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Synthesis and characterization of wholly aromatic polyamides containing pendent amino and cyano groups

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Summary

The new pyrazole-ring containing diamine monomer with amino and cyano groups, 1,3-di-*p*-aminophenyl-4-cyano-5-aminopyrazole (PYA), was prepared from 4-nitrobenzoyl chloride and 4-nitrophenyl hydrazine with 4 steps. The monomer was converted to polyamides with terephthaloyl chloride and isophthaloyl chloride. The amino and cyano groups on the pyrazole-ring were not affected during polymerization. The synthesized polyamides having intrinsic viscosities of 0.92-1.18 dL/g were amorphous, and soluble in polar aprotic solvents and boiling acetone and THF. The polymers had high glass transition temperatures and high thermal stability. 5% weight loss temperatures in nitrogen occurred around 490°C, but these polymers are partially degraded at 300°C in air due to the amino group on the pyrazole-ring.

Introduction

Wholly aromatic polyamides (aramides) are high performance polymeric materials with many characteristic physical and chemical properties due to chain stiffness and intermolecular hydrogen bonding of amide groups (1). One of the disadvantages of these polymers is limited solubility and processability. Much research efforts have been concentrated on increasing processability with minimal effect on thermal stability. Incorporation of substituents as pendent groups (2,3,4) and flexible units along backbone (5,6,7) is a typical approach to improve solubility and processability through modification of chemical structure. Introducing functional groups as substituents is even more interesting because they can be used to impart special functionality to high performance polymers.

In this paper, we describe the synthesis and characterization of new wholly aromatic polyamides which have rigid but kink-catenated pyrazole-ring with amino and cyano groups. The diamine was prepared by a facile method using inexpensive and widely used starting materials. The thermal behavior of the polar functional groups were also described.

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Experimental

Materials

Terephthaloyl chloride and isophthaloyl chloride were recrystallized from *n*-hexane. N,N-Dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and N-methylpyrrolidinone (NMP) were stirred in the presence of P_2O_5 overnight and then distilled under reduced pressure. Malononitrile was purified by vacuum distillation. Methylene chloride and 1,2-dichloroethane were stirred in the CaH_2 overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were obtained from Aldrich, Acros, and Junsei chemical company, and used without further purification.

General measurement

^1H NMR and ^{13}C NMR spectra of synthesized compounds were recorded on Brucker Fourier Transform AC 200 (200MHz) or AM 300 (300MHz) spectrometers. Chemical shifts of ^1H NMR were reported in unit, parts per million (ppm) relative to the singlet at 7.24ppm for chloroform-*d* or to the center line of the quintet at 2.49ppm for methyl sulfoxide-d_6. Splitting patterns designated as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), and m (multiplet). FTIR spectra of the monomers and the polymers were obtained with Bomem Michelson series FTIR spectrphotometer using KBr pellet or film. Viscosity of polymers was measured by a Canon-Ubbelohde type viscometer at 30°C. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system. DSC measure-ments were made using a closed cell at a heating rate of 10°C/min in N_2 atmosphere. TGA measurements were made at heating rate of 10°C/min in N_2 or air. The tensile strength of the polymers were measured on an Instron 1125 Universal Testing Machine with a full-scale load of 5kg and a crosshead speed of 5mm/min. The film was cut into dumb-bell-shaped specimens with a micro-dumb-bell cutting die, to produce specimens having width and thicknesses of 0.32cm and 0.075-0.10mm, respectively.

Monomer synthesis

(Hydroxy-4-nitrophenylmethylene)propanedinitrile, sodium salt (1)

A reaction kettle equipped with mechanical stirrer and an additional funnel was charged with 4-nitrobenzoyl chloride (27.8g, 0.150mol), malononitrile (9.91g, 0.150mol), and 300mL of methylene chloride. The reaction mixture was stirred vigorously and cooled at 0°C. Benzyltriethylammonium chloride (1.71g, 7.51mmol) as a phase transfer catalyst was dissolved in 5mL distilled water and added to the reaction kettle. 50mL of 6N NaOH solution was added dropwise to the cold reaction mixture over 8hrs. The reaction mixture was then stirred at room temperature for another 3hrs. The resulting yellow precipitate was filtered, washed repeatedly with methylene chloride, and dried *in vacuo* at 70°C for 24hrs. (29.2g, 82.1% yield): IR (KBr, cm^{-1}): 3430 (br, O-Na); 2205 (CN); 1590 (aromatic); 1520, 1350 (NO_2).

