Fully Conjugated and Soluble Polyazomethines

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ABSTRACT: Fully conjugated and soluble polyazomethines were synthesized by the polycondensation of aromatic dialdehydes with two kinds of diamines having a tetraphenylethylene structure, *cis*- and *trans*-1,2-bis(4-aminophenyl)-1,2-diphenylethylene (**4a** and **4b**). The structures of these diamines were determined using NMR and single crystal X-ray analysis. The diamines formed 1:1 complexes with toluene which was used as a recrystallization solvent. The polyazomethines, as precipitated, possessed inherent viscosities (η_{inh}) in the range from 0.83 to 0.98 dL/g. Polymers **6** and **7**, which were prepared from **4a** and terephthalaldehyde and from **4b** and isophthalaldehyde, respectively, gave flexible and tough orange films. These polymer films exhibited excellent solubility in common organic solvents such as benzene, chloroform, and THF. The molecular weights of the polymers increased 2- to 4-fold by postcuring at 200 °C. Although the crystallinity of polymer **6** was slightly higher than that of polymer **7**, these polymers were essentially amorphous. All of the polyazomethines showed excellent thermal stability with no significant weight loss up to approximately 350 °C, and the 5% weight loss temperatures in air were over 400 °C. The polymer films had glass transition temperatures over 260 °C.

Introduction

It has been well-known that fully conjugated polyazomethines formed from ordinary aromatic diamines and dialdehydes are precipitated even during the initial stage of the polymerization due to their rigid-rod chain structures,[1] although they are expected to exhibit excellent properties such as thermal stability, electric conductivity, nonlinear optical properties, or many other characteristics.[2−9] The resulting precipitates are insoluble in organic solvents and do not have self-standing film formability. Therefore, these interesting properties have so far been estimated using powdery or spin-coated samples in almost all cases. Recently, much effort has been put forth on synthesizing soluble polyazomethines with film formability.[10−17] Suematsu and co-workers reported the synthesis of some film-forming aromatic polyazomethines using *m*-cresol as a polymerization medium, whereas some polyazomethines precipitated from *m*-cresol as a colored powder during the polymerization process.[18] Other methods have been also reported to improve the processability of conjugated polyazomethines by modification and selection of the polymer structure, for example, unsymmetrical[19] or symmetrical[20,21] substitutions in the main chain aromatic rings with flexible alkyl or alkoxy side chains.

We now describe the synthesis, characterization, and properties of fully conjugated, soluble, and film-formable polyazomethines which were made from two types of diamines with a tetraphenylethylene structure and dialdehydes.

Results and Discussion

Monomer Synthesis. The diamines were prepared via several steps using 4-nitrobenzoyl chloride as a starting material. The synthetic route is illustrated in Scheme 1 together with melting points and yields. The Friedel-Crafts reaction of 4-nitrobenzoyl chloride with benzene catalyzed by aluminum chloride gave 4-nitrobenzophenone (**1**) in good yield. (4-Nitrophenyl)-phenyldichloromethane (**2**) was formed by the chlorination of the carbonyl group in **1** with phosphorus pentachloride. The coupling reaction of **2** using powdery Cu produced a mixture of two isomers, *cis*- and *trans*-1,2-bis(4-nitrophenyl)-1,2-diphenylethylene (**3**). The mixture, without being separated into each compound, was reduced with $SnCl_2$ dihydrate and concentrated HCl. Judging from the ^1H NMR spectrum (Figure 1a) measured in DMSO-d_6, the reduction products are found to consist of nearly equimolar amounts of two diamine isomers. The silica-gel TLC analysis using a mixture of hexane and ethyl acetate (1:1 vol/vol) as an eluent revealed that the two isomers had R_f values of 0.63 and 0.36. These two isomers were separated by column chromatography, and the ^1H NMR spectra of the compounds having R_f values of 0.63 and 0.36 are shown in parts b and c of Figure 1, respectively. Although it was easily anticipated that one of the isomers was *cis*-1,2-bis(4-aminophenyl)-1,2-diphenylethylene (**4a**) and the other was the *trans*-isomer (**4b**), they could not be exactly distinguished only using the ^1H and ^{13}C NMR spectroscopic data. The compound with an R_f value of 0.36 was recrystallized from toluene and the structure was determined by single crystal X-ray analysis. Refinement, described in the Experimental Section, results in the structure shown in Figure 2, and the X-ray crystal data are listed in Table 1. On the basis of this result, the compounds having R_f values of 0.36 and 0.63 were identified as diamines **4a** and **4b**, respectively. Interestingly, as can be seen from Figure 2, diamine **4a** forms a 1:1 complex with toluene which was used as a recrystallization solvent. This fact was also supported by the NMR spectrum of the diamine complex; that is, the signal at 2.29 ppm assigned to the methyl protons of toluene was observed with the integral area of three protons compared with those of 4 and 18 protons corresponding to amino and aromatic ones, respectively. The toluene molecule in the crystal is sandwiched between two molecules of the diamine and lies almost perpendicular to the molecular planes of the diamine. The four benzene rings of the diamine are neither coplanar nor perpendicular to one another but rather are twisted at some intermediate angle like blades of a propeller. The diamine is found to loosely include the toluene molecule as judged by the fact that the carbon atoms of the toluene have markedly larger anisotropic thermal ellipsoides at room temperature than those of

