Novel Linear and Hyperbranched Aromatic Polyamide with Phenylazometine Units for Chemical Recycling

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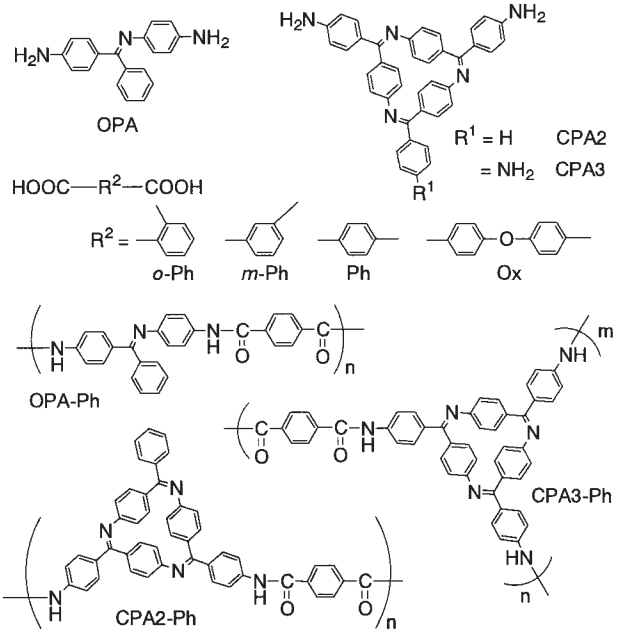
Novel linear and hyper-branched aromatic polyamides having phenylazomethine units were synthesized by the polycondensation of di- or triamine monomers containing azomethine bonds with dicarboxylic acids. The polymers obtained have a high solubility in DMF unlike polyphenylazomethines, a high thermal stability ($Td_{10\%} > 500\,^{\circ}C$), and is susceptible to a simple and selective acid catalyzed decomposition for chemical recycling.

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 hydrolyzed in an acid solution, are attractive polymers for recyclable plastics, but their very low solubility prevents their actual use as engineering materials. 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 to the aramid backbone should facilitate chemical degradation under mild conditions via hydrolysis of the azomethine bonds. Until now, various kinds of polymers including azomethine bonds have been synthesized and mainly investigated as a liquid crystalline polymers,[3] but their degradation has not been reported. We now report the synthesis and chemical degradation of novel linear and hyper-branched aromatic polyamides having phenylazomethine units, which act as a degradation site.

Using linear azomethine compound (OPA) and cyclic phenylazomethine trimers (CPAs)[4] 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, triphenylphosphite (TPP), and LiCl (Table 1).[5] The polymerization of OPA with *o*-phthalic acid (*o*-Ph) 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 91, 99, and 99% yields, respectively (Runs 2–4). The polymerization of CPA2 and CPA3 with dicarboxylic acids gave polyCPA2-Ph, -Ox, polyCPA3-Ph, and -Ox in 77–88% yields (Runs 5–8).[6] The polymers obtained have a high solubility in DMF, and the molecular weight was determined to be 20000–120000 (polystyrene standards) by GPC measurement using THF including 10 mM LiBr as an effluent.

In IR spectra of the polymers, two characteristic peaks attributed to stretching vibration of N–H and C=O in amide bonds appeared around 3350 and 1650 cm^{-1}, respectively (e.g., polyOPA-Ox: 3340 and 1657 cm^{-1}). The formation of amide bonds was also confirmed by ^1H NMR measurements. Especially, polyCPA3-Ph and -Ox gave relatively simple spectra due to the high symmetrical structure of the CPA3 units. 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 CPA3 monomer 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. On the other hand, the spectrum of polyOPA-Ox is complex and shows 8 peaks between 10–11 ppm attributed to the amide protons, because OPA is an asymmetrical compound. These 8 peaks are considered to appear due to the *E*/*Z* isomers in the azomethine

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	91 (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	CPA2	Ph	77 (polyCPA2-Ph)	2.0	521	2.6
6	CPA2	Ox	88 (polyCPA2-Ox)	4.5	490	
7	CPA3	Ph	79[a] (polyCPA3-Ph)	4.8	538	1.7
8	CPA3	Ox	86[a] (polyCPA3-Ox)	3.8	518	

[a] The reactions were stopped just before gelation.

bond and 2 kinds of bond combinations (head-to-tail and head-to-head) of the monomers in 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; 464 °C, polyCPA2-Ph; 521 °C). The bulky CPA is an effective unit for enhancement of the thermal stability. (2) The hyper-branched structure made the polymer more thermostable based on the cross-linking 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.