(Chloro-4-nitrophenylmethylene)propanedinitrile (2)

A 250mL round-bottomed flask was fitted with an additional funnel with a N_2 inlet. The assembly was charged with **1** (12.0g, 50.6mmol) and 80mL of 1,2-dichloroethane. $POCl_3$ (31.0g, 202mmol) was added dropwise for 1hr, and the mixture was refluxed for 10hrs. This reaction mixture was cooled to room temperature and 1,2-dicloroethane and the excess $POCl_3$ were distilled at reduced pressure. The solid residue was extracted with hot methylene chloride several times. The dark brown methylene chloride extracts were

combined, passed through a bed of Celite on a glass funnel, concentrated, passed through a short silica gel column eluted with methylene chloride. This eluate was concentrated to yield a yellow solid. This product was recrystallized from chloroform / *n*-hexane to give bright yellow crystal. (7.91g, 66.9% yield): m.p. 113-114°C. IR (KBr, cm^{-1}): 3097 (aromatic C-H); 2238 (CN); 1590, 1570 (aromatic); 1520, 1350 (NO_2). ^1H NMR ($CDCl_3$, ppm): 8.38, 8.34, 7.99, 7.95 (dd, 4H). ^{13}C NMR ($CDCl_3$, ppm): 161.48, 150.26, 147.57, 130.06, 124.17, 110.67, 110.48, 88.73.

1,3-di-*p*-nitrophenyl-4-cyano-5-aminopyrazole (**3**)

A 250mL round-bottomed flask was charged with 4-nitrophenyl hydrazine (4.20g, 27.4mmol), DABCO (1.54g, 13.7mmol), and 50mL of NMP. To this solution, stirred under N_2 and cooled to 0°C, was added, dropwise, a solution of **2** (6.40g, 27.4mmol) in 60mL of NMP. The solution was stirred under N_2 at 0°C for 1hr, heated at 70°C for 12hrs, cooled to room temperature and poured into an ice-water mixture to precipitate. This precipitation was filtered, washed repeatedly with water and dried *in vacuo*. (8.83g, 92.0% yield): m.p. 320-321°C (with decomposition). IR (KBr, cm^{-1}): 3430, 3320, 3220 (NH_2); 2220 (CN); 1648 (C=N); 1598 (aromatic); 1520, 1340 (NO_2). ^1H NMR (DMSO-d_6, ppm): 8.40, 8.36, 8.12, 8.08 (dd, 4H); 8.38, 8.32, 7.94, 7.88 (dd, 4H); 7.31 (s, 2H).

1,3-di-*p*-aminophenyl-4-cyano-5-aminopyrazole (**4**)

A slurry of **3** (8.30g, 23.7mmol), $SnCl_2$ (32g, 169mmol), and 180mL of 95% EtOH was stirred while 80mL of concentrated HCl was added slowly. After addition of HCl was over, the mixture was refluxed for 12hrs. Excess EtOH was evaporated and the remaining solution was poured into 300mL distilled water. The solution was basified with 10% NaOH solution and the precipitate was filtered off, washed with hot water and cold MeOH, and recrystallized from DMAc / H_2O (v/v=1:2) to give light brown product. (5.38g, 78.2% yield): m.p. 246-247°C. IR (KBr, cm^{-1}): 3400, 3340, 3210 (NH_2); 2205 (CN); 1620 (C=N); 1600, 1520 (aromatic). ^1H NMR (DMSO-d_6, ppm): 7.13, 7.10, 6.67, 6.64 (dd, 4H); 7.54, 7.51, 6.63, 6.60 (dd, 4H); 6.21(s, 2H); 5.34 (s, 2H), 5.30 (s, 2H). ^{13}C NMR (DMSO-d_6, ppm): 152.25, 149.97, 149.34, 148.72, 126.73, 125.83, 125.61, 118.98, 116.33, 113.75, 113.49, 69.65.

