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Soluble rigid rod-like polyimides and polyamides containing curable pendent groups

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Abstract

Soluble rod-like aromatic polyimides and polyamides containing curable pendent groups were synthesized. The polyimides (PIEANs) and polyamides (PAEANs) containing pendent enaminonitrile groups showed good thermal stability, and underwent curing reactions without the emission of volatile by-products above 300 °C to stable materials which were not soluble in any organic solvents. However, the polyimides (PIEONs) and polyamides (PAEONs) containing pendent enoxynitrile groups started to decompose around 300 °C, because of the instability of enoxynitrile groups. PAEONs underwent curing reactions around 420 °C in spite of the initial decomposition, but PIEONs exhibited only thermal degradation process. Thermal analyses of these polymers and the corresponding model compounds revealed that the curing of enaminonitrile groups proceeded via intermolecular crosslinking as well as intramolecular cyclization, while the enoxynitrile groups, known to undergo self-curing reaction, could not be cured by itself, and a reactive amine group was essential for the curing of the enoxynitrile groups.

Keywords: Polyimides; Polyamides; Enaminonitrile

1. Introduction

All aromatic polymers generally exhibit high thermal stability and excellent mechanical properties which make them find applications in many areas [1,2]. However, these polymers are difficult to process due to their high glass transition temperatures (T_gs), or high melting temperatures (T_ms), and limited solubilities in organic solvents [3,4]. One of typical examples of these aromatic polymers is aromatic polyamides that are processed in limited solvents such as concentrated H_2SO_4 or highly polar organic solvents containing an inorganic salt. Also, most of aromatic polyimides are processed in the form of the poly(amic acid) as a soluble precursor, and then cyclodehydrated to a stable polyimide by thermal and chemical treatment [5]. However, this process has several problems such as the instability of the poly(amic acid) and the emission of volatile by-products (often H_2O) on cyclization [6,7]. Because of these processing problems, a great deal of research on aromatic polyimides and polyamides has been directed toward the improvement of processability while maintaining desirable properties of these polymers [8–12]. The approaches involve the introduction of flexible linkages or bulky substituents, and the use of noncoplanar, alicyclic, or unsymmetrical monomers. For example, bulky substituents incorporated in rigid polymer chains interfere strong hydrogen bonding interaction in polyamides [13–18] and strong interchain interaction via charge-transfer or electronic polarization mechanism in polyimides [19–25], leading to increased solubility of the polymers.

Introducing a curable group into polymer chains is an effective way to convert polymeric or oligomeric materials to more stable forms without processing difficulty. Polyenaminonitriles (PEANs) [26–32] and polyenoxynitriles [33–35] are interesting curable polymers with good solubility and high thermal stability. These polymers have been known to undergo curing reactions thermally without emission of volatile by-products.

In this study, the new diamine monomers containing a pendent enaminonitrile group, [(3,5-diaminophenyl)phenylaminomethylidene]propanedinitrile

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(**4**), and a pendent enoxynitrile group, [(3,5-diaminophenyl)phenoxymethylidene]propanedinitrile (**6**), were synthesized and polymerized with several diacid chlorides and dianhydrides to produce aromatic polyamides and polyimides, respectively. Also, curing behavior of the polymers and the corresponding model compounds was investigated. The 'bulky' and 'curable' pendent groups were expected to allow easy processing and further modification of the rigid rod-like aromatic polymers.

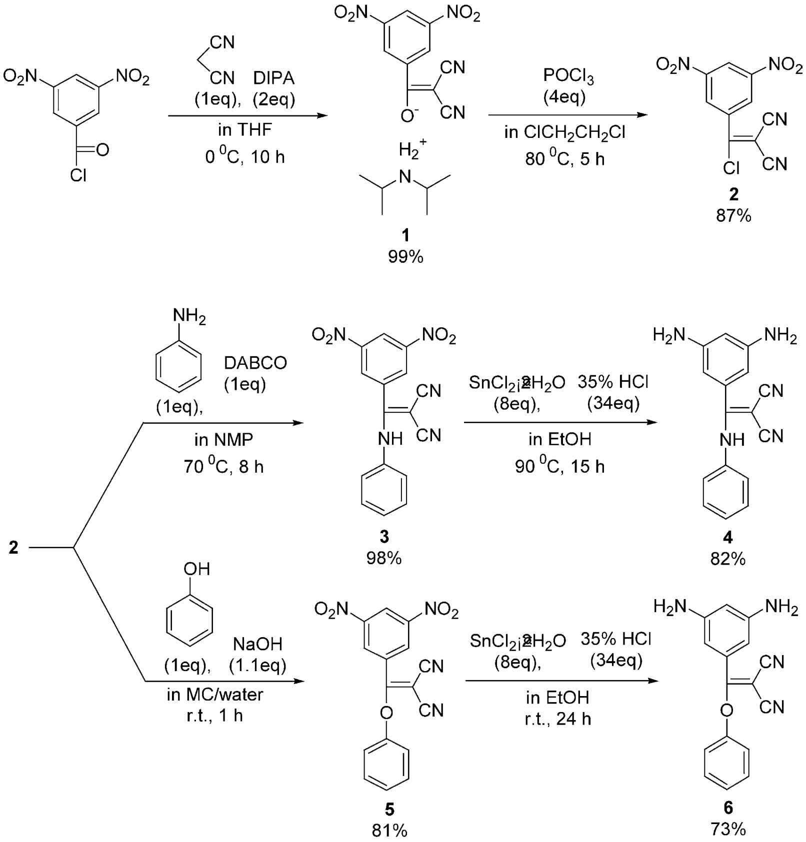
2. Results and discussion

2.1. Monomer syntheses

Two diamine monomers, **4** and **6**, were prepared according to the reaction sequence outlined in Scheme 1. The condensation of 3,5-dinitrobenzoyl chloride and malononitrile proceeded smoothly with slow addition of diisopropylamine as a base in THF and produced [(3,5-dinitrophenyl)hydroxymethylidene]propanedinitrile in high yield, while the condensation at previously reported base-catalyzed phase-transfer conditions resulted in low yield [36]. The chlorination of diisopropylammonium salt (**1**) was carried out with phosphorus oxychloride in 1,2-dichloroethane. The reaction of [(3,5-dinitrophenyl)chloromethylidene]propanedinitrile (**2**) with aniline in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as an acid acceptor gave the desired dinitro compound containing an enaminonitrile group (**3**). Unlike the synthesis of **3**, the dinitro compound containing an enoxynitrile group (**5**) was synthesized by interfacial reaction of **2** in dichloromethane with sodium phenoxide generated by the stirring of phenol and sodium hydroxide in distilled water. Because **5** was susceptible to nucleophilic attack by hydroxide ions remained in the crude product, the crude compound was dissolved in $CHCl_3$ and washed with 10% HCl solution before the recrystallization from $CHCl_3$/hexane. The two dinitro compounds, **3** and **5**, were reduced with $SnCl_2 \cdot 2H_2O$ and HCl to the corresponding diamine monomers, **4** and **6**, respectively. Reduction of the dinitro compound containing a pendent enoxynitrile group (**5**) was carried out at room temperature for 24 h, while reduction of the dinitro compound containing a pendent enaminonitrile group (**3**) was carried out at 90 °C for 15 h. The structures of the diamine monomers were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, and mass spectrometer.

2.2. Model reactions

Model reactions were conducted to investigate the reactivity of the diamine monomers as well as to obtain



Scheme 1.

the model compounds that can be used as a reference for structural and thermal characterization of the corresponding polymers. The diamine monomers, **4** and **6**, were reacted with benzoyl chloride or phthalic anhydride to give the corresponding model compounds (**7**, **8**, **9**, and **10**) as shown in Scheme 2. The diamide model compounds, **7** and **8**, were synthesized by solution condensation method in DMAc at room temperature, and the diimide model compounds, **9** and **10**, were synthesized by solution imidization method in NMP at 190 °C. The diamine monomer containing an enaminonitrile group (**4**) was converted to the diamide and diimide model compounds in high yield without any side reaction. The diamine monomer containing an enoxynitrile group (**6**) was also converted to the corresponding model compounds. Interestingly, the model compounds, **8** and **10**, were hydrolyzed into phenol and its counterpart in DMSO-d_6, although they were stable in powdery state or in solvents immiscible with water. The results of model reactions were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.