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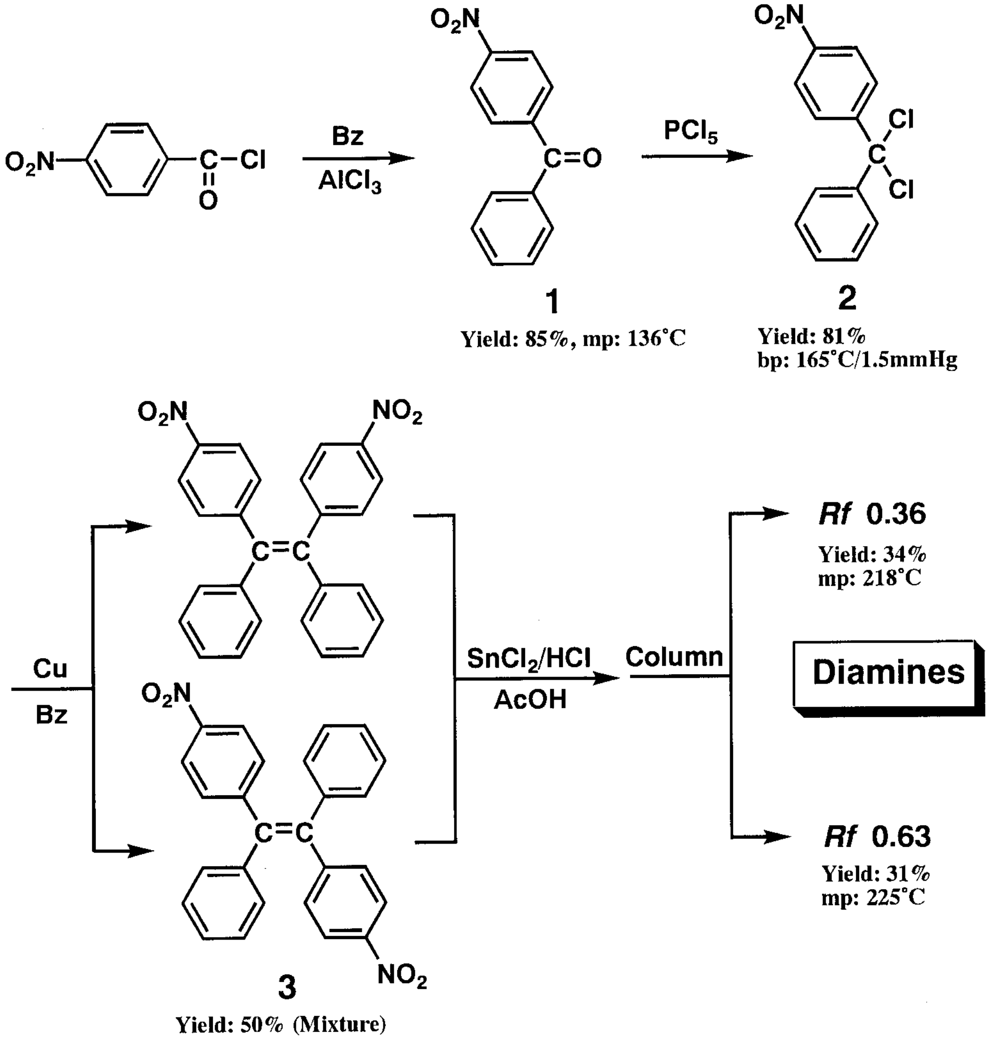
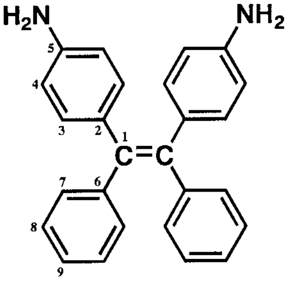
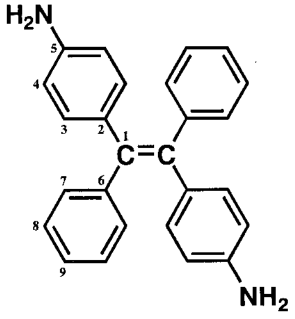
Scheme 1





Rf 0.36: 4a



Rf 0.63: 4b

the diamine. A further detailed X-ray analysis of the crystal showed that the diamine molecules were stacked in one direction and the toluene molecules were packed in the spaces as closely as their geometry allowed. Judging from the NMR spectrum of the diaimine **4b**, **4b** was also suggested to form the corresponding complex when it was recrystallized from toluene.

