Synthesis and Chemical Degradation of Thermostable Polyamide with Imine Bond for Chemical Recycling

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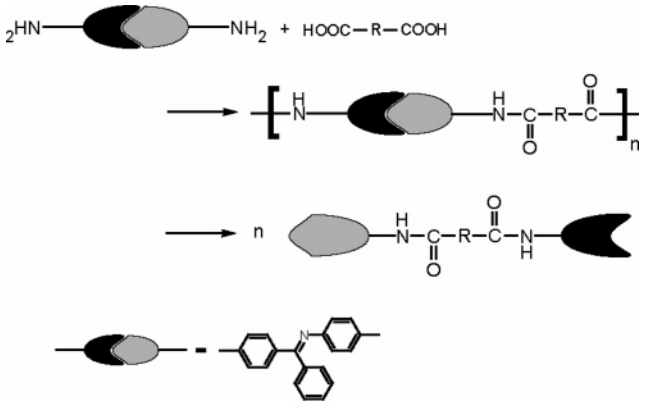
ABSTRACT: The mono-, di-, and triamino-substituted cyclic phenylazomethine (CPA) and diamino-substituted linear phenylazomethine (OPA) were synthesized in one-step via dehydration of aromatic amine and ketone in the presence of titanium tetrachloride. The linear and branched aromatic polyamides were prepared by the direct polycondensation of the di- or triamine monomers and various dicarboxylic acids in the presence of triphenyl phosphite and pyridine as condensation agents. Thermogravimetric analysis (TGA) revealed that the polymers had a high thermal stability. The temperature for a 10% weight loss determined by TGA was over 500 °C for some of the polymers. The hydrolysis property of the polymers was investigated using UV−vis spectroscopy. The spectra of the polymer solution in the presence of dilute sulfuric acid revealed that a simple and selective acid-catalyzed hydrolysis of azomethine bonds quantitatively occurred in mild conditions without cleavage of the amide bond, and more than 99% of the azomethine bonds were hydrated in less than 10 min at ambient temerature. The hydrolysis rate of the polymer was also determined. In polymer materials, these aromatic polyamides made it possible to relate high thermal stability with the decomposition property for effective chemical recycling.

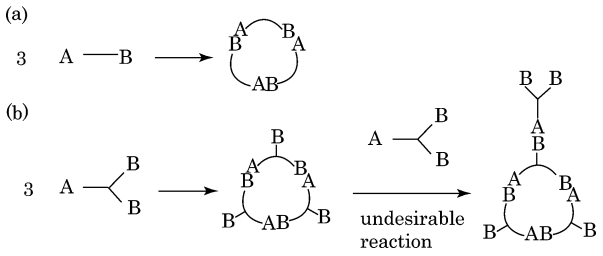
Introduction

Recently, polymers, which are chemically or biochemically degradable under mild conditions, have received much attention.[1] Polyphenylazomethines,[2] which have a high thermal stability and may be completely hydrated in an acid solution, are attractive polymers for recyclable plastics. The aromatic polyamide (aramid) is a useful engineering plastic having high thermal and chemical stabilities, but such properties make them difficult to dispose of as waste. The introduction of azomethine bonds into the aramid backbone should facilitate chemical degradation under mild conditions via hydrolysis of the azomethine bonds. Until now, various kinds of polymers containing azomethine bonds have been synthesized and mainly investigated as liquid crystalline polymers. In a previous papar, the degradation in poly(phenylazomethine)s has been reported.[3] On the basis of this idea, we now report the synthesis, thermostability, and chemical degradation of linear and branched aromatic polyamides having phenylazomethine units, which act as a degradation site (Scheme 1).

Scheme 1. Hydrolysis of Aromatic Polyamide Containing Phenylazomethine Bonds



Scheme 2. Formation of Cyclic Compounds in the Polymerization of (a) the AB Monomer or (b) the AB_2 Monomers



Results and Discussion

Synthesis of the Monomers. Hyperbranched polymers and dendrimers[4] have received much attention as novel high-performance polymers. These polymers were synthesized from multifunctional monomers. Especially, multifunctional cyclic compounds should be utilized as novel monomers because they have a cavity for molecular recognition. In general, cyclic compounds are obtained as a side product during the polymerization of the AB monomers (Scheme 2a).[5] On the other hand, during the polymerization of the AB_2-type monomers, the yield of each cyclic oligomer is too low to isolate[6] because undesirable reactions occur between the cyclic oligomers with monomers (Scheme 2b). However, if such cyclic compounds are obtained in a one-step synthesis, they will be supplied as novel multifunctional cyclic monomers for high-performance polymers and/or various functional polymers.[7]

Poly(phenylazomethine)s are synthesized by dehydration of diamines with dialdehydes/diketones.[8] On the other hand, in previous papers, we have reported the selective synthesis of cyclic phenylazomethine trimers via dehydration of aminophenyl ketones, which are AB-type monomers. In addition, we have also reported the selective synthesis of cyclic phenylazomethine triamino trimer via dehydration of 4,4′-diaminobenzophenone, which are AB_2-type monomers.[9] We tried the dehydration of the AB_2-type monomer with the AB-type monomer to obtain mono- and diamino-substituted cyclic CPAs.

