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Synthesis of Fully Conjugated Aromatic Polyazomethine from AB-type Monomer Using Soluble Precursor Method

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Summary: A new AB-type monomer, *N,N*-bistrimethylsilylated *p*-aminobenzaldehyde diethyl acetal was prepared *via* three steps from *p*-bromoaniline as a starting material. The two-stage polymerization involving a soluble precursor polymer process gave a poly(*p*-phenylenevinylene)-type polyazomethine, poly(1,4-phenylenenitrilomethylidyne). The first stage of polymerization was carried out in tetrahydrofuran or hexamethylphosphoramide containing water at room temperature. In the second stage, the polymer was thermally converted into the final polyazomethine by heating over 300°C to form a free-standing film. The film was reddish brown and insoluble in common organic solvents. The investigation of the first-stage products by means of MALDI-TOF mass spectroscopy proved the oligomers with 4-11 repeating units per molecule. From the ^{1}H-NMR analysis of the model reaction, the polymerization mechanism was found to be a stepwise polycondensation of 4-diethoxymethylaniline which was formed by removal of two silyl groups of the monomer.

Keywords: conjugated polymers, poly(1,4-phenylenenitrilomethylidyne), polyazomethine, polycondensation, soluble precursor

Introduction

It has been known that fully conjugated polyazomethines formed from aromatic diamines and aromatic dialdehydes precipitate even at the initial stage of the polymerization due to their rigid-rod chain structures,[1] although they are expected to exhibit excellent properties such as electric conductivity, nonlinear optical property, light-emitting property, or many other interesting characteristics.[2-8] Several approaches have been undertaken to improve the processibility of conjugated polyazomethines, for example by introducing various substituted benzene ring in the main chain,[9] by using monomers containing certain heterocyclic units such as thiophene,[8,10] phenylquinoxaline ring,[11,12] or monomers with cardo-structure,[13] tetraphenylethene,[14] and others.[15] Processibility of insoluble polymers has generally approached *via* two methodologies

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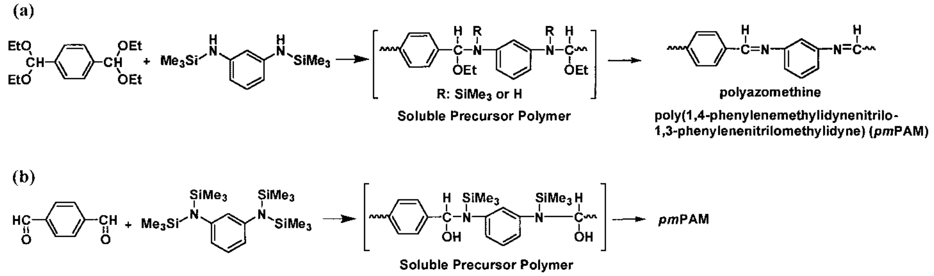
processing into thin film form, namely (a) the use of soluble precursor polymers which are thermally converted into insoluble materials after film formation,[16,17] and (b) chemical vapor deposition (CVD) involving co-sublimation of two or more reactive monomers which impinge on a substrate where they react, typically *via* a polycondensation mechanism, to form a polymer film.[18,19] The latter methodology, CVD, has been shown to be an effective and efficient means of producing polyazomethines with high conjugation lengths, and vacuum deposited aromatic polyazomethines were described for the preparation of organic light emitting devices.[20] Excellent examples of the former can be seen in the polyimide synthesis and poly(*p*-phenylenevinylene) (PPV) synthesis.[16] In 1987, we synthesized a full conjugated polyazomethine, poly(1,4-phenylenemethylidynenitrilo-1,3-phenylenenitrilomethylidyne) (*pm*PAM), using a soluble precursor method (see Scheme 1). The polyazomethine *pm*PAM was obtained by two different processes, namely (a) from terephthalaldehyde diethyl acetal and *N,N'*-bistrimethylsilylated 1,3-diaminobenzene,[21] and (b) from terephthalaldehyde and *N,N,N',N'*-tetrakistrimethylsilylated 1,3-diaminobenzene.[22] In both cases the resulting polyazomethine films were flexible but insoluble in common organic solvents.



Scheme 1. A soluble precursor methodology for a polyazomethine synthesis from: (a) terephthalaldehyde diethyl acetal and *N,N'*-bistrimethylsilylated 1,3-diaminobenzene; (b) terephthalaldehyde and *N,N,N',N'*-tetrakistrimethylsilylated 1,3-diaminobenzene.