The diamine complexes were not subjected to polycondensation and the other analyses such as IR, NMR, or the elemental analysis as described in the Experimental Section except for the melting point measurement, but the free diamines without recrystallization, which had been separated by column chromatography and then dried under vacuum, were used.

Synthesis of Polymers. According to Suematsu's report that *m*-cresol facilitated the polycondensation of diamine with aldehyde to give a homogeneous solution,[18] *m*-cresol was also adopted here as the polymerization solvent. The polycondensations of equimolar amounts of diamine and aldehyde were carried out at room temperature for 1 day while a slow stream of nitrogen was maintained. After an aliquot of the resulting polymer solution was cast on a glass plate, the solution was dried under reduced pressure upon heating in order to remove the reaction medium. If the polymer solution was poured into methanol, an orange powdery polymer quantitatively precipitated out. The reprecipitated polyazomethines possessed inherent viscosities

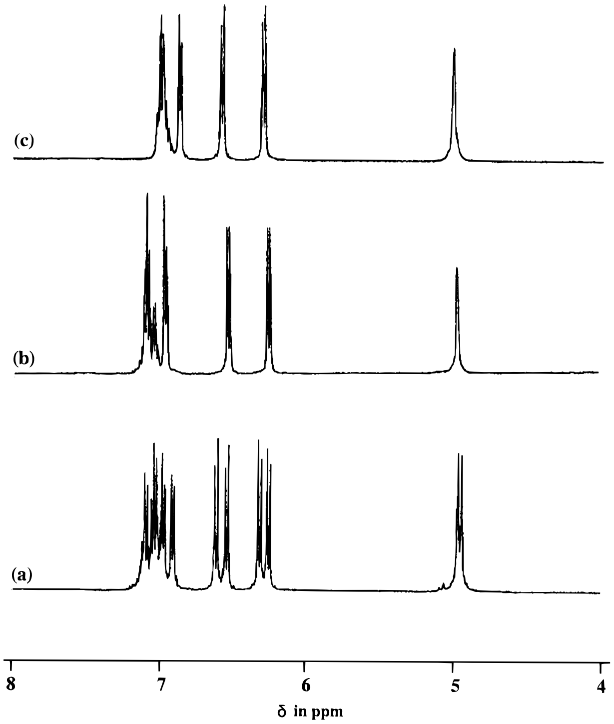


Figure 1. ^{1}H NMR spectra of diamines in DMSO-d_6: (a) mixture of two isomers; (b) diamine with R_f value of 0.63; (c) diamine with R_f value of 0.36.

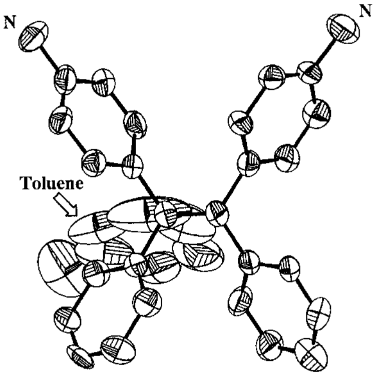


Figure 2. Perspective view of the diamine having R_f value of 0.36.

Table 1. X-ray Crystal Data for R_f 0.36 Diamine

formula	$C_{33}H_{30}N_2$
formula weight	454.61
crst color, habit	pale yellow, needles
cryst size (mm^3)	0.4 × 0.1 × 0.1
cryst system	triclinic (P1)
lattice params:	
a (Å)	9.475(7)
b (Å)	9.484(11)
c (Å)	17.314(34)
α (deg)	97.73(12)
β (deg)	97.12(10)
γ (deg)	119.25(7)
V (Å^3)	1312.32(30)

(η_{inh}) measured in concentrated H_2SO_4 which were in the range from 0.83 to 0.98 dL/g. The results along with the film quality of the polyazomethines are listed in Table 2.