Synthesis of model compound and polymerization

Model Compound (**5**)

A 25mL round-bottomed flask was charged with **4** (0.470g, 1.62mmol), benzoyl chloride (0.456g, 3.24mmol), and 9mL of DMAc. This mixture was stirred under N_2 at 0°C for 3hrs. To this solution, pyridine (0.356g, 3.24mmol) as an acid acceptor was added. After addition of pyridine, the solution was stirred at room temperature for 8hrs and poured into an ice-water mixture to precipitate a pale yellow solid that was filtered, washed with hot water and cold methanol repeatedly and dried *in vacuo*. (0.785g, 97.2% yield): m.p. 255-257°C. IR (KBr, cm^{-1}): 3330, 3210 (NH_2); 2210 (CN); 1650 (C=O of amide); 1600, 1520 (aromatic); 1530, 1415, 1320, 1250, 1182, 1108, 840, 703. ^1H NMR (DMSO-d_6, ppm): 10.47 (s, 1H), 10.42 (s, 1H); 8.00-7.82 (m, 10H); 7.59-7.48 (m, 8H); 6.76 (s, 2H).

PA1 (**6**)

A 50mL round-bottomed flask was charged with **4** (1.000g, 3.444mmol), terephthaloyl chloride (0.6993g, 3.444mol), and 17mL of DMAc. This mixture was stirred under N_2 at 0°C for 3hrs. To this solution, pyridine (0.356g, 3.24mmol) was added as an acid acceptor. After addition of pyridine, this solution was stirred at room temperature for 8hrs and poured into an ice-water mixture to precipitate pale yellow flakes that was filtered, washed

with hot water and hot methanol and dried *in vacuo*. (1.432g, 98.9% yield): The film was obtained from DMAc solution (10 wt% concentration). This viscous solution was cast on a glass plates and heated *in vacuo* at 80°C for 12hrs.: T_g (not detected until 370°C). [η] = 0.92 dL/g (DMAc at 30°C); IR (KBr, cm^{-1}): 3400-3100 (br, NH and NH_2); 2210 (CN); 1640 (C=O of amide); 1600, 1515 (aromatic); 1414, 1315, 1250, 1180, 1115, 836, 715. ^{1}H NMR (DMSO-d_6, ppm): 10.64 (s, 1H), 10.59 (s, 1H); 8.14 (s, 4H); 8.08-7.85 (m, 6H), 7.62, 7.57 (d, 2H); 6.80 (s, 2H).

PA2 (7)

The above procedure was repeated with isophthaloyl chloride. (1.428g, 98.6% yield): T_g 334°C. [η] = 1.18 dL/g (DMAc at 30°C). IR (KBr, cm^{-1}): 3400- 3100 (br, NH and NH_2); 2210 (CN); 1640 (C=O of amide); 1600, 1520 (aromatic); 1415, 1316, 1245, 1182, 1120, 835, 710. ^{1}H NMR (DMSO-d_6, ppm): 10.67 (s, 1H), 10.61 (s, 1H); 8.59 (s, 1H), 8.21, 8.17 (d, 2H), 7.73 (t, 1H); 8.02-7.85 (m, 6H), 7.61, 7.57 (d, 2H); 6.78 (s, 2H).

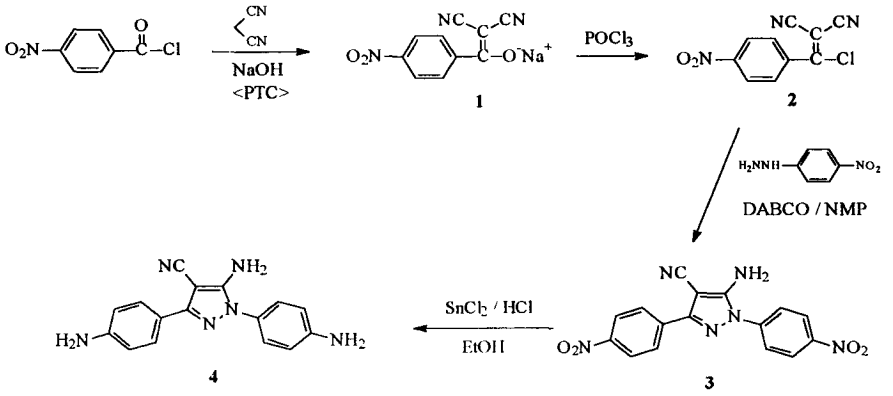
Results and discussion

Synthesis and characterization of monomer

Pyrazole-ring containing diamine monomer (**PYA, 4**) with the amino and cyano functional groups was prepared according to the reaction sequence of Scheme 1. This reaction was previously reported as a polymer forming reaction in the synthesis of polypyrazoles by Moore *et al* (8).