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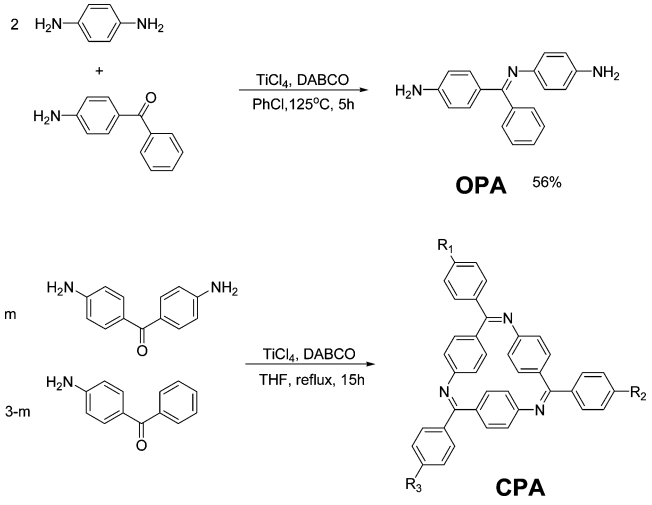
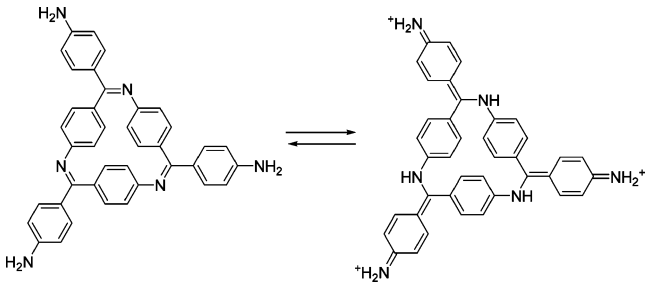
Scheme 3. Synthesis of Multifunctional Cyclic Phenylazotmethines (CPAs)



m	R_1	R_2	R_3	yield, %
3	NH_2	NH_2	NH_2	20 (CPA-3a)[9(c)]
2	NH_2	NH_2	H	11 (CPA-2a)
1	NH_2	H	H	19 (CPA-1a)
0	H	H	H	51 (CPA-0a)[9(c)]

Mono- and diamino-substituted CPAs (CPA-1a and -2a) were isolated in 19% and 11% yield, respectively, by dehydration with a mixture of 4,4′-diaminobenzophenone (AB_2 monomer) and 4-aminobenzophenone (AB monomer). Diamino-substituted linear phenylazomethine (OPA) was isolated in 56% yield by dehydration with a mixture of *p*-phenylenediamine and 4-aminobenzophenone. The yields (11% and 19%) are surprisingly high for the yield of the solo cyclic compound formed during the polymerization of the AB_2 with the AB-type monomer (Scheme 3). In addition, these results show that the intramolecular cyclization occurs much more preferentially than the linear oligomerization during this polymerization. This idea was supported by TOF-MS measurement as follows.

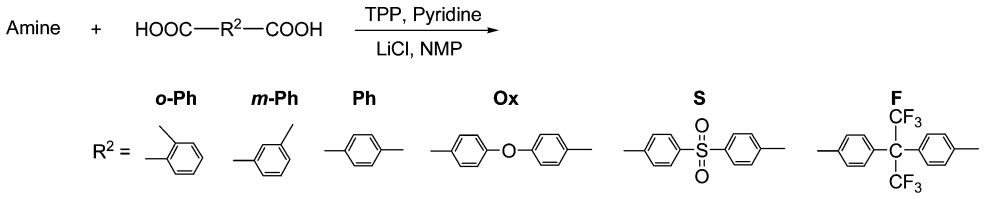
Scheme 4. Resonance of CPA-3A in Trifluoroacetic Acid



The TOF-MS measurement is useful for investigating the degree of polymerization of polymers. In general, two kinds of peaks, strong peaks attributed to linear oligomers and weak peaks to cyclic ones, appear in the spectra of the polymers. Interestingly, the spectrum of the reaction mixture during the polymerization of the AB_2 monomer with AB monomer shows only peaks attributed to oligomers with at least one cyclic structure (Figure 1). That is, most of the compounds formed in this reaction have a cyclic structure. This special phenomenon is considered to occur the easy formation of the cyclic oligomers, especially the cyclic trimer, CPA-3a, because a certain ratio of the oligomers greater the tetramer are expected to contain the cyclic trimer as a cyclic component.

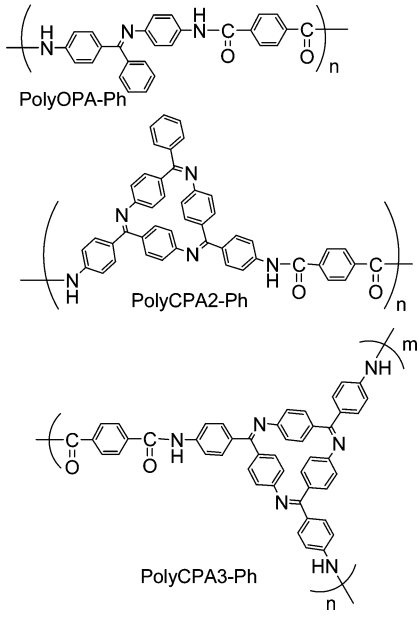
The ^{1}H NMR measurement shows that the structure of CPA-3a has high symmetrical structure in solution (Figure 2a). On

Table 1. Synthesis of Polyamide Having Phenylazomethine Units



Run	Amine	Carboxylic acid	Yield/%	Mw/x10^4	$Td_{10\%}$ /°C	DR /x10^{-2} s^{-1}
1	OPA	*o*-Ph	5	——	——	
2	OPA	*m*-Ph	94 (polyOPA-*m*-Ph)	3.0	459	
3	OPA	Ph	99 (polyOPA-Ph)	12.1	464	6.5
4	OPA	Ox	99 (polyOPA-Ox)	5.7	440	
5	OPA	S	99 (polyOPA-S)	4.8	437	
6	OPA	F	94 (polyOPA-F)	4.1	446	14
7	CPA2	Ph	98 (polyCPA2-Ph)	2.0	521	2.6
8	CPA2	Ox	99 (polyCPA2-Ox)	4.5	490	
9	CPA2	S	99 (polyCPA2-S)	5.1	457	
10	CPA2	F	99(polyCPA2-F)	5.3	450	2.8
11	CPA3	Ph	79 (polyCPA3-Ph)	4.8	538	1.7
12	CPA3	Ox	86[a] (polyCPA3-Ox)	3.8	518	

[a] Refer to 10(a) related to the critical conversion for gelation in the polymerization of A_2 and B_3 system.