Table 2. Synthesis of Polyazomethines with Tetraphenylethylene Structure[a]

polymer	diamine	dialdehyde	η_{inh} (dL/g)[b]	10^{-3} $\bar{M}_n$[c] reprecipitated	film[d]	film quality
5	**4a**	IPA	0.83	–	–	–[e]
6	**4a**	TPA	0.84	6.5	25.1	flexible
7	**4b**	IPA	0.98	9.7	22.7	flexible
8	**4b**	TPA	0.93	–	–	–[e]

[a] Polymerization: diamine, 1.00 mmol; dialdehyde, 1.00 mmol; solvent (m-cresol), 5 mL; room temperature; 1 day. [b] Reprecipitated polymer. Measured in concentrated H_2SO_4. [c] GPC (THF), polystyrene standards. [d] Cured at 80 °C for 1 h and 200 °C for 2 h under reduced pressure. [e] Precipitated during the polymerization reaction.

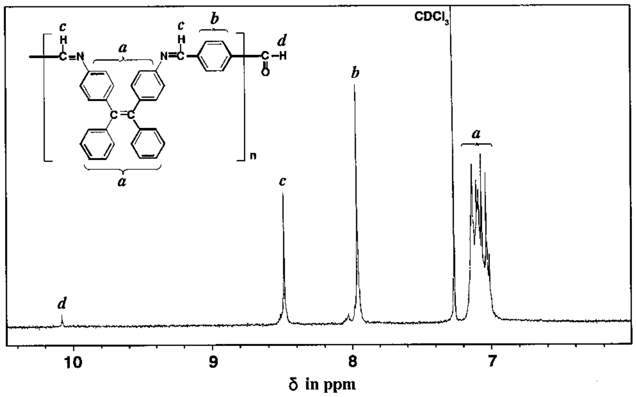


Figure 3. ^{1}H NMR spectrum of polymer **6** as reprecipitated and its assignment.

The polycondensations of **4a** and TPA (polymer **6**) and of **4b** and IPA (polymer **7**) homogeneously proceeded and the polymerization solutions provided flexible orange films, whereas polymers **5** and **8**, which were derived from **4a** and isopthalaldehyde (IPA) and from **4b** and terephthalaldehyde (TPA), respectively, were precipitated in the polymerization medium during the polymerization. At the present time, however, we cannot exactly explain the reason why the precipitate of polymers **5** and **8** was deposited. The excellent solubility of polymers **6** and **7** in NMR solvents such as deutrated chloroform made it possible to determine the ^{1}H NMR or the ^{13}C NMR spectrum and to investigate the structures. Figure 3 shows the ^{1}H NMR spectrum of the reprecipitated polymer **6** and its assignment. The number of protons corresponding to each resonance based on integration of the NMR spectrum is in good agreement with the proposed structure. The very small signal at 10.1 ppm (signal d) is attributed to the terminal aldehyde. We can easily estimate the degree of polymerization (DP) and the number-average molecular weight ($\bar{M}_n$) by measuring the signal-area ratio of the terminal aldehyde to the azomethine proton which appears at around 8.5 ppm (signal c). The DP and the $\bar{M}_n$ of the reprecipitated polymer **6** are 13.4 and 6.16 × 10^3, respectively. In the infrared spectrum of polymer **6** (Figure 4), a small peak at 1701 cm^{-1} due to an aldehyde group is observed and this is consistent with the NMR analysis. The infrared spectra of all the reprecipitated polymers and the films showed a strong C=N stretching at 1627 cm^{-1}.

The $\bar{M}_n$ of the soluble polyazomethines were also determined by gel permeation chromatography (GPC) (THF as the eluent) after calibration with standard polystyrenes, although their structures were somewhat different. The $\bar{M}_n$ of the reprecipitated polymer **6** measured by GPC was in fair agreement with that obtained by ^{1}H NMR. The GPC analysis revealed that the molecular weights of the polyazomethine films (polymers **6** and **7**) were about 2–4 times higher than those of the corresponding reprecipitated polymers, the

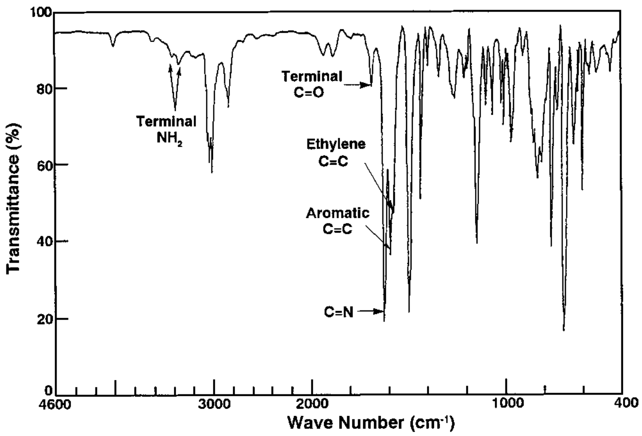


Figure 4. Infrared spectrum of polymer **6**.