4-Nitrobenzoyl chloride was reacted with malononitrile under basic, phase-transfer condition to provide the sodium salt of the enol (**1**). Reaction of this anhydrous salt **1** with $POCl_3$ produced the desired (chloro-4-nitrophenylmethylene)propanedinitrile (**2**) (9). Wallenfels had pointed out an analogy between the dicyanomethylidine group (=$C(CN)_2$) and the carbonyl oxygen atom (10). The two units have similar inductive and resonance effects, and show similar reactivity over many reactions. The pyrazole-ring formation was done by reacting **2** and 4-nitrophenyl hydrazine in the presence of DABCO as an acid acceptor (8). In the synthesis of **3**, it was observed that the reaction was extremely rapid. This fact led to the concern that this reaction might be so rapid that selectivity and regiochemical control might be lost, yielding two different regioisomers. However, the only one product **3** was obtained presumably because of poor nucleophilicity of secondary amine in 4-nitrophenyl hydrazine. Intermediate was not isolated, but cyclized to give stable pyrazole derivative. Dinitro compound **3** was reduced with stannous chloride and HCl to give corresponding diamine monomer **4**. In this reduction process, the amino and the cyano groups on the pyrazole-ring were not affected, and **4** was obtained with high yield. The overall yield of this four-step process was about 40%.

The structures of pyrazole-ring containing diamine monomer **4** was confirmed by spectroscopic data. FTIR spectrum of **4** shows peaks at absorption band at 3397 and 3338 cm^{-1} corresponding to primary amines, 3209 cm^{-1} to hydrogen bonding characteristics of the primary amines, 2205 cm^{-1} to CN stretching. ^{1}H NMR spectrum of **4** shows 5.34 and 5.30 ppm corresponding to four protons of two primary amines on the phenyl-rings, 6.21 ppm to two protons of primary amine on the pyazole-ring, 7.13-6.60 ppm with two doublets of doublet to eight protons of two phenyl rings. All of twelve carbon peaks are detected in ^{13}C NMR spectrum, and well matched with expectation.



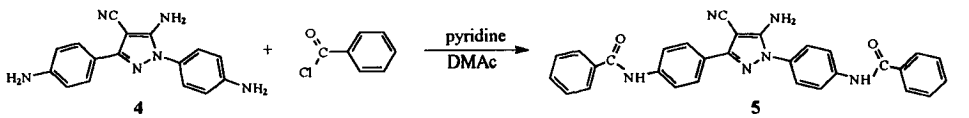
Scheme 1.

Model Reactions

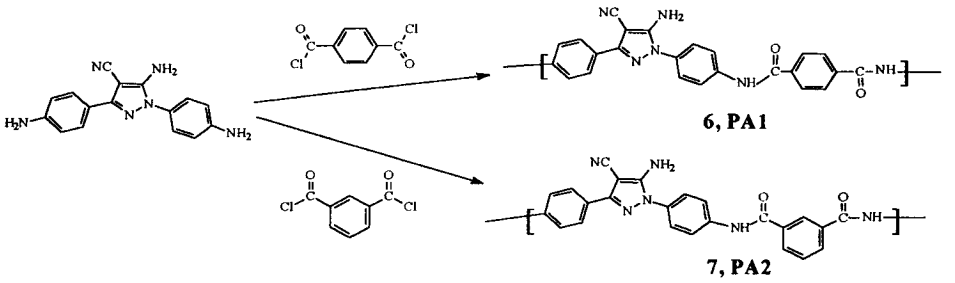
Model reaction was conducted to investigate the amine reactivity on the pyrazole-ring as well as to obtain a model compound which can be used as a reference for structural and thermal characterization of corresponding polymers. **4** was reacted with mono-functional benzoyl chloride to give model compound (**5**) with a quantitative yield (Scheme 2.).

