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Synthesis and Characterization of Poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid)

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ABSTRACT: Poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) (4) was prepared by the bulk polycondensation of 4-acetoxy-2,3,5,6-tetrafluorobenzoic acid (3). Polycondensation was conducted at 250 °C for 15 h and gave polymer with $\bar{X}_n$ of 135. Polymer 4 was characterized by elemental analysis, IR spectroscopy, differential scanning calorimetry, and wide-angle X-ray measurement. The crystal/nematic phase transition of polymer 4, which depends on the molecular weight, was observed at about 280 °C. Well-defined schlieren textures were observed in the nematic state. The phase transition temperature is 180° lower than that of poly(4-hydroxybenzoic acid). This thermal behavior of polymer 4 comes from fluorine substituents which decrease the dipole–dipole interaction among the polymer chains.

Introduction

Since thermotropic liquid-crystalline polymers (LCP) have shown promise as excellent engineering plastics due to their excellent mechanical properties, thermal stabilities, and chemical resistances, the synthesis of LCP has become of interest in recent years.[1] Among them, the thermotropic aromatic polyester, poly(4-hydroxybenzoic acid) (PHBA) has such a high melting point that melt processability is not feasible.[2] Therefore, various copolyesters of HBA with 5-hydroxynaphthoic acid (HNA)[3] or bisphenol terephthalate (BPT)[4] have been prepared to improve the processability.

Fluorine's small size, large electronegativity, low polarizability, and a large fluorine–fluorine repulsion lead to the interesting properties of fluoropolymers, such as good thermal stabilities, chemical resistances, small refractive indices, and weak cohesive forces between the molecules. Therefore, the introduction of fluorine atoms in PHBA would be expected to alter the physical properties of PHBA, such as solubility and thermal behavior, due to the decrease of cohesive forces between the molecules.

This article describes the successful synthesis and characterization of poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) by the self-polycondensation of 4-acetoxy-2,3,5,6-tetrafluorobenzoic acid.

Experimental Section

Materials. 2,3,5,6-Tetrafluorophenol (1) was purchased from Aldrich Co. and used without further purification. Acetyl chloride and triethylamine (TEA) were purified by distillation. Other reagents were obtained commercially and used as received.

4-Acetoxy-2,3,5,6-tetrafluorobenzoic Acid (3). This compound was prepared by carbonation of 2,3,5,6-tetrafluorophenol, followed by acetylation.

4-Hydroxy-2,3,5,6-tetrafluorobenzoic Acid Monohydrate (2). 2,3,5,6-Tetrafluorophenol (5 g, 0.03 mol) dissolved in freshly distilled dry tetrahydrofuran (THF) (15 mL) was added dropwise to a precooled (–65 to –60 °C) solution of *n*-butyllithium (42 mL of a hexane solution, 0.060 mol) in THF (120 mL). Time of addition was 15 min. After that, the mixture was stirred for 45 min at this temperature. Carbon dioxide was bubbled into the reaction mixture. One hour later the cooling bath was removed, and the reaction mixture warmed to room temperature with continued carbonation for 2 h. The mixture was then hydrolyzed with 6 M hydrochloric acid (90 mL) and phase separated, and the organic layer was dried over sodium sulfate. The solvent was distilled under reduced pressure to give white solids. Recrystallization from xylene produced white needles. The yield was 4.0 g (74%), mp 155–157 °C (lit.[5] 157 °C).

4-Acetoxy-2,3,5,6-tetrafluorobenzoic Acid (3). To a ice-cooled solution of 2 (5.32 g, 0.025 mol) and TEA (6 g, 0.055 mol) in THF (63 mL), a solution of acetyl chloride (2.5 g, 0.028 mol) in THF (32 mL) was added dropwise for 30 min. The mixture was stirred at 0 °C for 2 h, and then at room temperature for 2 h. The TEA·HCl was filtered, and the filtrate was diluted with water (100 mL), then acidified with 6 M hydrochloric acid. The solution was extracted with ether, and the combined organic layer was dried with Na_2SO_4. Evaporation of the solvent under reduced pressure gave white solids. Recrystallization from cyclohexane produced white needles. The yield was 3.8 g (60%), mp 129–130 °C. IR (KBr) 1805, 1716 cm^{-1} (C═O). ^{1}H NMR ($CDCl_3$): δ 8.67 (s, 1 H, –OH), 2.40 (s, 3 H, CH_3). ^{13}CNMR ($CDCl_3$): 165.86 (s, C═O), 163.58 (d, $^{13}J_{CF} = 1.4$ Hz, C═O), 19.88 (s, CH_3) ppm. Anal. Calcd for $C_9H_4F_4O_4$: C, 42.88; H, 1.60. Found: C, 42.59; H, 1.50.