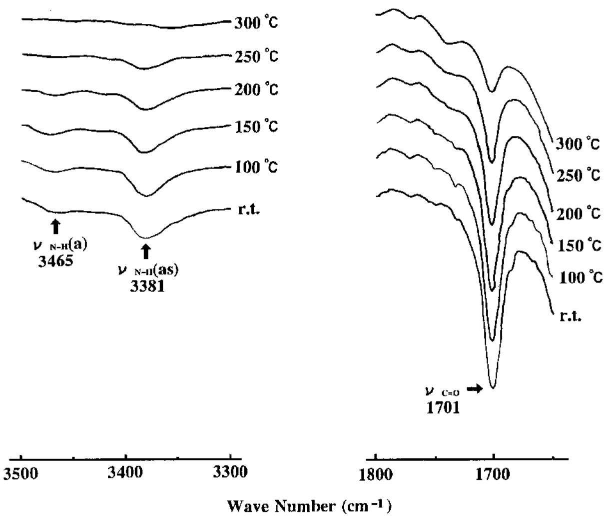


Figure 5. Dependencies of curing temperature on IR absorptions due to terminal NH$_2$ and CHO groups of repecipitated polymer **6**.

results of which are listed in Table 2. This fact suggested that the postpolymerization occurred during the film forming process, that is, the postcuring at 80 °C for 1 h and at 200 °C for 2 h. Although it is well-known that polyazomethines may undergo further polymerization in the solid state when postcured,[18,22] we could directly confirm it using GPC. Furthermore, this was also substantiated by IR and ^{1}H NMR spectroscopies. As can be seen from Figure 5, weak absorptions at 1701 cm^{-1} due to the terminal aldehyde group and at 3465 and 3381 cm^{-1} due to the terminal amino group of the reprecipitated polymer (polymer **6**) are gradually decreased by increasing the postcuring temperature. The signal at 10.1 ppm (signal *d*) attributed to the terminal aldehyde in the ^{1}H NMR of the corresponding postcured film was 4–5 times smaller than that of the precipitated polymer.

Properties of Polyazomethines. The solubility of the polymers was qualitatively investigated. The results are listed in Table 3. It is noteworthy that the polymer films (polymers **6** and **7**) exhibit high solubility in common organic solvents such as benzene, chloroform, or THF, whereas polymers **5** and **8** were soluble only in formic acid and concentrated H$_2$SO$_4$. The introduction of a tetraphenylethylene unit into the polyazomethines backbone would reduce the polymer–polymer interaction and significantly enhance the solubility.

Table 3. Solubility of Polyazomethine Films[a]

solvents	polymer **6**	polymer **7**
m-cresol	++	++
formic acid	++	++
concentrated H$_2$SO$_4$	++	++
N-methyl-2-pyrrolidone	++	++
N,*N*-dimethylformamide	+	++
N,*N*-dimethylacetamide	++	++
dimethyl sulfoxide	−	−
tetrahydrofuran	++	++
benzene	++	++
chloroform	++	++
acetone	+	+
methanol	−	−

[a] ++, soluble at room temperature; +, soluble on heating; −, insoluble even on heating.

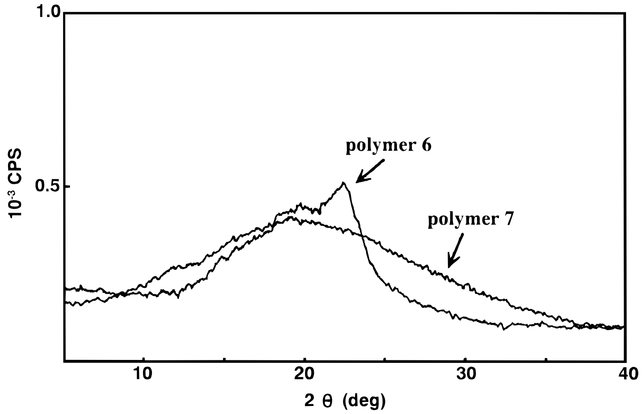


Figure 6. X-ray diffractograms of reprecipitated polymers **6** and **7**.

X-ray diffraction measurements of reprecipitated polymers **6** and **7** were carried out by a powder method at room temperature. In the X-ray diffraction patterns (Figure 6), no significant diffraction peaks are exhibited except for a broad halo. Although the crystallinity of polymer **6** seems to be slightly higher than that of polymer **7**, these polymers are essentially amorphous. The *d* spacings were calculated from the diffraction angles around the broad halo; the values of polymer **6** were 0.450 and 0.398, and that of polymer **7** was 0.462. The higher crystallinity of polymer **6** may be due to its better packed polymer structure than polymer **7**. Figure 7 shows a representation of the postulated structures which are based on some simplifying assumptions that the azomethine bond prefers a *trans* conformation, benzene rings are coplanar, etc. The polymer chains of polymer **6** seem to be aligned more regularly than those of polymer **7**.