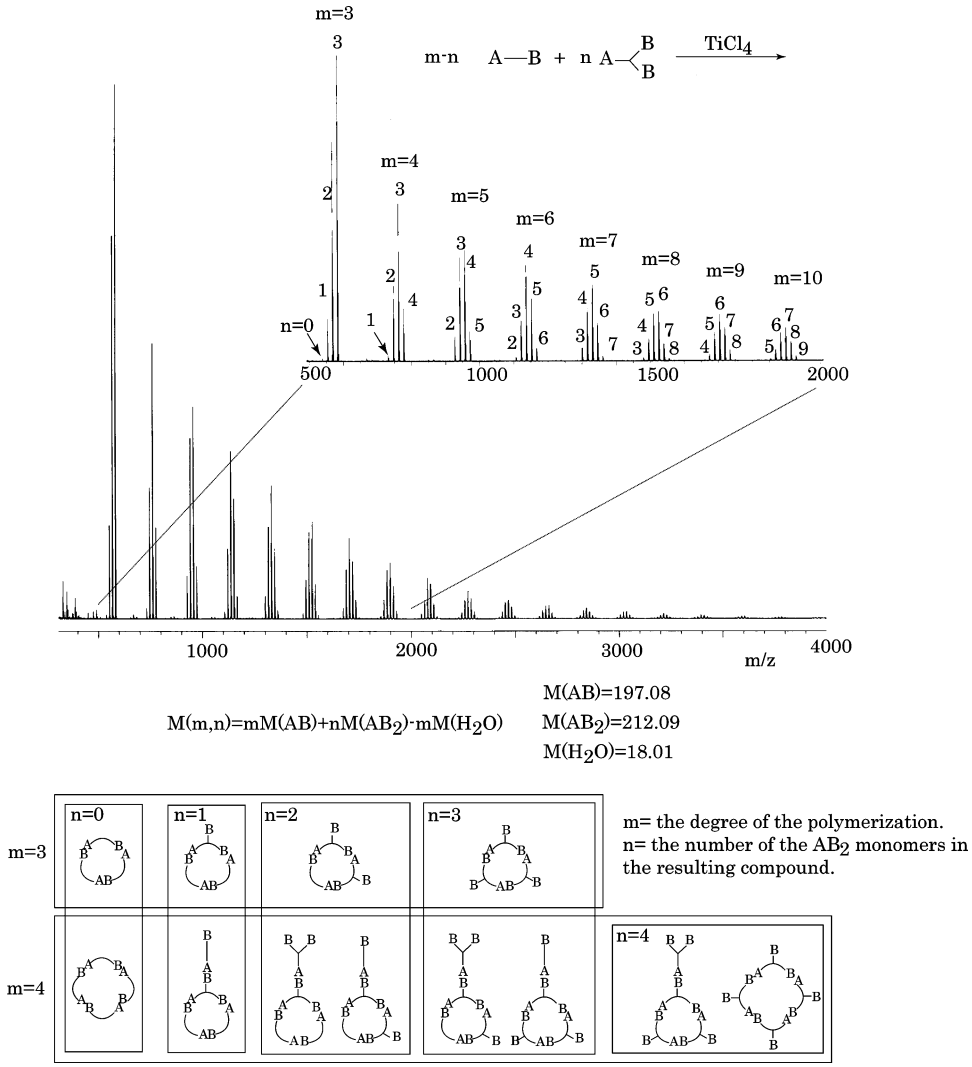


Figure 1. TOF-MS spectrum of the crude solution in the synthesis of CPA-2a and -1a.

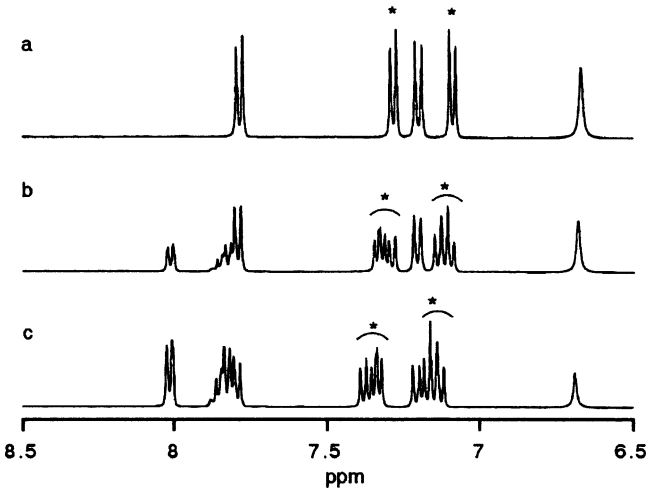


Figure 2. ^{1}H NMR spectra (270 Hz, DMSO-d_6) of (a) CPA-3a, (b) CPA-2a, and (c) CPA-1a. The marked peaks (*) are attributed to the protons at the three phenyl rings forming the cyclic structure of CPAs.