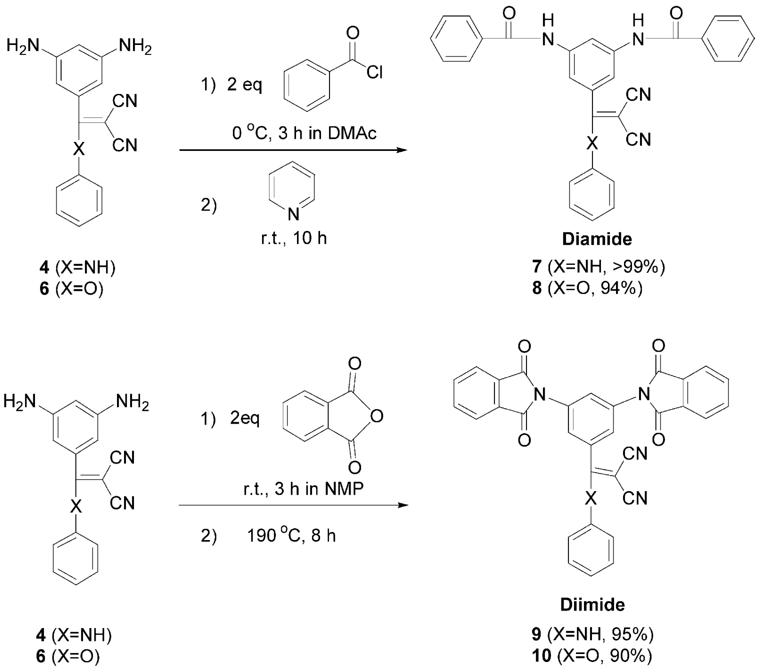
2.3. Polymer syntheses

Based on the results of the model reactions, several polyamides and polyimides were prepared from **4** and **6**. All the polymers were end-capped to exclude the end group effect on the curing. If the polymers were not end-capped, the curing reaction caused by the reactive end groups would make the curing process complicated. So, slightly excess amount of the diamine monomer was polymerized with diacid chloride or dianhydride, and monofunctional acid chloride or anhydride was added at the last stage of the polymerization.

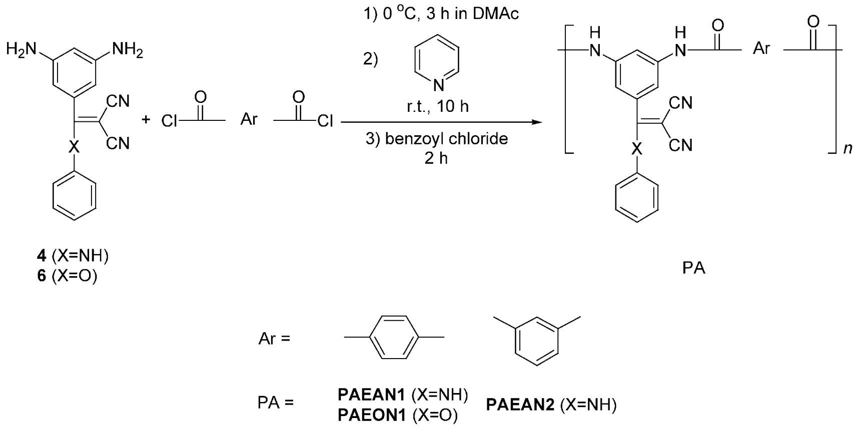
The polyamides containing enaminonitrile groups (PAEANs) were prepared by reacting **4** with terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC) at a concentration of 10 wt% solids in DMAc at room temperature, and benzoyl chloride was added as an end-capping reagent after the polymerization as shown in Scheme 3. Also, the polyamide containing enoxynitrile groups (**PAEON1**) was prepared by the same method from **6** and TPC. The polymerization proceeded homogeneously. All the end-capped polyamides were obtained as pale yellow flake on pouring of the reaction mixtures into water.

The synthesized polyamides were characterized by spectroscopic methods. Similar to the FTIR spectrum of **7**, **PAEAN2** showed characteristic absorption bands of the amide at 3262 and 1676 cm^{-1}, and the CN stretching at 2216 cm^{-1}. ^{1}H NMR spectra of the model compound **7** and **PAEAN2** are shown in Fig. 1. ^{1}H NMR spectrum of **PAEAN2** is consistent with its structure and shows similar patterns to **7**. Two peaks around 10.5 and 10.4 ppm correspond to NH proton of the enaminonitrile and the amide groups, respectively. These spectroscopic data confirmed that the polyamides were successfully synthesized and the both enaminonitrile and enoxynitrile groups were inert under the polymerization condition employed, as expected from the results of the model reactions.

The polyimides containing an enaminonitrile group (PIEANs) were prepared by solution imidization method from **4** with ODPA, BTDA, or PMDA as shown in Scheme 4. The polymerization was carried out by reacting slightly excess amount of diamine monomer **4** with the dianhydride at a concentration of 10 wt% solids in NMP. Poly(amic



Scheme 2.



Scheme 3.

acid) solution was formed by ring-opening polyaddition reaction at room temperature for 3 h. After dilution of the solution to 5 wt%, subsequent cyclodehydration by heating at 190 °C for 8 h and end-capping reaction of the resulting polyimides with phthalic anhydride at this temperature for 2 h gave the polyimides. The polymerization proceeded homogeneously without precipitation or gelation. All the end-capped polyimides were obtained as yellow flake on pouring of the reaction mixture into water/methanol (v/v = 1/1) mixture.

The structures of synthesized polyimides were confirmed by spectroscopic data. In the case of **PIEAN3**, the absorption bands at 1781, 1729, 1349, and 728 cm^{-1} corresponding to the imide bands were clearly observed. The CN stretching band at 2217 cm^{-1} proved the inertness of enaminonitrile group on solution imidization at 190 °C. ^{1}H NMR spectra of the model compound **9** and **PIEAN1** are shown in Fig. 2. ^{1}H NMR spectra of PIEANs showing similar patterns to that of the model compound were consistent with their structures. Also, all ^{1}H NMR spectra did not show amide and acid protons, which indicates complete imidization.

The polyimide containing an enoxynitrile group (**PIEON1**) was synthesized by taking the same method with **6** and ODPA. However, some enoxynitrile groups were decomposed into phenol and its counterpart. After the end-capped poly(amic acid) in NMP was formed, chemical imidization was carried out in the presence of pyridine and acetic anhydride at 70 °C for 12 h because of the instability of the enoxynitrile group at high temperature, but the decomposition of the enoxynitrile group was not completely avoided.