The degradation property of the polymers obtained ([polymer] $= 4.0 \times 10^{-5}$ M per imine unit) was investigated in an acidic solution (DMF : THF = 1 : 1 including 0.4 M sulfuric acid) at room temperature. The amide bond is not hydrolyzed under these conditions. In the UV-vis spectral measurement, the hydrolysis of the imine bond in the polymers was confirmed as the decrease in the absorption around 450 nm, which is attributed to the π-π^* transition of the imine bond. As an example, the spectral change in polyCPA3-Ph is shown in Figure 1a. The spectral change with an isosbestic point supports selective hydrolysis. The reaction obeys pseudo-first order kinetics, and the degradation rate (DR) in the hydrolysis of polyOPA-Ph, polyCPA2-Ph, and polyCPA3-Ph were calculated to be 6.5, 2.6, and 1.7×10^{-2} s^{-1}, respectively, from ΔOD in the absorption around 400 nm (Table 1 and Figure 1b). These rate constants show that over 99% of the imine bonds are hydrolyzed within 10 min.[7] 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}, CPA2: 1.1×10^{-2}, CPA3: 0.55×10^{-2} s^{-1}). The polymers are quickly hydrolyzed in acid solution, but are not decomposed under the milder acid conditions (the degradation rate of each polymer at pH > 3 was lower than 10^{-7} s^{-1}). The preferential formation of the degradation product A as shown in Figure 1c was confirmed by the ^{1}H NMR spectrum of the crude products during the hydrolysis of polyCPA3-A (Figure 1c). This result supports selective hydrolysis of the imines, not the amides in the degradation.

In conclusion, novel linear and hyper-branched polyamides having phenylazomethine units were synthesized by polycondensation of the di- or triamine monomer including azomethine bonds with dicarboxylic acids. The polymers have high solubility for DMF, a high thermal stability, and a simple and selective decomposition property in an acidic solution for chemical recycling.

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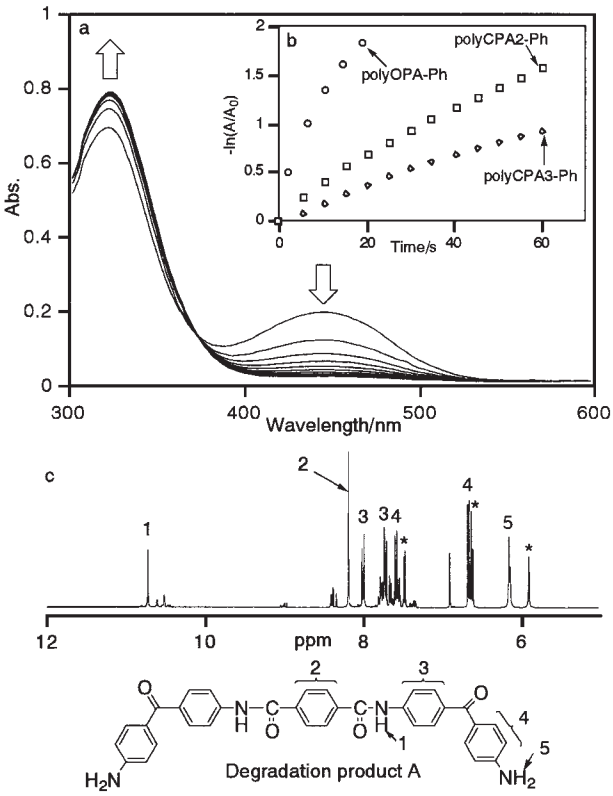

Figure 1. (a) UV-vis spectral change of polyCPA3-Ph in an acidic solution (DMF/THF = 1 : 1 including 0.4 M sulfuric acid) at room temperature for 10 min., (b) the relationship between-ln(A/A_0) and time, and (c) the ^{1}H NMR spectra of the crude products during the degradation of polyCPA3-Ph. The preferential formation of the degradation product A was confirmed by the spectrum, and the marked peaks (∗) were attributed to 4,4′-diaminobenzophenone.

References and Notes

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6 A typical synthetic procedure is as follows. CPA3 (0.200 g, 0.343 mmol), terephthalic acid (0.057 g, 0.343 mmol), and LiCl (0.306 g) were dissolved in *N*-methyl-2-pyrrolidinone (5.0 mL) – pyridine (3.7 mL) under N_2. TPP (0.213 g, 0.686 mmol) was added to the solution, and the mixture was stirred at 80 °C for 1.5 h. After polymerization, the entire mixture was poured into methanol (400 mL), the precipitate was filtered and washed with methanol. PolyCPA3-Ph (0.179 mg, 79%) was obtained after drying at 85 °C under vacuum for 12 h.

7 Molecular weight (Mw) of the product during hydrolysis was not correctly determined by GPC due to the low Mw.