It was found that the amino group on the pyrazole-ring was not reacted with benzoyl chloride and the cyano group on the pyrazole-ring was remained intact in low-temperature solution condensation This result was confirmed by FTIR and ^{1}H NMR spectra. ^{1}H NMR spectrum of **5** shows peaks at 10.47 and 10.42 ppm corresponding to two amide protons (C(=O)-NH-) as well as at 6.77 ppm corresponding to the unreacted primary amine protons on the pyrazole-ring. IR spectrum of **5** also shows absorption band at 3300 and 1650 cm^{-1} corresponding to the N-H and C=O amide stretching, respectively, as well as 2210 cm^{-1} to the CN stretching. Even though amine stretching region was not clearly resolved because of absorbed water by hygroscopic **5**, the trace of primary amine absorption can be seen in the IR spectrum.

The fact that the amino group attached on the pyrazole-ring did not react with acid chloride indicates poor nucleophilicity of the amine that is caused by strong electron withdrawing effect of the cyano group at the ortho position as well as electron deficient characteristics of pyrazole-ring. Thermal stability of this model compound was examined by TGA and DSC. The model compound was stable up to 370°C in nitrogen, and had no thermal transition except melting at 256°C. The result is somewhat unexpected because the amino and cyano groups on pyrazole-ring have a potential to undergo thermal reaction such as crosslinking or degradation. The unusual stability and inertness of the amino and cyano groups may stem from conjugative interaction of the amine with pyrazole-ring that is fortified with cyano group on the same ring.



Scheme 2.



Scheme 3.

Polymerization

The preparation of aromatic polyamides by low-temperature solution polycondesation has been well known. This method was used here to polymerize the diamine monomer **4** with terephthaloyl chloride and isophthaloyl chloride (Scheme 3.). Polymers obtained with this method formed fibrous bright-yellow precipitates up on pouring of the reaction mixture into stirring water. In all cases, the polymers were obtained with quantitative yields.

The formation of polyamides was confirmed by spectroscopic data. The FTIR spectra of the polymers show characteristic absorption bands of amide bonds at 3300 and 1640 cm^{-1}. The ^1H NMR spectra of the polymers show two sharp peaks of 10.47 and 10.42 ppm corresponding to amide protons (C(=O)-NH-). Moreover, it was confirmed that the amino and the cyano groups on the pyrazole-ring was remained intact during polymerization. The FTIR spectra show absorption band at 2210 cm^{-1} corresponding to the CN stretching, and the ^1H NMR spectra show the peaks at 6.79 (**PA1**) and 6.77 (**PA2**) ppm corresponding to the amino group on the pyrazole-ring. The IR and ^1H NMR spectra of the model compound and **PA1** are shown in Figure 1 and Figure 2, respectively.

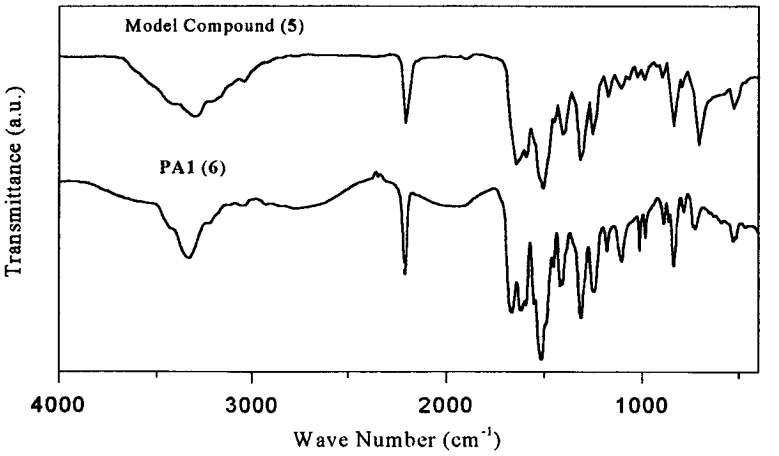


Figure 1. IR spectra of model compound (up) and **PA1** (bottom).