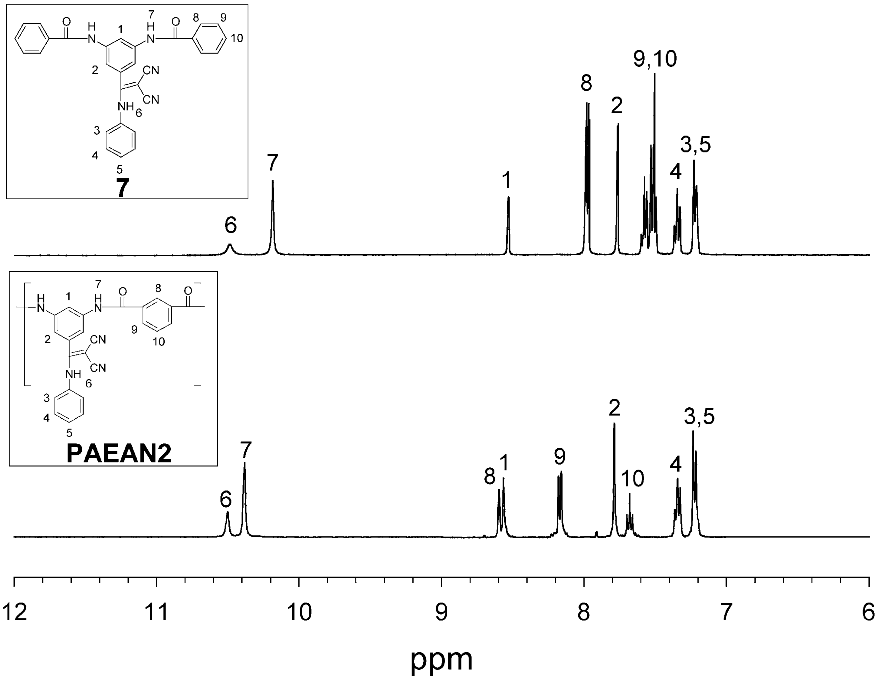
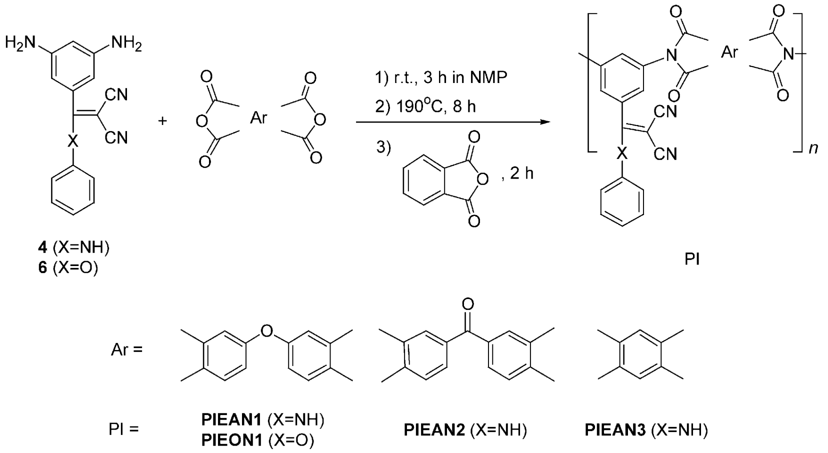


Fig. 1. ^{1}H NMR spectra of **7** and **PAEAN2** (400 MHz, in DMSO-d_6).



Scheme 4.

2.4. Physical and thermal properties

The inherent viscosities and thermal properties of the synthesized polymers are summarized in Table 1. The polymers had relatively low inherent viscosities ranging from 0.19 to 0.37 dL/g, presumably because of the addition of slightly excess amount of the diamine monomer compared to diacid chloride or dianhydride to obtain end-capped polymers. The synthesized polymers showed good solubility in polar aprotic solvents such as NMP, DMAc, and DMSO (Table 2). Bulky pendent groups incorporated in a rigid polymer chain are known to enhance the solubility of the polymers by reducing strong hydrogen bonding interaction in polyamides or strong inter-chain interaction via charge-transfer or electronic polarization mechanism in polyimides. In the case of the polymers containing the enaminonitrile groups, the enaminonitrile hydrogen atoms are able to form hydrogen bonds with amide-type solvents having proton accepting functional groups [30]. **PIEAN3**, which has the most rigid chains, dissolved in amide-type solvents on heating. After cooling, **PIEAN3** remained in NMP solution, while it turned into a gel in DMAc. The polymers were insoluble or partially soluble in acetone, tetrahydrofuran, toluene, and chlorinated solvents such as chlorobenzene and chloroform even at elevated temperatures. Unlike polyamides, polyimides were soluble in *m*-cresol on heating. The films, prepared by solution casting from *N*,*N*-dimethylacetamide solutions of the polymers, were somewhat brittle. However, strong polymer films were made after the heat-curing of the polymers containing enaminonitrile groups (PIEANs, PAEANs).

The four kinds of polymers synthesized in this study have reactive secondary amine at different position, i.e. in the main chain amide linkage and/or in the pendent

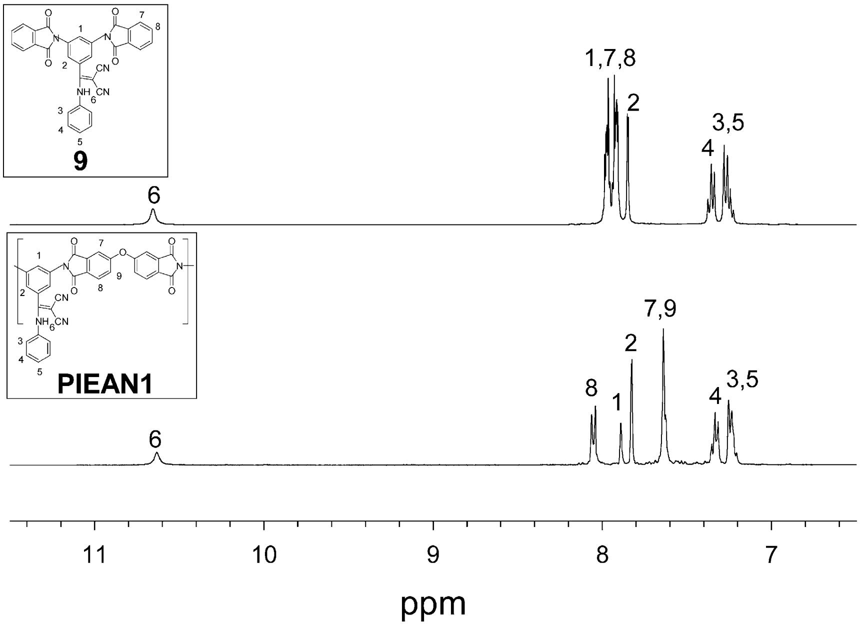


Fig. 2. ^{1}H NMR spectra of **9** and **PIEAN1** (400 MHz, in DMSO-d_6).

Table 1
Inherent viscosities and thermal properties of the synthesized polymers

Polymer	η_{inh}[a] (dL/g)	T_{max}[b] (°C)	ΔH[c] (J/g)	T_d[d] (°C)		CY[e] (%)
				In N_2	In air	
PAEAN1	0.37	353	218	456	448	74
PAEAN2	0.32	355	219	445	441	75
PAEON1	0.24	422	68	317	–	54
PIEAN1	0.20	363	201	530	533	61
PIEAN2	0.19	364	191	517	517	63
PIEAN3	0.30	375	188	527	489	63
PIEON1	0.32	N/D	N/D	372	–	55

N/D: not detected.

[a] Inherent viscosity, measured with a concentration of 0.5 g/dL in DMAc at 30 °C except for **PIEAN3** (in NMP).

[b] Temperature at maximum of the exothermic peak, measured by DSC with a heating rate of 10 °C/min.

[c] Enthalpy of the exothermic transition, measured by DSC with a heating rate of 10 °C/min.

[d] Five percent weight loss temperature, measured by TGA with a heating rate of 10 °C/min.

[e] Char yield, measured by TGA with a heating rate of 10 °C/min (calculated as the percentage of solid residue after heating from room temperature to 800 °C in N_2).

enaminonitrile group except for the polyimides containing a pendent enoxynitrile group (PIEONs), but all the polymers have a dicyanovinylidene group at the same position as shown in Scheme 5. Especially, the curing study of the polyamides and the polyimides containing pendent enoxynitrile groups (PAEONs and PIEONs) should clarify the role of the secondary amine groups in the curing reaction.

Thermal properties of the model compounds and the synthesized polymers were studied with DSC, TGA, and FTIR, and the results are summarized in Tables 1 and 3.