The thermal properties were evaluated by the 5% weight loss temperature (T_5) measured using thermogravimetric analysis (TGA) in N$_2$ and the glass transition temperature (T_g) measured using thermomechanical analysis (TMA) with a penetration probe. The polyazomethines had good thermal stability and the T_5's of polymers and **7** were 455 °C and 395 °C, respectively. Polymer **6** possessed a T_g at 292 °C and polymer **7** at 258 °C.

Experimental Section

Material. Commercial-grade *m*-cresol was purified by fractional distillation under reduced pressure. Benzene was purified by shaking with concentrated H$_2$SO$_4$, then with water, an aqueous solution of NaOH, and water, followed by drying with CaCl$_2$ and fractional distillation over CaH$_2$. Terephthalaldehyde and isophthalaldehyde were purchased from the Tokyo Kasei Co. and purified by recrystallization from water.

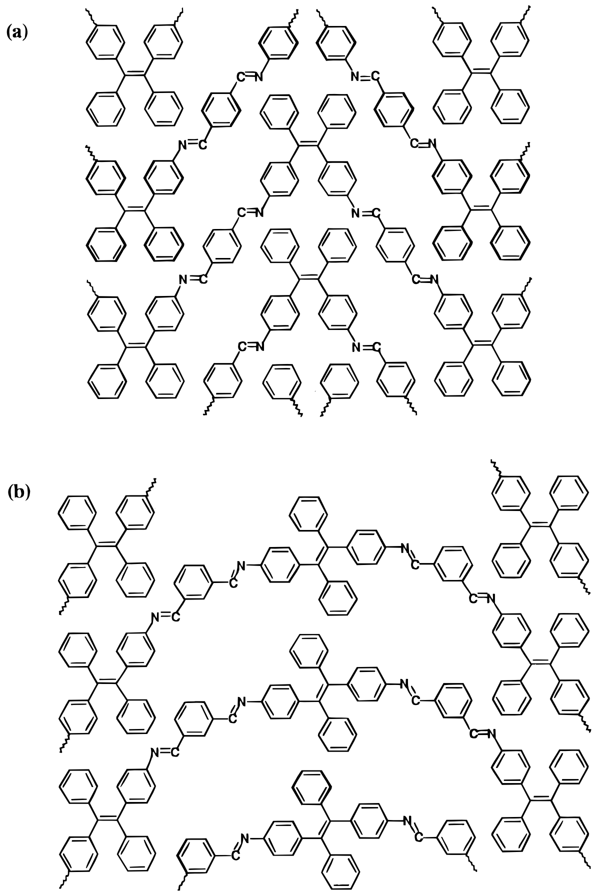


Figure 7. A representation of the postulated structures which are based on some simplifying assumptions: (a) polymer **6**; (b) polymer **7**.

Measurement. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-EX 400WB spectrometer operating at 400 and 100 MHz, respectively. Proton and carbon signals in the ^{1}H and ^{13}C NMR spectra were assigned in H,H-COSY, H,C-COSY, and NOESY (eliminating the J correlation). Signals were singlet where no multiplicity occurred. The internal standard was tetramethylsilane. J values are given in hertz. IR spectra were obtained using Jasco VALOR-III and JEOL JIR-100 Fourier-transform infrared spectrometers. The UV−vis spectra of the polymer films were recorded using a Jasco Ubest-50 spectrophotometer at room temperature in air. Melting points were taken on a Seiko Instruments TG/DTA 220 thermal analyzer. The molecular weight was analyzed using a JASCO 800 gel permeation chromatograph equipped with an RI detector and Shodex KF-806M columns in THF at 50 °C; molecular weight calculations were made on the basis of polystyrene standards. Inherent viscosities were measured in 0.5 g/dL concentrated H_2SO_4 solutions of the reprecipitated polymers at 30 °C using an Ostwald viscometer. Elemental analyses were made using a Perkin-Elmer CHN 2400 elemental analyzer. Thermogravimetric analyses were performed using a Seiko TG/DTA 220 thermal analyzer at a heating rate of 10 °C in a N_2 atmosphere. Thermomechanical analyses were made using a Seiko Instruments TMA/SS 100 equipped with a penetration probe of 1.0 mm diameter at an applied constant load of 10 g (stress, 0.125 MPa) and at a heating rate of 10 °C in air. X-ray diffraction spectra of the reprecipitated polymers were obtained by the powder method using a Rigaku RAD III diffractometer with graphite monochromated Cu Kα radiation at 40 kV−25 mA and 2 deg/min.