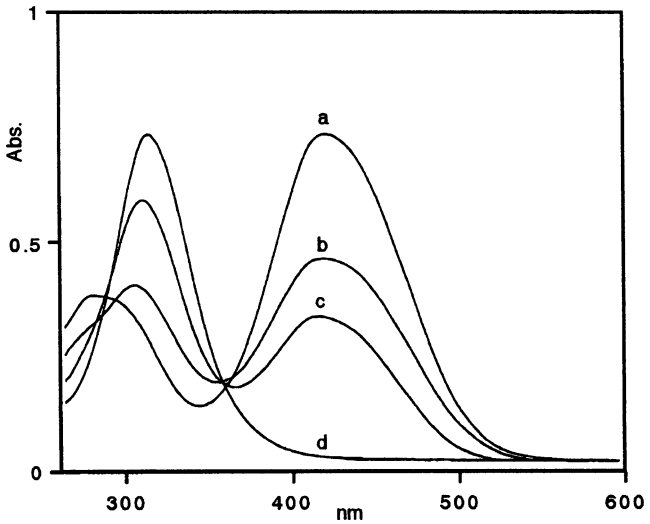


Figure 3. UV−vis spectra of (a) CPA-3a, (b) CPA-2a, (c) CPA-1a, and (d) CPA-0a in trifluoroacetic acid.

the other hand, in the spectra of CPA-1a and -2a, peaks attributed to the protons at the three phenyl rings forming the cyclic part appear as three pairs of doublet based on the asymmetrical structure (Figure 2b,c).

The UV−vis spectra give useful information about the structure and/or π-conjugation of the molecules. The spectrum of CPA-0a, which has no amino groups, in trifluoroacetic acid shows an absorption at 320 nm, which is based on the $\pi-\pi^*$ transition of the protonated imine part (Figure 3d). On the other hand, a new absorption at 420 nm appeared in the spectra of CPA-3a, -2a, and -1a (Figure 3a−c). This absorption is analogous to one based on a quinoidal structure, and the

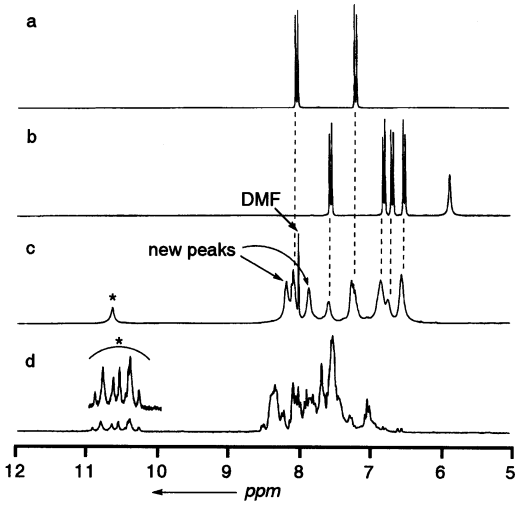


Figure 4. [1]H NMR spectra of (a) oxybis(benzoic acid), (b) CPA-3a, (c) polyCPA3-Ox, and (d) polyOPA-Ox. The indicated peaks (*) are attributed to amide protons.

absorption was enhanced by the increase in the number of amine groups in the CPAs. Therefore, the absorption is based on the resonance with the quinoidal-type structure, as shown in Scheme 4.

Synthesis of Polymers. Using a linear azomethine compound (OPA) and cyclic phenylazomethine trimers (CPAs) as a di- or triamine monomer, novel aromatic polyamides having azomethine units were synthesized by polycondensation with some dicarboxylic acids in the presence of pyridine, triphenyl phosphite (TPP), and LiCl (Table 1).[10] The polymerization of OPA with *o*-phthalic acid did not proceed because of steric hindrance (run 1), but those with iso-, terephthalic acid, and oxybis(benzoic acid) (*m*-Ph, -Ph, and Ox) proceeded to give the corresponding polymers (polyOPA-*m*-Ph, polyOPA-Ph, and polyOPA-Ox) in 94%, 99%, and 99% yields, respectively (runs 2, 3, and 4). The polymerization of CPA2 and CPA3 with the dicarboxylic acids gave polyCPA2-Ph, -Ox, polyCPA3-Ph, and -Ox in 79−99% yields (runs 7, 8, 11, and 12). The molecular weight was determined to be 20 000−120 000 (polystyrene standards) by GPC measurement using DMF including 10 mM LiBr as an effluent.

The formation of amide bonds in each polymer was confirmed by [1]H NMR measurements. Especially, polyCPA3-Ph and -Ox have relatively simple spectra due to the highly symmetric structure of the CPA-3a units. As shown in Figure 4c, only one peak attributed to the amide proton appeared at 11.6 ppm in the spectrum of polyCPA3-Ox. The peak at 5.95 ppm attributed to the amine proton of a CPA-3a monomer (Figure 4b) disappeared during the polymerization. In addition, new peaks at 7.9 and 8.2 ppm attributed to aromatic protons were confirmed in the spectrum of the polymer compared to the spectra of the monomers (Figure 4a,b). On the other hand, the spectrum of polyOPA-Ox is complex and shows eight peaks between 10 and 11 ppm attributed to the amide protons (Figure 4d) because OPA is an asymmetric compound. These eight peaks are considered to appear due to the *E*/*Z* isomers in the azomethine bond and the two kinds of bond combinations (head-to-tail and head-to-head) of the monomers during the polymerization.