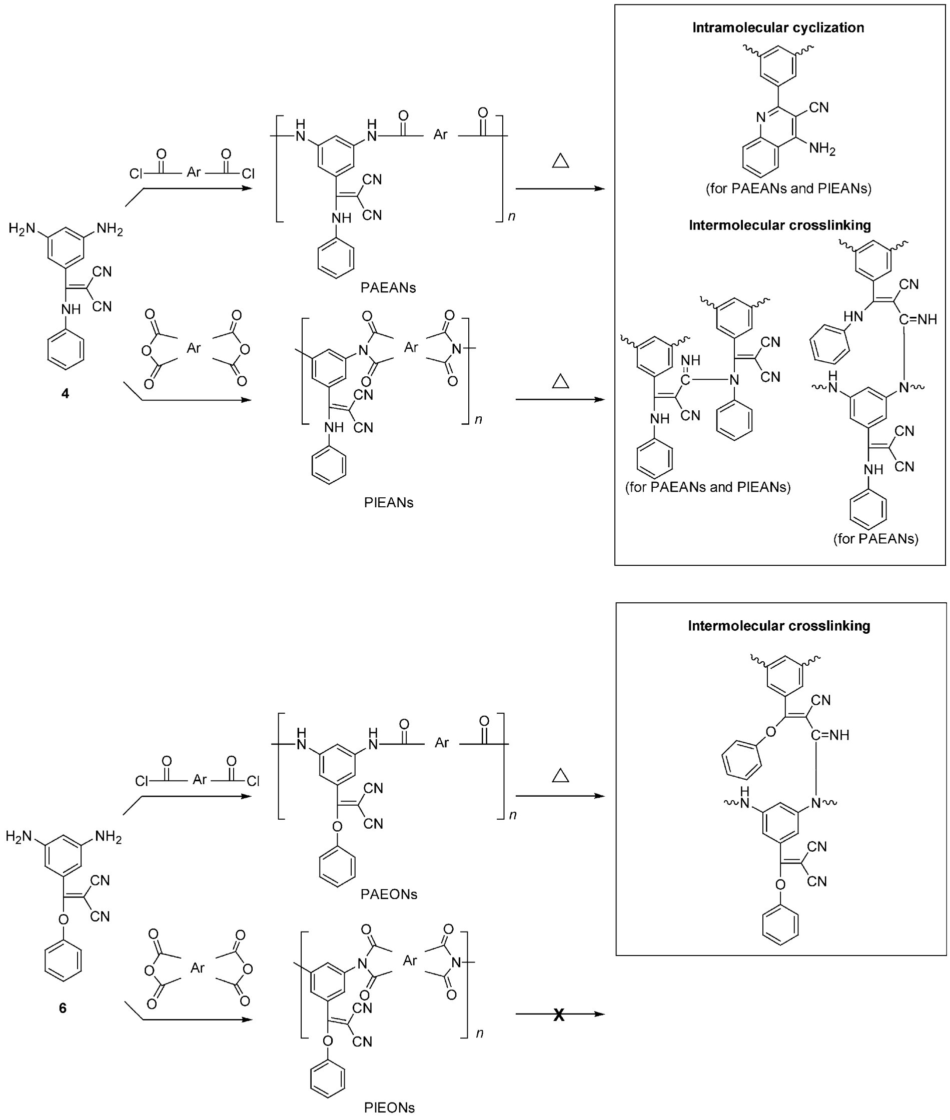
The DSC results of the model compounds shown in Fig. 3 revealed the importance of reactive amine groups and the occurrence of intermolecular crosslinking. The model compounds **7**, **8**, and **9** that contain a reactive secondary amine group underwent curing around 355, 380, and 356 °C, respectively, but the model compound **10** which has only tertiary amine in the imide ring did not show any curing behavior. It is clear that, unlike the enaminonitrile group, the enoxynitrile group which was previously reported to undergo curing is not self-curable.

The representative DSC results of the polymers shown in Fig. 4 also reveal that the reactive secondary NH in the pendent enaminonitrile group or in the main chain amide linkage is essential for the curing reaction. **PAEAN1** and **PIEAN3** exhibit a broad and irreversible exothermic peak around 353 and 375 °C, respectively. The FTIR spectra of **PAEAN1** subjected to thermal curing at 350 °C display a shift of the enamine N–H stretching band at 3346 cm^{-1} to the primary amine stretching band at 3374 cm^{-1}, a decrease in the intensity of the C≡N band at 2215 cm^{-1}, and a new appearance of the C=N band at 1635 cm^{-1} as shown in Fig. 5. Similarly, the FTIR spectra of **PIEAN3** display a shift of the enamine N–H stretching band at 3326 cm^{-1} to the primary amine stretching band at 3383 cm^{-1}, a decrease in the intensity of the C≡N band at 2217 cm^{-1}, and a new appearance of the C=N band at 1636 cm^{-1} after heat curing at 370 °C. These spectral results are consistent with the structure of the cured polymer by intermolecular crosslinking and intramolecular cyclization. Although initial decomposition of **PAEON1** is detected before 300 °C, DSC analysis shows a broad peak corresponding to the curing process around 420 °C. Curing reaction of **PAEON1** having secondary amine in the amide linkage can proceed only via intermolecular crosslinking. As expected, **PIEON1**, which has no reactive amine groups in the polymer, exhibits only thermal degradation process. These results clearly indicate that intermolecular crosslinking is a part of the curing process for the polymers containing enaminonitrile groups (Scheme 5). All the cured PAEANs, PIEANs, and PAEONs

Table 2
Solubilities of the synthesized polymers

Polymer	Solubility[a]						
	NMP	DMAc	DMSO	*m*-Cresol	THF	Toluene	Chlorobenzene
PAEAN1	++	++	++	+−	−	−	−
PAEAN2	++	++	++	+−	−	−	+−
PAEON1	++	++	++	+−	+−	−	+−
PIEAN1	++	++	++	+	−	−	−
PIEAN2	++	++	++	+	−	−	−
PIEAN3	+	+	+−	−	−	−	−
PIEON1	++	++	+−	+	−	−	−

[a] Key: ++, soluble at room temperature; +, soluble on heating; +−, partially soluble on heating; −, insoluble.



Scheme 5.

were not soluble in any solvents (even in concentrated H_2SO_4).

TGA analyses (Fig. 6) of the polymers showed that **PAEAN1** has higher char yield after heat treatment up to 800 °C, although initial decomposition temperature of

Table 3
Thermal properties of the model compounds

Compound	T_m[a] (°C)	T_{max}[b] (°C)	ΔH[c] (J/g)
7	283–285	355	220
8	109–111	380	95
9	300–302	356	177
10	230–232	N/D	N/D

N/D: not detected.

[a] Measured by DSC with a heating rate of 20 °C/min.

[b] Temperature at maximum of the exothermic peak, measured by DSC with a heating rate of 20 °C/min.

[c] Enthalpy of the exothermic transition, measured by DSC with a heating rate of 20 °C/min.

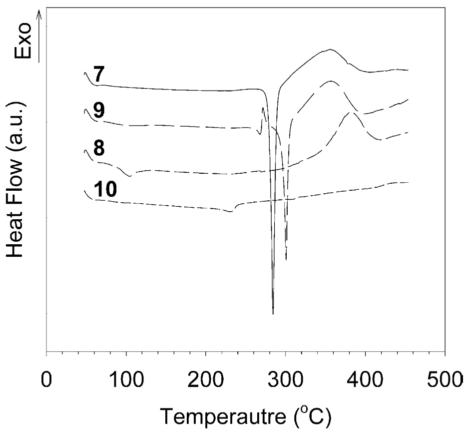


Fig. 3. DSC curves of the model compounds (in N_2, heating rate: 20 °C/min).

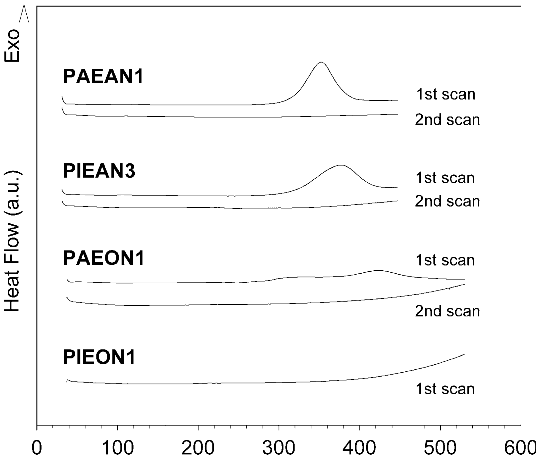


Fig. 4. DSC curves of the four representative polymers (in N_2, heating rate: 10 °C/min).