Monomer Synthesis. 4-Nitrobenzophenone (1). In a 1-L three-necked flask equipped with a reflux condenser and a nitrogen inlet were placed 185.6 g (1.00 mol) of 4-nitrobenzoyl chloride and 600 mL of distilled benzene. A slow stream of nitrogen gas was maintained, and the mixture was stirred at room temperature until *p*-nitrobenzoyl chloride was entirely dissolved. The flask was cooled by dipping into an ice-water bath, and then 150.0 g (1.12 mol) of aluminum chloride was gradually added to the solution. After the mixture became homogeneous, the temperature was elevated to room temperature, then the mixture was stirred for 2 h and then for 4 h at reflux temperature. The reaction mixture was concentrated by evaporation, and the residue was poured over ice in a beaker. The precipitate was filtered and washed with an aqueous NaOH solution and then water. The resulting solid was recrystallized twice from ethanol to give 4-nitrobenzophenone as a pale-yellow crystallite (191 g, 85%): mp 136 °C; IR-(KBr) 1640(C=O), 1510 and 1340 (NO_2) cm^{-1}.

(4-Nitrophenyl)phenyldichloromethane (2). In a 200-mL three-necked flask equipped with a reflux condenser and a nitrogen inlet were placed 50 g (0.22 mol) of **1** and 57 g (0.27 mol) of phosphorus pentachloride. A slow stream of nitrogen gas was maintained, and the temperature was gradually elevated to 140 °C. The mixture was continuously heated at that temperature for 24 h. After the produced phosphorus oxychloride was removed by evaporation under reduced pressure, the residue was fractionally distilled and the orange fraction was collected (50 g, 81%): bp 161 °C (1.5 mmHg); IR-(liquid film) 1510 and 1340 (NO_2) cm^{-1}.

***cis*- and *trans*-1,2-Bis(4-nitrophenyl)-1,2-diphenylethylene (3).** In a 500-mL round-bottom flask equipped with a reflux condenser were placed 50 g (0.18 mol) of **2**, 600 mL of distilled benzene, and 30 g (0.47 mol) of powdery Cu which had been treated with 200 mL of acetone containing 0.5 g of iodine. The mixture was heated at reflux temperature for 24 h with magnetic stirring. The hot solution was filtered and the filtrate was cooled to room temperature. The resulting precipitate was filtered and then recrystallized from acetic acid to give a mixture of *cis*- and *trans*-isomers (**3**) as a yellow solid (70 g, 57%); IR(KBr) 1510 and 1340 (NO_2) cm^{-1}. Anal. Calcd for $C_{26}H_{18}N_2O_4$: C, 73.93; H, 4.27; N, 6.64. Found: C, 73.92; H, 4.52; N, 6.95.

***cis*- and *trans*-1,2-Bis(4-aminophenyl)-1,2-diphenylethylene (4a and 4b).** In a 500-mL round-bottom flask equipped with a reflux condenser were placed 10 g (0.024 mol) of **3** and 100 mL of acetic acid. To the solution a mixture of concentrated HCl (70 mL) and $SnCl_2$ dihydrate (56 g, 0.025 mol) was added and then heated at 100 °C for 6 h with magnetic stirring. After the flask was cooled in an ice-water bath, the reaction mixture was made slightly basic with an aqueous NaOH solution. The resulting precipitate was filtered and dried under reduced pressure. Reduced products were extracted with dried acetone from the solid. The extract was evaporated to dryness. Recrystallization of the resulting solid from toluene gave a mixture of *cis*- and *trans*-1,2-bis(4-aminophenyl)-1,2-diphenylethylene (**4a** and **4b**) as a pale yellow solid. The two isomers were separated by column chromatography (Silica gel 60) using a mixture of ethyl acetate and hexane (1:1 vol/vol) as an eluent. The isomers were distinguished by ^{1}H-NMR, ^{13}C-NMR, and X-ray crystallographic analysis.