The thermogravimetric analysis (TG) of the polymers shows a clear relationship between the structure and the thermal stability (Table 1). That is, (1) the thermal stability increased by the introduction of the bulky CPA units in the aramid backbone ($Td_{10\%}$: polyOPA-Ph; 463 °C, polyCPA2-Ph; 521 °C). The bulky CPA is an effective unit for enhancement of the thermal stability. (2) The branched structure made the polymer more thermostable based on the network between the branches ($Td_{10\%}$: polyCPA3-Ph; 538 °C). (3) The thermal stability of the polymers decreased about 20−30 °C by introduction of the ether bond in the backbone.

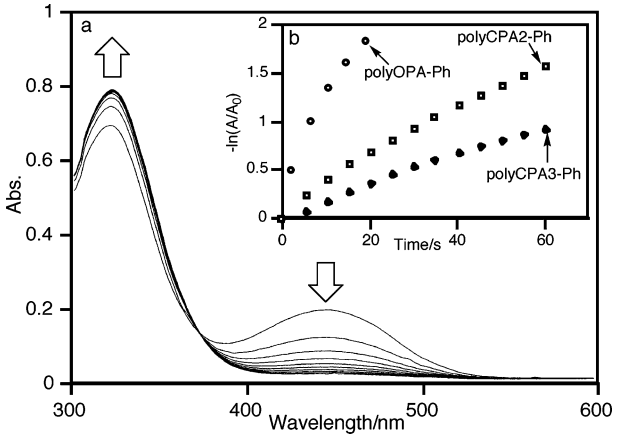


Figure 5. (a) UV−vis spectral change in polyCPA3-Ph in an acidic solution (DMF/THF = 1:1 including 0.4 M sulfuric acid). (b) Relationship between $-\ln(A/A_0)$ and time.

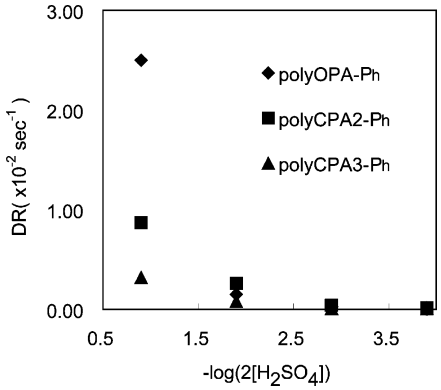


Figure 6. Relationship between the concentration of sulfuric acid and degradation rate (DR). The DR of each polymer in the area $-\log[2(H_2SO_4)] > 3$ was less than 10^{-7} s^{-1}.

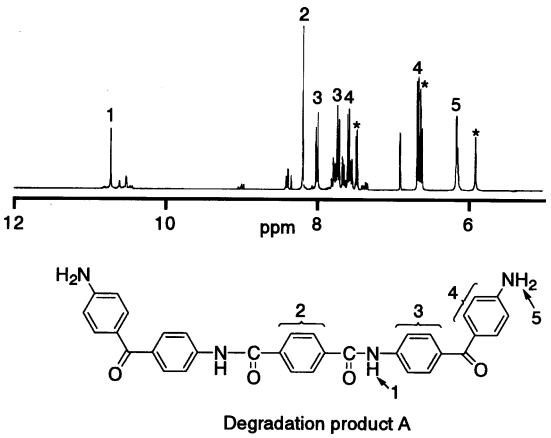


Figure 7. [1]H NMR spectra of the crude products during the hydrolysis of polyCPA3-Ph. The preferential formation of hydrolysate A was confirmed by the spectrum, and the marked peaks (*) were attributed to 4,4′-diaminobenzophenone.

The degradation property of the obtained polymers was investigated in an acidic solution at room temperature.[11] A typical procedure is as follows. The resulting polymer ([polymer] = 4.0×10^{-5} M per imine unit) was dissolved in a solvent (DMF:THF = 1:1 mixture), and a 3 mL polymer solution was

then placed in a 1 cm quartz cell. 200 μL of diluted sulfuric acid (concentrated sulfuric acid:H_2O = 1:2 mixture) was added to the cell using microsyringe. The spectra changed with an isosbestic point. The absorption around 450 nm, attributed to the $\pi-\pi^*$ transition of the imine bond, decreased. As an example, the spectral change of polyCPA3-Ph is shown in Figure 5a. After the hydrolysis, ^{1}H NMR suggested the structure of a hydrolysate. It is revealed that the amide bond is not hydrated under these conditions and that the azomethine bond obviously preferentially cleaves into an amine and a ketone.

The reaction selectively proceeds and obeys pseudo-first-order kinetics. The degradation rates (DR) during the hydrolysis of polyOPA-Ph, polyCPA2-Ph, and polyCPA3-Ph were calculated to be 6.5×10^{-2}, 2.6×10^{-2}, and 1.7×10^{-2} s^{-1}, respectively, from the change for the absorption around 450 nm (Table 1 and Figure 5b). These rate constants show that over 99% of the imine bonds are hydrated within 10 min. The molecular weight (M_w) of the product during hydrolysis was not correctly determined by GPC due to the low M_w. The degradation rates of the obtained polymers correspond to those of the imine monomers (the degradation rate of the monomer: OPA, 5.8×10^{-2} s^{-1}; CPA2, 1.1×10^{-2} s^{-1}; CPA3, 5.5×10^{-3} s^{-1}) under the same conditions for the polymer hydrolysis experiment. The polymers are quickly hydrated in acid solution but are not decomposed under the milder acid conditions (the degradation rate of each polymer in pH >3 was less than 10^{-7} s^{-1} (Figure 6)).

The preferential formation of degradation product A as shown in Figure 7 was confirmed by the ^{1}H NMR spectrum of the crude products during the hydration of polyCPA3-Ph (Figure 7). This result supports the selective hydration of the imines and not the amides during the degradation.