Polymer Synthesis. A typical example of the polymerization follows. Monomer 1 was placed in a polymerization ampule equipped with gas inlet and outlet tubes. The ampule was heated in a metal bath to 130 °C. Temperature was raised to 150 °C at a heating rate 10 °C/min, then to 250 °C at a heating rate 20 °C/min. A vacuum was applied, and then a flow of nitrogen was introduced to maintain the pressure at 60 mmHg. The reaction mixture was held at 250 °C for several hours. The cold reaction product was mechanically powdered, extracted with boiling acetone, and dried in vacuo at 150 °C for 24 h. IR (KBr) ν 1786 (C═O), 1145 cm^{-1} (C—O). Anal. Calcd for $(C_7F_4O_4)_n$: C, 43.77. Found: C, 43.59.

Molecular Weight Analysis. The degree of polymerization was determined by the end group analysis described in ref 6. Polymer (0.03 g) was suspended in a 7 wt % aqueous KOH solution (2.3 mL). The mixture was refluxed for 3 h. The clear solution was cooled and was acidified with concentrated H_3PO_4 (0.4 mL). A dilution to 3.7 mL with deionized water provided the stock solution.

Stock solutions were analyzed with respect to acetic acid by using a Shimadzu GC-14A gas chromatograph with FID equipped with a thermon-3000 (60–80 mesh) glass column. Thus, 1-μm samples were injected with an injector temperature of 250 °C, a column temperature of 110 °C, a detector temperature of 250 °C, and a helium flow rate 30 cm^3/min. Propionic acid (250 ppm) was used as an internal standard. Assuming one acetoxy end group per chain, number average molecular weights were then calculated according to the following formula:

$$M_n = \frac{(60 \times 10^6)\ (\text{g of polymer})}{(\text{ppm AcOH})\ (\text{mL of stock solution})}$$

Measurements. Infrared, NMR, and Thermal Analysis. The infrared spectra were recorded on a Hitachi I-5020 FT-IR

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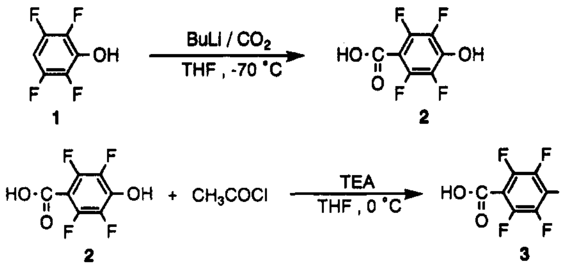
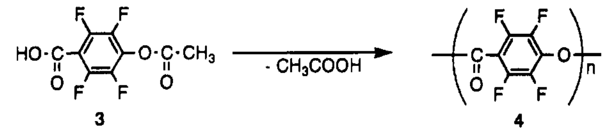
Scheme I



Scheme II



spectrometer, and the NMR spectra on a Hitachi R-22 (90 MHz) instrument. Thermal analyses were performed on a Seiko SSC 5000 thermal analyzer at a heating rate 10 °C/min for thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) of the samples was performed by use of a DSC 200 (Seiko Instruments and Electronics Ltd.) at a heating rate of 20 °C/min under an N_2 purge.

X-ray Diffraction Measurements. X-ray diffraction experiments were carried out by a RAD-rA diffractometer (Rigaku Denki Co. Ltd.) equipped with a heating device. Wide-angle X-ray diffraction (WAXD) traces were obtained by a step-scanning method using a scintillation counter system: the step width and fixed time were programmed for steps of 0.05 deg every 4 s. Changes in WAXD patterns during stepwise heating and cooling processes were recorded in the temperature range from 26 to 300 °C. WAXD photographs were taken using a flat camera.