4a: 34%; mp 218 °C (from toluene); $R_f = 0.36$ (silica gel, hexane−ethyl acetate (1:1 vol/vol)) ^{1}H NMR δ (DMSO-d_6) 4.98 (4H, NH_2), 6.31 (4H, d, $J_{4,3} = 7$, H-4), 6.61 (4H, d, $J_{3,4} = 7$, H-3), 6.91 (4H, dd, $J_{7,8} = 8$, $J_{7,9} = 2$, H-7), 7.01 (2H, dd, $J_{9,8} = 7$, $J_{9,7} = 2$, H-9), 7.05 (4H, dd, $J_{8,7} = 8$, $J_{8,9} = 7$, H-7); ^{13}C NMR δ (DMSO-d_6) 113.1 (C-4), 125.6 (C-9), 127.3 (C-8), 130.9 (C-7), 131.3 (C-2), 131.4 (C-3), 138.5 (C-1), 144.6 (C-6), 146.7 (C-5). The atom labeling used here is the same as that used in Scheme 1. IR (KBr) 3474, 3418, 3384, 3340, 3210, 3047, 3025, 1621, 1595, 1574, 1511, 1279, 1180, 835, 805, 748, 701 cm^{-1}. Anal. Calcd for $C_{26}H_{22}N_2$: C, 86.19; H, 6.08; N, 7.73. Found: C, 85.96; H, 6.27; N, 7.95.

4b: 31%; mp 225 °C (from toluene); $R_f = 0.63$ (silica gel, hexane−ethyl acetate (1:1 vol/vol)) ^{1}H NMR δ (DMSO-d_6) 4.96 (4H, NH_2), 6.25 (4H, d, $J_{4,3} = 8$, H-4), 6.53 (4H, d, $J_{3,4} = 8$, H-3), 6.98 (4H, dd, $J_{7,8} = 7$, $J_{7,9} = 2$, H-7), 7.06 (2H, dd, $J_{9,8} = 7$, $J_{9,7} = 2$, H-9), 7.11 (4H, dd, $J_{8,7} = 7$, $J_{8,9} = 7$, H-8); ^{13}C NMR δ (DMSO-d_6) 113.1 (C-4), 125.6 (C-9), 127.4 (C-8), 130.8 (C-7), 131.1 (C-2), 131.5 (C-3), 138.5 (C-1), 144.8 (C-6), 146.7 (C-5). The atom labeling used here is the same as that used in Scheme 1. IR (KBr) 3469, 3378, 3050, 3026, 1620, 1514, 1285, 1179, 829, 763, 702 cm^{-1}. Anal. Calcd for $C_{26}H_{22}N_2$: C, 86.19; H, 6.08; N, 7.73. Found: C, 86.27; H, 5.97; N, 8.02.

X-ray Crystallographic Analysis of 4a. A pale yellow crystal recrystallized from toluene was mounted on a glass fiber. All measurements were made on a Mac Science MXC 18 diffractometer with graphite monochromated Cu Kα radiation and a 12-kW rotating anode generator. Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25°. The data were collected using the $\omega-2\theta$ scan technique. Scans of $(1.37 + 0.30 \tan \theta)°$ were made at a speed of 32.0 deg/min (in ω). The data were corrected for Lorentz and polarization effects, and the structure was solved by a direct method (SIR92).[23] All calculations were performed using a CRYSTAN crystallographic software package from the Mac Science Corp.

Polycondensation and Film Preparation. In a 30-mL three-necked flask containing *m*-cresol (5 mL) were placed the diamine (1.00 mmol) and the dialdehyde (1.00 mmol) while a slow stream of nitrogen was maintained. The mixture was mechanically stirred at room temperature for 1 day. An aliquot of the polymerization solution was cast on a glass plate and then heated under vacuum at 80 °C for 1 h and at 200 °C for 2 h. The remainder of the polymer solution was poured into methanol. The reprecipitated polymer was dried under reduced pressure at room temperature for 1 day.

Concluding Remarks

Two kinds of novel diamines having a tetraphenylethylene structure, *cis*- and *trans*-1,2-bis(4-aminophenyl)-1,2-diphenylethylene (**4a** and **4b**), were synthesized and the structures were analyzed by the NMR and single crystal X-ray measurements. The structures of these diamines were determined using NMR and single crystal X-ray analysis. Interestingly, the diamines formed 1:1 complexes with toluene which was used as the recrystallization solvent. Fully conjugated, soluble, and film-forming polyazomethines were prepared in *m*-cresol by polycondensation of the diamines with aromatic dialdehydes, terephthalaldehyde (TPA) and isophthalaldehyde (IPA). The precipitated polyazomethines possessed inherent viscosities (η_{inh}) in the range from 0.83 to 0.98 dL/g. Polymers **6** and **7**, which were prepared from **4a** and TPA, and from **4b** and IPA, respectively, gave flexible and tough orange films. These polymer films exhibited high solubility in common organic solvents. The molecular weights of the polymers increased 2- and 4-fold by postcuring at 200 °C. The crystallinity of polymer **6** was slightly higher than that of polymer **7**, but these polymers were essentially amorphous. All of the polyazomethines showed excellent thermal stability with no significant weight loss up to approximately 350 °C and the 5% weight loss temperatures in air were over 400 °C. Polymer **6** possessed a T_g at 292 °C and polymer **7** at 258 °C.

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