Conclusion

In conclusion, we first synthesized the mono- and diamino-substituted cyclic phenylazomethine trimer (CPA-1a and -2a) during the polymerization of AB_2-type and AB monomers and isolated in 11% and 19% yields, respectively. The π-conjugation elongation of the multifunctional CPAs in trifluoroacetic acid was confirmed by UV−vis spectroscopy. Linear and branched polyamides containing phenylazomethine units were synthesized by polycondensation of the di- or triamine monomer including azomethine bonds with dicarboxylic acids. The polymers have a high thermal stability and a simple and selective decomposition property in an acidic solution for chemical recycling. In polymer materials, these aromatic polyamides made it possible to harmonize the high thermal stability with the decomposition property for effective chemical recycling. This strategy can be adapted not only to polyamides but also to other thermostable polymers and engineering plastics. In this paper, we proposed a new approach for the chemical recycling of thermostable polymers.

Experimental Section

Measurements. The infrared (IR) spectra were recorded using a JASCO FT/IR-410 Fourier transform infrared spectrophotometer. The ^{1}H NMR spectra were recorded using a JEOL Ex-270. MALDI-TOF MS data were obtained using a Ultraflex TOF/TOF MALDI mass spectrometer (Bruker Daltonics) in the positive ion mode. A dithranol was used as the matrix. The thermogravimetric analysis (TGA) was carried out with a Rigaku Thermo plus2 TG-DTA TG8120 at a heating rate of 10 K min^{-1} in nitrogen. Gel permeation chromatography (GPC) was performed on a Shimazhu HPLC LC-10AD fitted with polystyrene−divinylbenzene columns (two Shodex KD-804 and KD-802) and a Shimazhu SPA-M10A VP diode array detector in DMF containing 10 mM lithium bromide as the eluent. The UV−vis spectra were recorded using a Shimazhu UV-3100PC.

Materials. All reagents were purchased from Aldrich, Merck, or Kanto Chemicals and were used without further purification. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere.

Synthesis of OPA. 4-Aminobenzophenone (4.00 g, 20.3 mmo1), *p*-phenylenediamine (4.89 g, 40.6 mmo1), and DABCO (6.82 g, 60.8 mmo1) were dissolved in chlorobenzene (400 mL) under a nitrogen atmosphere. Titanium tetrachloride (2.89 g, 15.2 mmol) was added in a dropwise manner. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 5 h. Disappearance of the 4-aminobenzophenone was confirmed by TLC. After cooling, the precipitate was removed by filtration. The filtrate was concentrated; the OPA (3.24 g, 11.3 mmol, 56% yield) was isolated by silica gel column chromatography (hexane:ethyl acetate = 1:1−1:3, including 1% Et_3N, R_f = 0.24 in the solution of ethyl acetate:hexane = 1:1). OPA: ^{1}H NMR (270 MHz, DMSO-d_6 , TMS standard, ppm): *E* isomer: δ 7.34−7.26 (m, 5H), 7.05 (d, J = 7.6 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 6.32 (d, J = 8.9 Hz, 2H), 6.27 (d, J = 8.9 Hz, 2H), 5.63 (s, 2H), 4.68 (s, 2H). *Z* isomer: δ 7.59 (d, J = 7.8 Hz, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.38 (dd, J = 7.4 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 6.45 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 8.9 Hz, 2H), 6.36 (d, J = 8.9 Hz, 2H), 5.35 (s, 2H), 4.80 (s, 2H).^{13}C NMR (67.5 MHz, DMSO-d_6, TMS standard, ppm): *E* isomer: δ 164.89, 151.03, 143.88, 140.74, 137.68, 129.93, 128.91, 127.87, 127.00, 122.38, 113.96, 112.78. *Z* isomer: δ 165.25, 148.91, 144.44, 141.02, 140.91, 130.53, 129.73, 128.73, 127.66, 122.38, 113.96, 112.9. IR (KBr): 3410 ($\nu_{as}NH_2$), 3335 (ν_sNH_2), 1632 (νC═N), 1589 (phenyl). EI-MS 287 $[M]^+$. Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.12; H, 6.11; N, 14.26. OPA is a mixture of *E*/*Z* geometric isomers. The ratio *E*/*Z* = 3.6/1 was confirmed by integration of the amine protons in the ^{1}H NMR spectra.

Synthesis of CPA-2a. $TiCl_4$ (1.01 g, 5.30 mmol) was added to a mixture of 4,4′-diaminobenzophenone (1.00 g, 4.71 mmo1), 4-aminobenzophenone (0.47 g, 2.36 mmo1), and DABCO (2.38 g, 21.2 mmo1) in anhydrous THF (250 mL) under a nitrogen atmosphere. White fumes were generated upon the addition of $TiCl_4$. The reaction mixture was heated in an oil bath at 90 °C for 5 h. After cooling, $TiCl_4$ (2.02 g, 10.6 mmo1) and DABCO (4.76 g, 42.4 mmol) were further added in the reaction mixture, and the solution was heated again in an oil bath at 90 °C for 10 h. Disappearance of the monomers was confirmed on TLC, and the precipitate was removed by filtration. The filtrate was concentrated; CPA-2a (0.118 g, 0.21 mmol, 11% yield) was isolated by silica gel column chromatography (dichloromethane:ethyl acetate = 1:0−3:1, including 1% Et_3N, R_f = 0.5 in the solution of ethyl acetate:dichloromethane = 1:2). CPA-2: ^{1}H NMR (270 MHz, DMSO-d_6 , TMS standard, ppm): δ 7.75 (d, J = 7.0 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.46 (dd, 7.0 Hz, 2H), 7.43 (d, J = 8.6 Hz, 4H), 6.74 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H), 6.67 (d, J = 8.1 Hz, 2H), 6.56 (d, J = 8.6 Hz, 4H), 6.45 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 8.6 Hz, 2H), 6.39 (d, J = 8.1 Hz, 2H), 5.78 (s, 4H). ^{13}C NMR (67.5 MHz, DMSO-d_6 , TMS standard, ppm): δ 169.82, 169.10, 168.82, 152.68, 152.17, 151.48, 151.39, 137.59, 130.91, 130.70, 130.22, 130.01, 129.35, 128.25, 128.03, 127.36, 127.29, 127.23, 125.20, 119.48, 119.22, 118.59, 112.62. IR (KBr): 3462 ($\nu_{as}NH_2$), 3374 (ν_sNH_2), 1621 (νC═N), 1587 (phenyl). FAB-MS 568 $[M]^+$. HRMS Calcd for $C_{39}H_{29}N_5$: 567.2423. Found: 567.2420.

