11-AAU); (▲) CopB30; (◆) CopB50; (■) CopB70; (+) polyacrylamide.

molar ratio of these groups in the copolymer seemed to influence the extent of hydrogen bonding. It is envisaged that the CopB50 system is mainly associated with interchain hydrogen bonding initially and is gradually transformed to intrachain hydrogen bonding on aging. The aging effect of polyelectrolytes has generally been attributed to conformational changes that lead to a diminished hydrodynamic volume as a function of time [10, 12, 14, 17]. Such changes will eventually lead to the most thermodynamically stable polymer conformation, and its viscosity will be constant thereafter in the absence of biodegradation of the copolymer.

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