Polarized Optical Microscopy. The specimen which was held between thin microscope cover slips was placed on the hot plate kept at the desired temperatures. When the specimen had melted, the upper cover slip was slid to prepare thin films, followed by quenching into liquid N_2. Phase transitions of the polymer during heating and cooling processes were examined using the polarized optical microscope equipped with a hot stage (Linkam Co., TH-600RMS).

Results and Discussion

Synthesis of Monomer. A new monomer, 4-acetoxy-2,3,5,6-tetrafluorobenzoic acid (3) was prepared by the reactions shown in the Scheme I.

4-Hydroxy-2,3,5,6-tetrafluorobenzoic acid (2) was obtained by the lithiation of 2,3,5,6-tetrafluorophenol (1), followed by carbonation of the lithium salt. Compound 2 was converted to monomer 3 in 60% yield by treatment with acetyl chloride in the presence of triethylamine (TEA). The structure of 3 was assigned on the basis of elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The IR spectrum showed characteristic absorptions at 1805 and 1716 cm^{-1} due to C=O stretching (Figure 1). The ^{1}H NMR spectrum of 3 consists of two singlets at 2.40 (3 H)) and 8.67 (1 H) that were assigned to the acetyl and carboxyl protons. Furthermore, the ^{13}C NMR resonances of C=O in 3 were observed at 163.58 (d $^{13}J_{CF}$ = 1.4 Hz) and 165.86 ppm.

Synthesis of Polyester. The synthesis of poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) (4) was carried out by the bulk polymerization of 3 (Scheme II). Since the melting point of monomer 3 is 130 °C, which is lower than that of 4-acetoxybenzoic acid (190 °C), polymerization was initiated at 130 °C. In order to avoid distillation of the monomer, reaction temperature was raised slowly to 150 °C at a heating rate 10 °C/h, then to 250 °C at a heating rate 20 °C/h. This operation resulted in the formation of oligomers. Next, a vacuum was applied, and then a flow of nitrogen was introduced to maintain the pressure at 60 mmHg. Polycondensation was allowed to continue for several hours at 250 °C. During polymerizations, sublimation of monomer 3 was still observed, and it was recovered. The results of all polycondensations are summarized in Table I. The number-average degree of polymerization $\bar{X}_n$ was determined by end-group analysis using gas chromatography. The $\bar{X}_n$ increased with increasing the polymerization time, and the polycondensation at 250 °C for 15 h gave polymer with $\bar{X}_n$ of 135.

Table I
Synthesis of Poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) (4)

no.	time,[a] h	yield,[b] %	$\bar{X}_n$[c]	$\bar{M}_n$
1	0	78	15	2880
2	1	80	25	4800
3	3	80	33	6340
4	5	82	61	11700
5	10	84	96	18400
6	15	84	135	25900

[a] Monomer was preheated at 130–150 °C (heating rate 10 °C/h). [b] After extraction with acetone. [c] The end-group analysis by gas chromatography.