Synthesis of CPA-1a. $TiCl_4$ (0.810 g, 5.70 mmol) was added to a mixture of 4,4′-diaminobenzophenone (0.538 g, 2.53 mmo1), 4-aminobenzophenone (1.00 g, 5.07 mmo1), and DABCO (1.28 g, 11.4 mmo1) in anhydrous THF (270 mL) under a nitrogen atmosphere. White fumes were generated upon the addition of $TiCl_4$. The reaction mixture was heated in an oil bath at 90 °C for 5 h. After cooling, $TiCl_4$ (0.540 g, 3.38 mmo1) and DABCO (1.28 g, 11.4 mmol) were further added in the reaction mixture, and the solution was heated again in an oil bath at 90 °C for 10 h. Disappearance of the monomers was confirmed on TLC, and the precipitate was removed by filtration. The filtrate was concentrated;

CPA-1a (0.264 g, 0.481 mmol, 19% yield) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:3−1:1, including 1% Et_3N, R_f = 0.6 in the solution of ethyl acetate: dichloromethane = 1:2). CPA-1a: ^{1}H NMR (270 MHz, DMSO-d_6 , TMS standard, ppm): δ 7.77 (d, J = 6.8 Hz, 4H), 7.55 (t, J = 7.0 Hz, 2H), 7.48 (dd, 6.8, 7.0 Hz, 4H), 7.44 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 8.1 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 8.1 Hz, 2H), 6.48 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 8.1 Hz, 2H), 5.79 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, TMS standard, 50 °C, ppm): δ 169.85, 169.58, 168.86, 152.58, 151.87, 151.38, 137.45, 130.87, 130.69, 129.95, 129.32, 128.19, 127.99, 127.27, 125.03, 119.41, 118.77, 118.51, 112.56. IR (KBr): 3461 ($\nu_{as}NH_2$), 3345 (ν_sNH_2), 1611 (νC═N), 1588 (phenyl). FAB-MS 552 $[M]^+$. HRMS Calcd for $C_{39}H_{29}N_5$: 552.2314. Found: 552.2311.

Synthesis of PolyOPA-*m*-Ph. In a flask, OPA (0.300 g, 1.04 mmo1), isophthalic acid (0.173 g, 1.04 mmo1), and LiCl (0.123 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.713 g, 2.30 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 95 °C for 3 h. After the temperature was adjusted to room temperature, the solution was poured into mehano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyOPA-*m*-Ph (0.411 mg, 94%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3318 (νNH), 1656 (νC═N), 1594 (phenyl), 1516(νC═O), 841, 702. Anal. Calcd for $C_{27}H_{19}N_3O_2 + H_2O$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.84; H, 4.78; N, 9.33.

Synthesis of PolyOPA-Ph. In a flask, OPA (0.200 g, 0.696 mmo1), terephthalic acid (0.116 g, 0.696 mmo1), and LiCl (0.098 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (1.4 mL), and then pyridine (1.0 mL) and triphenyl phosphite (TPP) (0.432 g, 1.39 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 95 °C for 3 h. After the temperature was decreased to room temperature, the solution was poured into methano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyOPA-Ph (0.288 mg, 99%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3398 (νNH), 1650 (νC═N), 1594 (phenyl), 1514 (νC═O), 922, 772, 693.

Synthesis of PolyOPA-Ox. In a flask, OPA (0.200 g, 0.696 mmo1), 4,4′-oxybis(benzoic acid) (0.180 g, 0.696 mmo1), and LiCl (0.141 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.432 g, 1.39 mmo1) were added to the flask under a nitrogen atmosphere. The solution was stirred at 100 °C for 5 h. After the temperature was decreased to room temperature, the solution was poured into methano1 (500 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyOPA-Ox (0.350 mg, 99%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3309 (νNH), 1654 (νC═N), 1595 (phenyl), 1512 (νC═O), 1239 (Ar−O−Ar), 844, 759, 700. Anal. Calcd for $C_{33}H_{23}N_3O_3 + H_2O$: C, 75.13; H, 4.78; N, 7.96. Found: C, 74.74; H, 5.50; N, 7.74.

Synthesis of PolyOPA-S. In a flask, OPA (0.300 g, 1.04 mmo1), 4,4′-dicarboxydiphenyl sulfone (0.320 g, 1.04 mmo1), and LiCl (0.123 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.713 g, 2.30 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 100 °C for 3 h. After the temperature was decreased to room temperature, the solution was poured into mehano1 (500 mL) to precipitate the polymer. The polymer was collected by fi1tered and washed with methanol. PolyOPA-S (0.575 mg, 99%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3353 (νNH), 1656 (νC═N), 1597 (phenyl), 1516 (νC═O), 1320 (νSO_2), 844, 703. Anal. Calcd for $C_{33}H_{23}N_3O_4S + H_2O$: C, 68.86; H, 4.38; N, 7.30; S, 5.57. Found: C, 68.31; H, 4.32; N, 6.92; S, 5.33.