PAEAN1 is lower than that of **PIEAN3**. Unlike PIEANs, PAEANs have secondary amine groups in the main chains that provide higher degree of crosslinking for PAEANs, leading to higher char yield. The enthalpy values of the exothermic transitions of these two polymers also support that the amine group in the amide linkage participates in the curing reaction. ΔH of **PAEAN1** having both enaminonitrile group and amide linkage is higher than that of **PIEAN3** having only enaminonitrile group as shown in Table 1. The polymers containing enoxynitrile group, **PAEON1** and **PIEON1**, have lower thermal stability than the polymers containing enaminonitrile group, **PAEAN1** and **PIEAN3**.

PAEON1 started to decompose with emission of volatile product before heat-curing, which may stem from low thermal stability of the enoxynitrile group. Compared to the enoxynitrile group, the enaminonitrile group is a more efficient curable group with better thermal and hydrolytic stability.

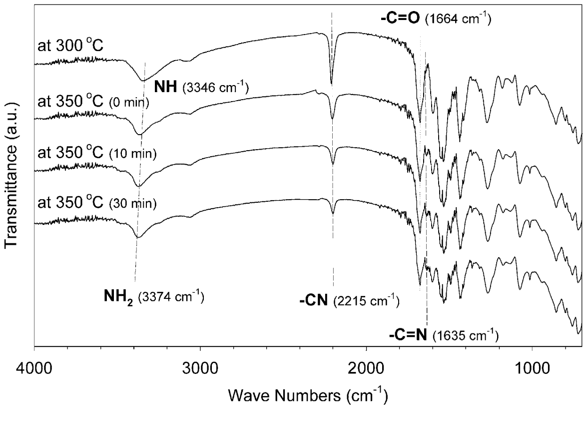


Fig. 5. FTIR spectra of **PAEAN1** (thin film) after heat-curing at 350 °C.

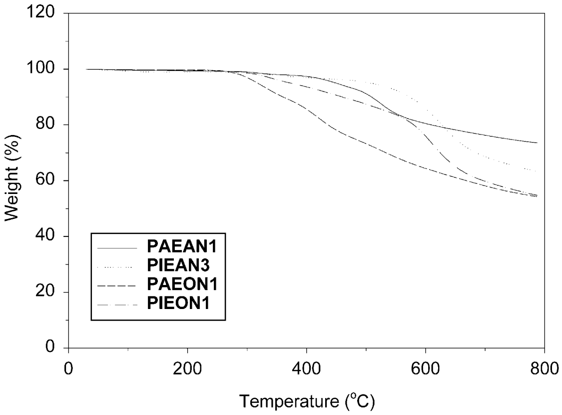


Fig. 6. TGA curves of the four representative polymers (in N_2, heating rate: 10 °C/min).

3. Conclusions

Aromatic polyamides and polyimides containing pendent enaminonitrile or enoxynitrile groups, PAEANs, PIEANs, PAEONs, and PIEONs, were synthesized. All the synthesized polymers with inherent viscosities ranging from 0.19 to 0.37 dL/g showed good solubility in polar aprotic solvents. PAEANs and PIEANs had good thermal stability and underwent curing reaction without the emission of volatile fragment above 300 °C to stable materials that were not soluble in any solvents. However, PAEONs and PIEONs started to decompose around 300 °C because of the instability of the enoxynitrile groups.

The curing behavior of the four kinds of end-capped polymers and the corresponding model compounds indicates that the curing reaction of the enaminonitrile group proceeds via intermolecular crosslinking as well as intramolecular cyclization, but the enoxynitrile group cannot be cured by itself and a reactive amine group is essential for curing.

4. Experimental section

4.1. Materials

3,5-Dinitrobenzoylchloride purchased from Aldrich was used as received. Malononitrile was distilled under reduced pressure, and $POCl_3$ was distilled under atmospheric pressure. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was sublimed in vacuo at 60 °C. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were recrystallized from *n*-hexane. 4,4′-Oxydiphthalic anhydride (ODPA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) were recrystallized from acetic anhydride and then dried in vacuo at 150 °C for 24 h. *N*,*N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were stirred in the presence of P_2O_5 overnight and then distilled under reduced pressure.

Chlorobenzene was stirred in the CaH_2 overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were used without further purification.

4.2. Measurements

FTIR spectra of the compounds were obtained with a Bruker EQUINOX-55 spectrophotometer using KBr pellet or film. ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds were recorded on Bruker Fourier Transform AVANCE 400 (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) spectrometers. Chemical shift of NMR was reported in part per million (ppm) using tetramethylsilane as an internal reference. Splitting patterns designated as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), m (multiplet), and br (broaden). Elemental analysis was carried out with a FISONS EA 1108 Analyzer. Inherent viscosity data were obtained with 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. Melting points (mp) and temperatures for curing reactions of the synthesized compounds were obtained with DSC instrument at a heating rate of 10 °C/min or 20 °C/min in N_2. TGA measurements were made at a heating rate of 10 °C/min in N_2 or air.

4.3. Monomer syntheses

4.3.1. [(3,5-Dinitrophenyl)hydroxymethylidene]propanedinitrile diisopropylammonium salt (*1*)

3,5-Dinitrobenzoyl chloride (30.0 g, 0.130 mol) and malononitrile (8.19 mL, 0.130 mol) were dissolved in 400 mL of tetrahydrofuran (THF) in a dried 1000 mL three-necked flask equipped with a mechanical stirrer. Diisopropylamine (DIPA) (36.4 mL, 0.260 mol) in 100 mL of THF was slowly added to the flask at 0 °C over 9 h, and the mixture was stirred for an additional hour. Precipitated diisopropylamine hydrochloride salt was filtered. THF solvent was evaporated, and oil-like crude product was poured into ethyl ether. After 1 day, the precipitate was filtered, washed with ethyl ether, and dried in vacuo at room temperature for 12 h to give the desired yellow product (**2**) (46.2 g, 98.5% yield): mp 113–115 °C. FTIR (KBr, cm^{-1}): 3100 (aromatic C–H); 3035 (N–H of amine salt); 2993, 2877 (aliphatic C–H); 2202, 2184 (–CN); 1654, 1625, 1597 (aromatic C=C and C=N); 1549, 1347 (NO_2). ^{1}H NMR ($CDCl_3$, 400.13 MHz, ppm): 9.03 (t, 1H, $J=1.94$ Hz); 8.89 (d, 2H, $J=1.99$ Hz); 7.94 (s, 2H, $\mathrm{N}H_2^+$); 3.47 (septet, 2H, $J=6.33$ Hz); 1.40 (d, 12H, $J=6.52$ Hz). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): 184.49, 148.17, 141.94, 127.77, 120.47, 120.00, 119.46, 51.59, 47.98, 19.14. HRMS (*m/e*): calcd for $C_{16}H_{19}N_5O_5$, 361.1386; found 361.1356.

4.3.2. [(3,5-Dinitrophenyl) chloromethylidene]propanedinitrile (**2**)

1 (40.0 g, 0.111 mol) was dissolved in 200 mL of 1,2-dichloroethane in a dried 500 mL two-necked flask. $POCl_3$ (41.4 mL, 0.444 mol) was added dropwise to the flask at room temperature. After all of $POCl_3$ had been added, a reflux condenser was attached to the flask and the mixture was boiled to 80 °C for 5 h. Excess $POCl_3$ and solvent were distilled under reduced pressure. The crude product was dissolved into methylene chloride (MC), and the insoluble salt was filtered. The product was purified by silica column chromatography using methylene chloride (MC) as an eluent. Evaporation of MC gave the yellow powdery product that was dried in vacuo at room temperature for 12 h (26.8 g, 86.7% yield): mp 125–127 °C. FTIR (KBr, cm^{-1}): 3094 (aromatic C–H); 2238 (–CN); 1627, 1592 (aromatic C=C and C=N); 1542, 1344 (NO_2). ^{1}H NMR ($CDCl_3$, 400.13 MHz, ppm): 9.26 (t, 1H, $J=2.62$ Hz); 8.94 (d, 2H, $J=2.63$ Hz). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): 161.11, 148.95, 135.33, 128.56, 122.83, 110.17, 109.84, 90.93. HRMS (*m/e*): calcd for $C_{10}H_3ClN_4O_4$, 277.9843; found 277.9845.