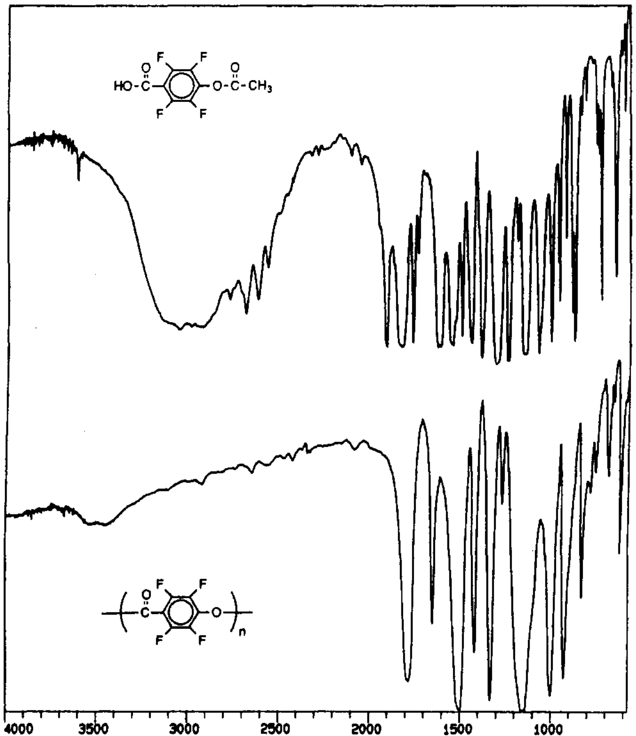


Figure 1. IR spectra of 4-acetoxy-2,3,5,6-tetrafluorobenzoic acid (3) and poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) (4).

Polymer Characterization. The polymer was confirmed to be the corresponding poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) 4 by means of infrared spectroscopy and elemental analysis. The IR spectra exhibited characteristic absorptions at 1786 and 1145 cm^{-1} due to C=O and C—O—C stretching (Figure 1). Elemental analysis also supported the formation of the expected polymer.

Polymer 4 was a faint gray solid and insoluble in all common solvents. The thermal stability of the polymer was examined by thermogravimetry (TG) under nitrogen. Typical traces for polymers with the different degrees of polymerization are shown in Figure 2. A two-stage characteristic with a relatively fast loss of weight between

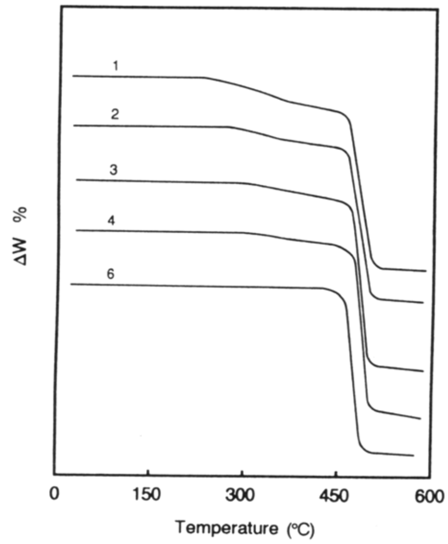


Figure 2. TG traces for polymers (**4**) with different degrees of polymerization in nitrogen.

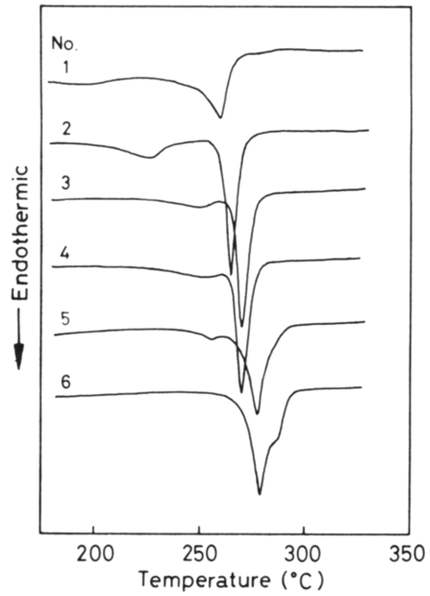


Figure 3. DSC traces of polymers (**4**) (no. 1–6).

280 and 350 °C and above 450 °C was observed for the polymer with $\overline{X}_n$ of 15 (no. 1). This two-stage characteristic disappeared gradually with increasing $\overline{X}_n$. Similar behavior was observed for studies of the thermal degradation of PHBA. Kricheldorf et al. interpreted the first weight loss as further condensation of the oligomers which led to elimination of acetic acid and larger molecules such as 4-acetoxybenzoic acid, 4-hydroxybenzoic acid, and 4-phenoxybenzoic acid phenyl ester might also appear as volatile byproducts.[7] Therefore, it can be assumed that the first weight loss of polymer **4** is also attributed to further condensation of the oligomers. The degradation temperature for 10% weight loss was 455 °C in nitrogen.