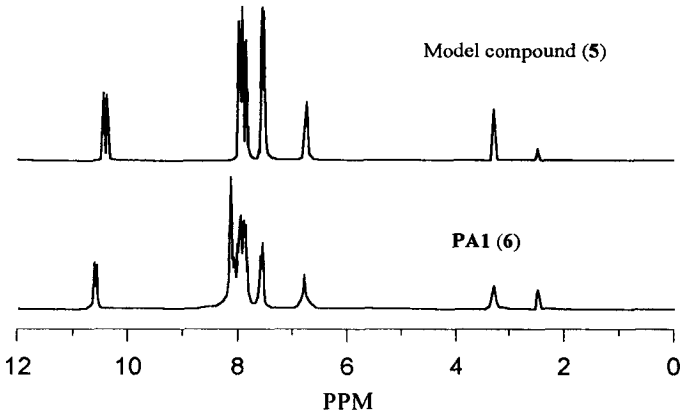


Figure 2. ^{1}H NMR spectra of model compound (up) and **PA1** (bottom).

Characterization of polyamides

The solubility of the polyamides was tested in various solvents. **PA1** and **PA2** are well soluble in polar aprotic solvents such as NMP, DMAc, DMF, and DMSO, and in phenolic solvents such as *m*-cresol. The two polymers are partially soluble in acetone and THF at room temperature, but dissolved in boiling acetone and THF. The intrinsic viscosities of **PA1** and **PA2** are 0.92 and 1.18 dL/g, respectively. These polymers give fingernail-creasable, transparent, and mechanically tough films on casting.

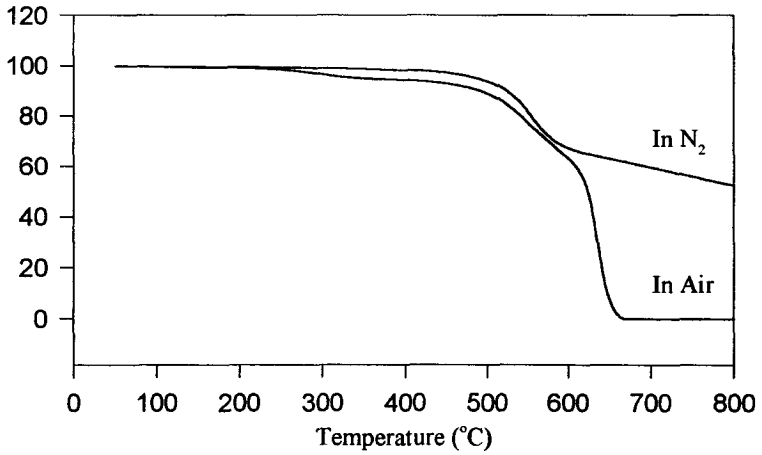


Figure 3. TGA curves of **PA1**.

The thermal behavior of these polyamides was studied by TGA and DSC. The 5% weight loss temperatures of **PA1** and **PA2** are 490 and 489°C in nitrogen, and 401 and 393°C in air, respectively. In the case of TGA analysis in air, the sudden 4% weight loss occurred near 300°C, which is equal to the weight of amino group in the repeating unit. This result indicates that the amino group on the pyrazole-ring may be degraded thermooxidatively at 300°C in air. The TGA curves of **PA1** are shown in Figure 3. The T_g of the **PA2**, determined by DSC, is 334°C. However, the T_g of **PA1** is not detected up to 370°C by DSC. Generally, para-linked polymers have higher T_g than meta-linked ones due to chain rigidity (1). Therefore, the T_g of **PA1** may be over 370°C. The tensile strength of **PA1** and **PA2** was 746 kg/cm^2 (73.1 MPa), and 663 kg/cm^2 (65.0 MPa), respectively.

Conclusions

Wholly aromatic polyamides containing amino and cyano functional groups in the pyrazole-ring were synthesized from new diamine monomer by using low-temperature solution condensation method. The synthesized polymers are amorphous and soluble in polar aprotic solvents as well as in boiling acetone and THF. They had high molecular weight and good thermal and mechanical properties. Surprisingly, the amino and cyano groups on the pyrazole-ring were thermally stable and did not undergo any curing reaction..

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