4.3.3. [(3,5-Dinitrophenyl) phenylaminomethylidene]propanedinitrile (**3**)

Aniline (3.92 mL, 43.1 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (4.83 g, 43.1 mmol) were dissolved in 30 mL of NMP in a dried 250 mL two-necked flask. **2** (12.0 g, 43.1 mmol) dissolved in 50 mL of NMP was added to the flask slowly. After the mixture was stirred at room temperature for 1 h, it was heated to 70 °C for 8 h. The mixture was poured into distilled water containing small amount of concentrated HCl. The precipitate was filtered, washed with water, and dried in vacuo at 40 °C over P_2O_5 for 12 h. The yellow powdery product was purified by recrystallization from acetone/methanol. Alternatively, it was added into methanol and stirred for 30 min. The insoluble product was filtered and separated from the soluble side-product (14.1 g, 97.7% yield): mp 266–268 °C. FTIR (KBr, cm^{-1}): 3243 (–NH– of enaminonitrile); 3129, 3099, 3063 (aromatic C–H); 2227, 2211 (–CN); 1611, 1571, 1494, 1469, 1421 (aromatic C=C and C=N); 1551, 1343 (NO_2). ^{1}H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.80 (s, 1H, N*H* of enaminonitrile); 8.97 (t, 1H, $J=2.12$ Hz); 8.89 (d, 2H, $J=2.12$ Hz); 7.39–7.25 (m, 5H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 164.36, 148.52, 137.22, 135.89, 130.67, 129.61, 128.39, 126.24, 121.92, 117.42, 114.16, 54.20. HRMS (*m/e*): calcd for $C_{16}H_9N_5O_4$, 335.0655; found 335.0651.

4.3.4. [(3,5-Diaminophenyl) phenylaminomethylidene]propanedinitrile (**4**)

A slurry of **3** (8.00 g, 23.9 mmol), tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) (43.1 g, 191 mmol), and 140 mL of absolute ethanol in 250 mL two-necked flask was stirred while concentrated HCl (71.1 mL, 813 mmol) was added slowly. After addition of HCl was over, a reflux condenser was installed and the mixture was boiled to 90 °C for 15 h. Excess ethanol was evaporated, and the remaining solution was poured into ice water. The solution was basified with 10% NaOH solution up to pH 7–8. The resulting precipitate was filtered, washed with distilled water, and dried in vacuo at 80 °C over P_2O_5 for 12 h. The precipitate was added into 250 mL of ethyl acetate (EA) and stirred for 1 h. After the insoluble tin compound was filtered, EA in the filtrate was evaporated. The deep yellow product was purified by recrystallization from ethanol/distilled water (5.39 g, 82.1% yield): mp 212–214 °C. FTIR (KBr, cm^{-1}): 3424, 3382 ($-NH_2$); 3298 (–NH– of enaminonitrile); 2210 (–CN); 1602, 1563, 1530, 1457, 1389 (aromatic C=C and C=N). ^1H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.09 (s, 1H, N*H* of enaminonitrile); 7.33–7.28 (m, 2H, aromatic of pendent phenyl); 7.20–7.13 (m, 3H, aromatic of pendent phenyl); 6.03 (t, 3H); 4.70 (s, 4H, N*H* of aromatic diamine). ^{13}C NMR (DMSO-d_6, 100.62 MHz, 100 °C, ppm): 169.09, 148.74, 137.81, 132.87, 128.03, 125.57, 123.73, 116.21, 114.17, 103.41, 102.40, 52.13. HRMS (*m*/*e*): calcd for $C_{16}H_{13}N_5$, 275.1171; found 275.1173.

4.3.5. [(3,5-Dinitrophenyl)phenoxymethylidene]propanedinitrile (**5**)

Phenol (3.55 g, 37.7 mmol) and sodium hydroxide (1.58 g, 39.5 mmol) were dissolved in 35 mL of distilled water in 250 mL one-necked flask equipped with a mechanical stirrer, and the mixture was stirred at room temperature for 30 min. **2** (10 g, 35.9 mmol) in 35 mL of MC was added to the flask. After the mixture was stirred rapidly at room temperature for 1 h, MC was evaporated at room temperature. The resulting precipitate containing water was filtered, washed with water, and dried in vacuo at room temperature over P_2O_5 for 12 h. After the precipitate was dissolved in 200 mL of $CHCl_3$, small amount of NaOH, which had remained in the precipitate, was extracted with 10% HCl solution (50 mL×3). The product was recrystallized from $CHCl_3$/hexane to give yellow powder (9.78 g, 81.1% yield): mp 154–156 °C. FTIR (KBr, cm^{-1}): 3106, 3092 (aromatic C–H); 2235 (–CN); 1606, 1596, 1575, 1488, 1459 (aromatic C=C and C=N); 1547, 1347 (NO_2); 1232, 1202 (C–O–C of enoxynitrile). ^1H NMR (DMSO-d_6, 400.13 MHz, ppm): 9.06 (d, 2H, $J=2.00$ Hz); 8.90 (t, 1H, $J=2.17$ Hz); 7.37–7.35 (m, 4H, aromatic of pendent phenyl); 7.20–7.18 (m, 1H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 176.15, 153.34, 148.00, 131.23, 130.34, 130.14, 126.98, 122.44, 120.63, 112.52, 110.66, 73.38. HRMS (*m*/*e*): calcd for $C_{16}H_8N_4O_5$, 336.0495; found 336.0481.

4.3.6. [(3,5-Diaminophenyl)phenoxymethylidene]propanedinitrile (**6**)

A slurry of **5** (7.5 g, 22.3 mmol), tin(II) chloride dihydrate ($SnCl_2\cdot 2H_2O$) (40.2 g, 178 mmol), and 130 mL of absolute ethanol in 250 mL two-necked flask was stirred while concentrated HCl (66.3 mL, 758 mmol) was added slowly. Then, the mixture was stirred at room temperature for additional 24 h. Excess ethanol was evaporated, and the remaining solution was poured into ice water. The solution was basified with 10% NaOH solution up to pH 7–8. The resulting precipitate was filtered, washed with distilled water, and dried in vacuo at room temperature over P_2O_5 for 24 h. The precipitate was added to 250 mL of ethyl acetate (EA) and stirred for 1 h. After the insoluble tin compound was filtered, EA in the filtrate was evaporated. The orange-colored product was purified by recrystallization from THF/hexane (4.51 g, 73.1% yield): mp 171–173 °C. FTIR (KBr, cm^{-1}): 3473, 3440, 3380, 3361 ($-NH_2$); 2228 (–CN); 1622, 1549, 1487, 1457 (aromatic C=C and C=N); 1287, 1222 (C–O–C of enoxynitrile). ^1H NMR (DMSO-d_6, 400.13 MHz, ppm): 7.35–7.31 (m, 2H, aromatic of pendent phenyl); 7.17–7.10 (m, 3H, aromatic of pendent phenyl); 6.03 (d, 2H, $J=1.88$ Hz); 5.92 (t, 1H, $J=1.81$ Hz); 5.12 (s, 4H, N*H* of aromatic diamine). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 182.45, 154.56, 149.67, 129.89, 128.89, 125.54, 119.31, 113.32, 112.20, 103.59, 103.13, 70.07. HRMS (*m*/*e*): calcd for $C_{16}H_{12}N_4O$, 276.1011; found 276.1013.

4.4. Model reactions

All model reactions were carried out under dry argon atmosphere.