Thermal Properties. DSC curves of the as-synthesized polymer **4** (no. 1–6) samples are shown in Figure 3. All of the specimens exhibit an endothermic peak in the temperature range from 250 to 280 °C. Above this endothermic peak, the well-defined nematic texture was observed under a polarized optical microscope as shown in Figure 4, which was obtained at 330 °C from polymer **4** (no. 6). The scale of the schlieren texture is about 30 μm.

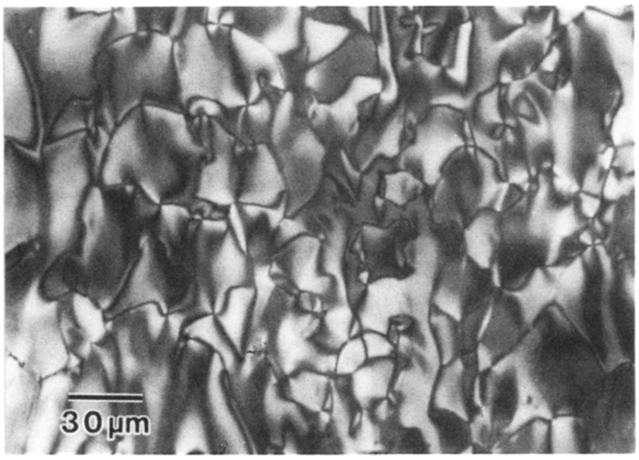


Figure 4. Polarized optical micrograph of polymer **4** (no. 6) observed above 280 °C (between crossed polarizers).

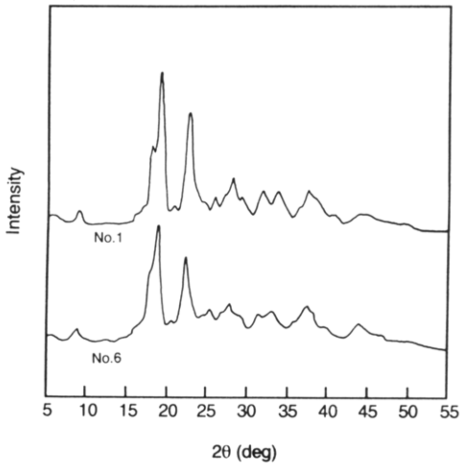


Figure 5. WAXD traces of polymer **4** (no. 1 and 6).

Economy et al.[6] reported that nematic textures of PHBA were observed at temperatures of 450–470 °C. Therefore, the phase transition temperatures of polymer **4** are ca. 180° lower than those of PHBA. The decrease of the phase transition temperature seems to come from the fluorine's properties; large electronegativity, low polarizability, and large fluorine–fluorine repulsion. These fluorine's characteristics reduce the dipole–dipole interaction among polymer **4** chains.

The phase transition temperatures increase with increasing $\overline{X}_n$. The crystallite sizes formed in polymer **4** depend on the molecular weight. The tendency of its thermal property is analogous to that of PHBA.[6]

Structure of Polymer 4. WAXD traces of polymers (no. 1 and 6) are shown in Figure 5. These profiles are almost identical. The values of *d* spacing for the reflections observed in them are summarized in Table II. These values were measured from the WAXD photographs taken at room temperature. The values for both samples are coincident within the limits of experimental error. These results suggest that the crystalline structures formed in polymer **4** are almost same regardless of $\overline{X}_n$.

Phase Transition of Polymer 4. DSC curves of polymer **4** (no. 4) for heating and cooling processes are shown in Figure 6. Two endothermic peaks are observed in the first heating process (a). And the DSC curve of the cooling process (b) exhibits a large exothermic peak at 200 °C. The DSC curve of the second heating process (c) clearly shows two endothermic peaks at 220 and 250 °C; the lower endothermic peak is larger than that of the first

Table II
Observed X-ray *d* Spacings of Poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) (4) (No. 1 and No. 6)

observed *d* spacing no. 1 (nm)	relative intensity[a]	observed *d* spacing no. 6 (nm)	relative intensity
0.990	w	0.995	vw
		0.633	w
0.538	vw	0.541	w
0.471	vs	0.473	vs
0.389	vs	0.395	s
0.359	vw	0.355	m
0.343	w		
0.315	m	0.317	m
0.300	w		
0.275	w		
0.262	m	0.266	m
0.245	vw	0.250	w
0.236	m	0.237	m

[a] Key: vw, very weak; w, weak; m, medium; s, strong; vs, very strong.