Synthesis of PolyOPA-F. In a flask, OPA (0.300 g, 1.04 mmo1), 2,2-bis(4-carboxyphenyl)hexafluoropropane (410 g, 1.04 mmo1), and LiCl (0.123 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.713 g, 2.30 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 100 °C for 3 h. After the temperature was adjusted to room temperature, the solution was poured into mehano1 (500 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyOPA-F (0.635 mg, 94%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3317 (νNH), 1656 (νC═N), 1597 (phenyl), 1515 (νC═O), 849, 701.

Synthesis of PolyCPA2-Ph. In a flask, CPA-2a (0.100 g, 0.176 mmo1), terephthalic acid (0.029 g, 0.176 mmo1), and LiCl (0.123 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.109 g, 0.352 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 95 °C for 3 h. After the temperature was adjusted to room temperature, the solution was poured into methano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyCPA2-Ph (0.121 mg, 98%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3335 (νNH), 1664 (νC═N), 1593 (phenyl), 1521 (νC═O), 962, 846, 700. Anal. Calcd for $C_{47}H_{31}N_5O_2 + 2H_2O$: C, 76.93; H, 4.81; N, 9.54. Found: C, 76.53; H, 4.67; N, 8.68.

Synthesis of PolyCPA2-F. In a flask, CPA-2a (0.100 g, 0.176 mmo1), 2,2-bis(4-carboxyphenyl)hexafluoropropane (0.069 g, 0.176 mmo1), and LiCl (0.123 g) were dissolved in *N*-methyl-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.109 g, 0.352 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 100 °C for 7 h. After the temperature was adjusted to room temperature, the solution was poured into mehano1 (500 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyCPA2-F (0.162 mg, 99%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3364 (νNH), 1670 (νC═N), 1594 (phenyl), 1514 (νC═O), 848, 702.

Synthesis of PolyCPA2-S. In a flask, CPA-2a (0.100 g, 0.176 mmo1), 4,4′-dicarboxydiphenyl sulfone (0.054 g, 0.176 mmo1), and LiCl (0.123 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.109 g, 0.352 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 80 °C for exactly 75 min. After the temperature was decreased to room temperature, the solution was poured into methano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyCPA2-S (0.148 mg, 99%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3355 (νNH), 1672 (νC═N), 1592 (phenyl), 1520 (νC═O), 1315 (νSO_2), 847, 688. Anal. Calcd for $C_{53}H_{35}N_5O_4S + 2H_2O$: C, 72.84; H, 4.50; N, 8.01; S, 3.67. Found: C, 72.60; H, 4.32; N, 7.22; S, 3.77.

Synthesis of PolyCPA2-Ox. In a flask, CPA-2a (0.100 g, 0.176 mmo1), 4,4′-oxybis(benzoic acid) (0.046 g, 0.176 mmo1), and LiCl (0.123 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (2.0 mL), and then pyridine (1.5 mL) and triphenyl phosphite (TPP) (0.109 g, 0.352 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 80 °C for exactly 75 min. After the temperature was adjusted to room temperature, the solution was poured into mehano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyCPA2-Ox (0.140 mg, 99%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3340 (νNH), 1357 (νC═N), 1593 (phenyl), 1512 (νC═O), 1236 (−O−), 845, 700. Anal. Calcd for $C_{53}H_{35}N_5O_3 + 2H_2O$: C, 77.07; H, 4.76; N, 8.48. Found: C, 76.74; H, 4.46; N, 8.03.

Synthesis of PolyCPA3-Ph. In a flask, CPA-3a (0.200 g, 0.343 mmo1), terephthalic acid (0.057 g, 0.343 mmo1), and LiCl (0.306 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (5.0 mL), and then pyridine (3.7 mL) and triphenyl phosphite (TPP) (0.213 g, 0.686 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 80 °C for exactly 75 min.

After the temperature was adjusted to room temperature, the solution was poured into methano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyCPA3-Ph (0.179 mg, 79%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3337 (νNH), 1661 (νC═N), 1591 (phenyl), 1523 (νC═O), 845, 689. Anal. Calcd for $C_{63}H_{39}N_6O_6 + 3H_2O$: C, 73.46; H, 4.40; N, 8.16. Found: C, 73.85; H, 4.58; N, 10.10.

Synthesis of PolyCPA3-Ox. In a flask, CPA-3a (0.150 g, 0.257 mmo1), 4,4′-oxybis(benzoic acid) (0.066 g, 0.257 mmo1), and LiCl (0.230 g) were dissolved in *N*-methy1-2-pyrrolidinone (NMP) (3.8 mL), and then pyridine (2.8 mL) and triphenyl phosphite (TPP) (0.160 g, 0.515 mmo1) were charged into the flask under a nitrogen atmosphere. The solution was stirred at 80 °C for exactly 2 h and 25 min. After the temperature was decreased to room temperature, the solution was poured into mehano1 (400 mL) to precipitate the polymer. The polymer was collected by filtration and washed with methanol. PolyCPA3-Ox (0.207 mg, 86%) was obtained after drying at 85 °C under vacuum for 12 h. IR (KBr): 3345 (νNH), 1654 (νC═N), 1593 (phenyl), 1515 (νC═O), 1237 (−O−), 845, 759.

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