4.4.1. Model compound of the polyamide containing pendent enaminonitrile group (**7**)

4 (0.200 g, 0.726 mmol), benzoyl chloride (0.204 g, 1.45 mmol), and 3.7 mL of DMAc were added to a dry 25 mL two-necked flask, and this mixture was stirred at 0 °C for 3 h. After pyridine (0.118 mL, 1.45 mmol) as an acid acceptor was added, the mixture was stirred at room temperature for 10 h. The solution was poured into distilled water, and the resulting precipitate was filtered, washed with distilled water and methanol repeatedly, and dried in vacuo at 80 °C for 12 h (0.305 g, 99.7% yield): mp 281–283 °C. FTIR (KBr, cm^{-1}): 3300 (–NH– of enaminonitrile and amide); 2217 (–CN); 1655 (C=O of amide); 1602, 1538, 1495, 1450, 1418 (aromatic C=C and C=N). ^1H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.49 (s, 1H, N*H* of enaminonitrile); 10.19 (s, 2H, N*H* of amide); 8.54 (t, 1H, $J=1.88$ Hz); 7.99 (dd, 4H, $J=6.98$ Hz, $J=1.64$ Hz); 7.77 (d, 2H, $J=1.88$ Hz); 7.59–7.50 (m, 6H, aromatic of benzoyl); 7.35–7.33 (m, 2H, aromatic of pendent phenyl); 7.24–7.22 (m, 3H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 167.69, 165.86, 139.98, 137.73, 134.51, 132.74, 131.93, 129.04, 128.51, 127.81, 127.12, 124.80, 117.20, 116.07, 114.96, 114.58, 52.94. HRMS (*m*/*e*): calcd for $C_{30}H_{21}N_5O_2$, 483.1695; found 483.1691.

4.4.2. Model compound of the polyamide containing pendent enoxynitrile group (**8**)

The above procedure was repeated with the following quantities of reagents: **6** (0.200 g, 0.724 mmol), benzoyl chloride (0.204 g, 1.45 mmol), and 3.7 mL of DMAc. After the filtration, the product was washed with distilled water and distilled water/methanol (v/v = 1/2) mixture repeatedly and dried in vacuo over P_2O_5 at room temperature for 24 h (0.330 g, 94.1% yield): mp 119–121 °C. FTIR (KBr, cm^{-1}): 2233 (–CN); 1659 (C=O of amide); 1602, 1543, 1488, 1449, 1417 (aromatic C=C and C=N); 1274, 1243 (C–O–C of enoxynitrile). ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): 8.40 (s, 2H, N*H* of amide); 8.19 (s, 1H); 7.77 (s, 2H); 7.70 (d, 4H, J = 7.39 Hz); 7.46 (t, 2H, J = 7.39 Hz); 7.35 (t, 4H, J = 7.70 Hz); 7.22 (t, 2H, J = 7.81 Hz); 7.07 (t, 1H, J = 7.40 Hz); 6.93 (d, 2H, J = 7.90 Hz). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): 180.31, 166.27, 154.11, 139.56, 133.80, 132.29, 130.04, 129.59, 128.70, 127.13, 126.21, 119.72, 116.06, 115.56, 113.27, 110.78, 71.81. HRMS (*m*/*e*): calcd for $C_{30}H_{20}N_4O_3$, 484.1535; found 484.1532.

4.4.3. Model compound of the polyimide containing pendent enaminonitrile group (**9**)

A dry 25 mL two-necked flask was equipped with a Dean–Stark trap connected to a water-cooled condenser. **4** (0.200 g, 0.726 mmol), phthalic anhydride (0.215 g, 1.45 mmol), and 3.6 mL of NMP were added to the flask, and this mixture was stirred for 3 h. Temperature was raised up to 190 °C and the mixture was stirred for 8 h while chlorobenzene as an azeotroping reagent was added periodically. The solution was poured into distilled water, and the resulting precipitate was filtered, washed with distilled water and methanol repeatedly, and dried in vacuo over P_2O_5 at 80 °C for 12 h (0.370 g, 95.2% yield): mp 298–300 °C. FTIR (KBr, cm^{-1}): 3242 (–NH– of enaminonitrile and amide); 2219 (–CN); 1781, 1722 (C=O of imide); 1599, 1561, 1496, 1464 (aromatic C=C and C=N); 1358 (C–N of imide); 719 (C=O bending of imide). ^1H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.65 (s, 1H, N*H* of enaminonitrile); 7.99–7.91 (m, 9H); 7.85 (d, 2H J = 1.73 Hz); 7.38–7.34 (m, 2H, aromatic of pendent phenyl); 7.28–7.23 (m, 3H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 166.46, 165.74, 137.41, 134.89, 133.31, 132.76, 131.40, 128.90, 127.43, 127.36, 127.11, 125.06, 123.58, 116.64, 114.11, 53.57. HRMS (*m*/*e*): calcd for $C_{32}H_{17}N_5O_4$, 535.1281; found 535.1285.

4.4.4. Model compound of the polyimide containing pendent enoxynitrile group (**10**)

The above procedure was repeated with the following quantities of reagents: **6** (0.200 g, 0.724 mmol), phthalic anhydride (0.215 g, 1.45 mmol), and 3.6 mL of NMP. But, the precipitate was dried in vacuo over P_2O_5 at room temperature for 24 h (0.350 g, 90.1% yield): mp 240–242 °C. FTIR (KBr, cm^{-1}): 2228 (–CN); 1783, 1724 (C=O of imide); 1600, 1566, 1449 (aromatic C=C and C=N); 1364 (C–N of imide); 718 (C=O bending of imide). ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): 8.05 (t, 1H, J = 1.89 Hz); 7.98–7.93 (m, 4H); 7.86 (d, 2H, J = 1.87 Hz); 7.84–7.79 (m, 4H); 7.35–7.31 (m, 2H, aromatic of pendent phenyl); 7.19–7.15 (m, 1H, aromatic of pendent phenyl); 7.05–7.02 (m, 2H, aromatic of pendent phenyl). ^{13}C NMR ($CDCl_3$, 100.62 MHz, ppm): 178.25, 166.21, 154.10, 134.94, 133.42, 131.19, 130.28, 129.75, 126.70, 126.35, 124.72, 124.15, 119.68, 112.14, 110.52, 73.26. HRMS (*m*/*e*): calcd for $C_{32}H_{16}N_4O_5$, 536.1121; found 536.1113.

4.5. Polymerizations

All polymerization reactions were carried out under dry argon atmosphere.

4.5.1. Polyamide from **4** and TPC (**PAEAN1**)

To a dry 50 mL three-necked flask equipped with a mechanical stirrer, **4** (0.50000 g, 1.8161 mmol), TPC (0.36868 g, 1.8160 mmol), and 8.3 mL of DMAc were added, and this mixture was stirred at 0 °C for 3 h. After pyridine (0.29377 mL, 3.6322 mmol) as an acid acceptor was added, the mixture was stirred at room temperature for 10 h. Benzoyl chloride (0.00511 g, 0.036322 mmol) as an end-capping reagent was added, and the mixture was stirred at room temperature for additional 2 h. The solution was poured into distilled water, and the resulting precipitate was filtered, washed with distilled water and methanol repeatedly, and dried in vacuo at 80 °C for 12 h: FTIR (thin film, cm^{-1}): 3275 (–NH– of enaminonitrile and amide); 3088 (aromatic C–H); 2215 (–CN); 1664 (C=O of amide); 1605, 1558, 1445 (aromatic C=C and C=N). ^1H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.48 (s, 1H, N*H* of enaminonitrile); 10.36 (s, 2H, N*H* of amide group); 8.60 (t, 1H, J = 1.68 Hz); 8.13 (s, 4H, aromatic of terephthaloyl); 7.80 (d, 2H, J = 1.56 Hz); 7.38–7.35 (m, 2H, aromatic of pendent phenyl); 7.25–7.23 (m, 3H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 167.08, 165.12, 139.80, 137.65, 137.25, 133.45, 129.03, 127.93, 127.15, 124.82, 117.01, 116.31, 115.02, 114.37, 51.90.

4.5.2. Polyamide from **4** and IPC (**PAEAN2**)

The above procedure was repeated with the following quantities of reagents: **4** (0.50000 g, 1.8161 mmol), IPC (0.36868 g, 1.8160 mmol), and 8.3 mL of DMAc: FTIR (thin film, cm^{-1}): 3262 (–NH– of enaminonitrile and amide); 3071 (aromatic C–H); 2216 (–CN); 1676 (C=O of amide); 1623, 1603, 1566, 1528, 1472, 1439, 1406 (aromatic C=C and C=N). ^1H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.50 (s, 1H, N*H* of enaminonitrile); 10.38 (s, 2H, N*H* of amide); 8.60 (s, 1H); 8.56 (s, 1H); 8.17 (dd, 2H, J = 7.76 Hz, J = 1.48 Hz); 7.79 (d, 2H, J = 1.72 Hz); 7.68 (t, 1H, J = 7.77 Hz); 7.36–7.32 (m, 2H, aromatic of pendent phenyl); 7.23–7.22 (m, 3H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 167.30, 165.34, 139.86, 137.67, 134.78, 132.17, 131.05, 128.99, 128.77, 127.25, 127.15, 124.76, 117.17, 116.19, 114.87, 114.57, 52.55.