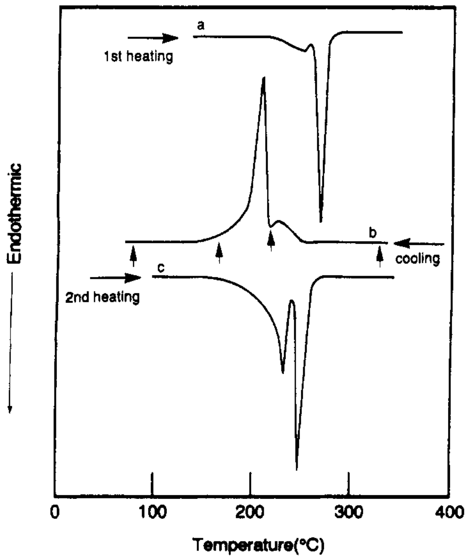


Figure 6. DSC traces of polymer 4 (no. 4) for heating and cooling processes.

heating process. The thermal behavior of all other samples is similar to those of polymer 4. In particular, the DSC profiles of the second heating process are almost the same, regardless of $\overline{X}_n$. The result is attributable to polymerization during the first heating process.

The WAXD traces were observed at various temperatures denoted by arrows on the DSC curve of the cooling process in Figure 6. Polymer 4 (no. 4) was heated rapidly up to 320 °C in the nematic state, and then the sample was cooled at 10 °C/min to the desired temperatures.

WAXD traces for the cooling process from 320 °C are shown in Figure 7. The WAXD curve obtained at 320 °C is broad, exhibiting a nematic profile. Many sharp reflections are observed in the WAXD curve obtained at 220 °C which is the temperature between two exothermic peaks. The WAXD profile at 220 °C is similar to those obtained below the lower exothermic peak, 170 °C and room temperature (RT). But, intensity of the reflection at 2θ = ca. 18° (d = ca. 0.49 nm) decreases in the WAXD curves of 170 °C and RT, where they are observed as a shoulder. On the other hand, the intensity of the reflection at 2θ = ca. 19° (d = ca. 0.47 nm) increases with cooling.

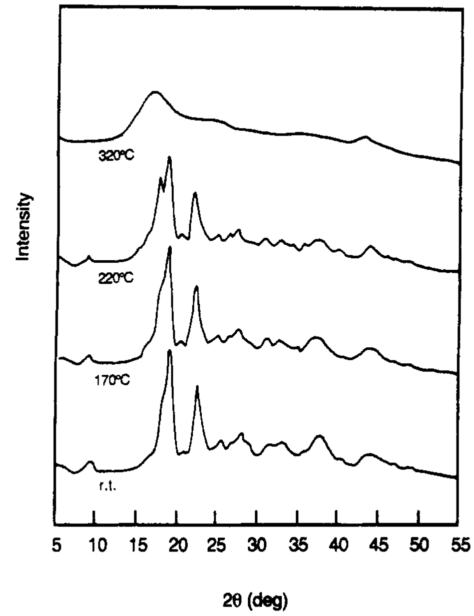


Figure 7. WAXD traces of polymer 4 (no. 4) in cooling process.

In the case of PHBA, Yoon et al.[8] have suggested that it exhibits a crystal/smectic transition at 300 °C. It is assumed that a polymorphism occurs through the exothermic peak of 210 °C in polymer 4. The structure formed at the temperature range between the two exothermic peaks may be a smectic one. However, the assignment is tentative and further investigation of the structure is under way.

In summary, our studies indicate that poly(4-hydroxy-2,3,5,6-tetrafluorobenzoic acid) (4) with high molecular weights can be readily prepared by the bulk polycondensation of 4-acetoxy-2,3,5,6-tetrafluorobenzoic acid (3). The phase transition temperature to a nematic state is about 180° lower than that of PHBA. A well-defined schlieren texture was observed in the nematic phase above 280 °C.

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