*4.5.3. Polyamide from **6** and TPC (**PAEON1**)*

To a dry 25 mL three-necked flask equipped with a mechanical stirrer, **6** (0.30000 g, 1.0858 mmol), TPC (0.22042 g, 1.0857 mmol), and 5.0 mL of DMAc were added, and this mixture was stirred at 0 °C for 3 h. After pyridine (0.17564 mL, 2.1716 mmol) as an acid acceptor was added, the mixture was stirred at room temperature for 10 h. Benzoyl chloride (0.00305 g, 0.021716 mmol) as an end-capping reagent was added, and the mixture was stirred at room temperature for additional 2 h. The solution was poured into distilled water, and the resulting precipitate was filtered, washed with distilled water and methanol repeatedly, and dried in vacuo over P_2O_5 at room temperature for 24 h: FTIR (thin film, cm^{-1}): 3220 (–NH– of enaminonitrile and amide); 3096 (aromatic C–H); 2232 (–CN); 1666 (C=O of amide); 1607, 1548, 1445 (aromatic C=C and C=N); 1278, 1243 (C–O–C of enoxynitrile). ^{1}H NMR (DMSO-d_6, 400.13 MHz, ppm): 10.74 (s, 2H, N*H* of amide group); 8.54 (s, 1H); 8.10 (s, 4H aromatic of terephthaloyl); 7.96 (s, 2H); 7.40–7.36 (m, 2H, aromatic of pendent phenyl); 7.29–7.27 (m, 2H, aromatic of pendent phenyl); 7.22–7.28 (m, 1H, aromatic of pendent phenyl).

*4.5.4. Polyimide from **4** and ODPA (**PIEAN1**)*

A dry 50 mL three-necked flask was equipped with a Dean–Stark trap connected to a water-cooled condenser and a mechanical stirrer. **4** (0.50000 g, 1.8161 mmol), ODPA (0.56336 g, 1.8160 mmol), and 9.3 mL of NMP were added into the flask, and this mixture was stirred for 3 h. The poly(amic acid) solution was diluted with 9.3 mL of NMP, and temperature was raised up to 190 °C. The mixture was stirred at this temperature for 8 h while chlorobenzene as an azeotroping reagent was added periodically. Phthalic anhydride (0.00538 g, 0.036322 mmol) as an end-capping reagent was added, and the mixture was stirred at 190 °C for additional 2 h. The solution was poured into distilled water/methanol (v/v = 1/1) mixture, and the resulting precipitate was filtered, washed with distilled water and methanol repeatedly, and dried in vacuo over P_2O_5 at 80 °C for 12 h: FTIR (thin film, cm^{-1}): 3227 (–NH– of enaminonitrile); 2215 (–CN); 1779, 1722 (C=O of imide); 1651, 1602, 1567, 1528, 1472, 1442 (aromatic C=C and C=N); 1353 (C–N of imide); 1237 (C–O–C); 746 (C=O bending of imide). ^{1}H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.63 (s, 1H, N*H* of enaminonitrile); 8.06 (d, 2H, $J = 8.92$ Hz); 7.89 (t, 1H, $J = 1.80$ Hz); 7.83 (d, 2H, $J = 1.84$ Hz); 7.66–7.63 (m, 4H); 7.36–7.32 (m, 2H, aromatic of pendent phenyl); 7.26–7.21 (m, 3H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 166.49, 165.72, 165.57, 160.91, 137.38, 134.38, 134.18, 132.71, 128.91, 128.80, 127.44, 127.05, 127.11, 126.29, 125.05, 124.94, 116.57, 113.94, 114.03, 53.00.

*4.5.5. Polyimide from **4** and BTDA (**PIEAN2**)*

The above procedure was repeated with the following quantities of reagents: **4** (0.50000 g, 1.8161 mmol), BTDA (0.58517 g, 1.8160 mmol), and 9.5 mL of NMP: FTIR (thin film, cm^{-1}): 3227 (–NH– of enaminonitrile); 2213 (–CN); 1780, 1725 (C=O of imide); 1675 (C=O of BTDA); 1597, 1566, 1528, 1471, 1434, 1405 (aromatic C=C and C=N); 1355 (C–N of imide); 720 (C=O bending of imide). ^{1}H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.66 (s, 1H, N*H* of enaminonitrile); 8.28 (d, 2H, $J = 7.72$ Hz); 8.23 (s, 1H); 8.18 (d, 2H, $J = 7.68$ Hz); 7.96 (t, 1H, $J = 1.80$ Hz); 7.89 (d, 2H, 1.68); 7.37–7.33 (m, 2H, aromatic of pendent phenyl); 7.27–7.22 (m, 3H, aromatic of pendent phenyl). ^{13}C NMR (DMSO-d_6, 100.62 MHz, ppm): 193.35, 166.53, 165.81 (2C), 141.78, 137.41, 136.02, 134.69, 134.49, 132.68, 131.85, 128.96, 128.90, 127.71, 127.18, 125.08, 124.10, 124.00, 116.62, 114.11, 52.81.

*4.5.6. Polyimide from **4** and PMDA (**PIEAN3**)*

The above procedure was repeated with the following quantities of reagents: **4** (0.50000 g, 1.8161 mmol), PMDA (0.39611 g, 1.8160 mmol), and 7.8 mL of NMP: FTIR (thin film, cm^{-1}): 3273 (–NH– of enaminonitrile); 2217 (–CN); 1781, 1729 (C=O of imide); 1602, 1566, 1456 (aromatic C=C and C=N); 1349 (C–N of imide); 728 (C=O bending of imide). ^{1}H NMR (DMSO-d_6, 400.13 MHz, 100 °C, ppm): 10.71 (s, 1H, N*H* of enaminonitrile); 8.41 (s, 2H); 8.04 (t, 1H, $J = 1.84$ Hz); 7.94 (d, 2H, $J = 1.76$ Hz); 7.39–7.35 (m, 2H, aromatic of pendent phenyl); 7.29–7.24 (m, 3H, aromatic of pendent phenyl).

*4.5.7. Polyimide from **6** and ODPA (**PIEON1**)*

A dry 25 mL three-necked flask was equipped with a Dean–Stark trap connected to a water-cooled condenser and a mechanical stirrer. **6** (0.30000 g, 1.0858 mmol), ODPA (0.33681 g, 1.0857 mmol), and 5.5 mL of NMP were added to the flask, and this mixture was stirred for 3 h. The poly(amic acid) solution was diluted with 5.5 mL of NMP, and temperature was raised up to 190 °C. The mixture was stirred at this temperature for 8 h while chlorobenzene as an azeotroping reagent was added periodically. Phthalic anhydride (0.00322 g, 0.021716 mmol) as an end-capping reagent was added, and the mixture was stirred at 190 °C for additional 2 h. The solution was poured into distilled water/methanol (v/v = 1/1) mixture, and the resulting precipitate was filtered, washed with distilled water and methanol repeatedly, and dried in vacuo over P_2O_5 at room temperature for 24 h: FTIR (thin film, cm^{-1}): 2232, 2196 (–CN); 1782, 1728 (C=O of imide); 1605, 1569, 1475, 1447 (aromatic C=C and C=N); 1355 (C–N of imide); 1277, 1236 (C–O–C); 745 (C=O bending of imide). ^{1}H NMR (DMSO-d_6, 400.13 MHz, ppm): 8.07 (br, 2H); 7.95 (s, 2H); 7.83 (s, 1H); 7.63 (br, 4H); 7.35–7.27 (br, 4H, aromatic of pendent phenyl); 7.19 (br, 1H, aromatic of pendent phenyl).

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