Optical properties such as a second harmonic generation (SHG) and a refractive phenomenon are known to depend strongly on the orientation degree of a net dipole moment of the monomer unit. Common polyazomethines prepared from two kinds of monomers, namely dialdehydes and diamines, have two azomethine linkages per a repeating unit. The dipole moments are counterbalanced each other (Figure 1(a)) when the discussion on the polymer structure is limited to one dimension. However, if an appropriate AB-type monomer is used, we can synthesize a polyazomethine having oriented dipole moments (Figure 1(b)), which is expected to show interesting properties, for example, a large intensity in SHG.

In the present article we report the synthesis of a new AB-type monomer, *N,N*-bistrimethylsilylated *p*-aminobenzaldehyde diethyl acetal, and the preparation of a fully conjugated polyazomethine, poly(1,4-phenylenenitrilomethylidyne), with oriented dipole moments using a soluble precursor route. The structure of the precursor polymer has been investigated using matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). On the basis of ^{1}H-NMR analysis of the model reaction, a polymerization mechanism is proposed.

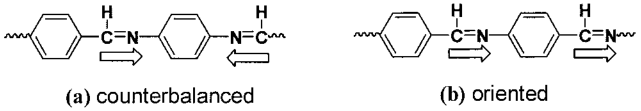


Fig. 1. The direction of dipole moments in the polyazomethines synthesized from: (a) a dialdehyde and a diamine (*counterbalanced*); and (b) an AB-type monomer (*oriented*).

Experimental Parts

Chemicals and Solvents

p-Bromoaniline, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS), bromoethane, magnesium, triethoxymethane, chloral hydrate, deuterated chloroform ($CDCl_3$), deuterated *N,N*-dimethylformamide (DMF-d_7) and hexamethylphosphoramide (HMPA) were used as received (Tokyo Kasei Organic Chemicals or Sigma Aldrich Chemical Co.). Tetrahydrofuran (THF) and hexane were refluxed with CaH_2 and then fractionally distilled. 1,8,9-Anthracenetriol (dithranol) as a matrix for MALDI-TOF MS was analytical-grade material (Sigma Aldrich Chemical Co.), used as supplied.

Characterization

Infrared spectra were obtained with a JASCO VALOR III Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were run on solutions in $CDCl_3$ or DMF-d_7 and recorded using a JEOL JNM-LA 500 spectrometer. Dichloromethane was used as the internal standard for both monomer and polymers (δ(^{1}H)=5.306 ppm; δ(^{13}C)=53.37 ppm). MALDI-TOF MS experiments were performed on a Voyager-DE PRO-T system (Applied Biosystems). The desorption/ionization was induced by a pulsed N_2 laser emitting at 337 nm with a 3 ns pulse width. The mass spectra were obtained at 20 kV accelation voltage and recorded in linear and in reflection mode. 1,8,9-Anthracenetriol (dithranol) was used as the matrix. The samples for MALDI-TOF MS analysis were prepared by mixing adequate volumes of the matrix solution (dithranol, 1 mg/mL in THF) and the polymer solution (the polymer, 1mg/1mL in THF) to obtain a 1:1 v/v ratio. Then 1 μL of the mixture was spotted on the sample holder and slowly dried to allow matrix crystallization. The instrument was calibrated using a mixture of angiotensin (peak at 1297.51 g/mol), ACTHs (peaks at 2094.46, 2466.72, and 3660.19 g/mol), and insuline (peak at 5734.59 g/mol). Spectra were collected as the averages of 200 scans.

Monomer Synthesis

***N,N*-Bistrimethylsilylated *p*-bromoaniline (2):** The compound **2** was prepared *via* two steps from *p*-bromoaniline according to a modified method of the literature.[23] Yield: 30% based on *p*-bromoaniline. Bp: 81°C/1mmHg (lit., [24] 106°C/1.2mmHg). ^{1}H NMR ($CDCl_3$, 500MHz): δ= 0.09 (18H, s, $Si(C\underline{H}_3)_3$), 6.79 (2H, d, H^2 and H^6, $J_{2,3}$=$J_{6,5}$=8Hz), 7.33 (2H, d, H^3 and H^5, $J_{3,2}$=$J_{5,6}$=8Hz). ^{13}C NMR ($CDCl_3$, 125MHz): δ= 2.0 ($Si(CH_3)_3$), 116.8 (C^4), 131.5 (C^3 and C^5), 131.8 (C^2 and C^6), 147.2 (C^1).

***N,N*-Bistrimethylsilylated *p*-aminobenzaldehyde diethyl acetal (3):** In a 2-L four-necked flask equipped with a Dimroth condenser, a mechanical stirrer, a dropping funnel, and a nitrogen inlet was placed 6.1 g (0.25 mol) of magnesium. The whole apparatus was dried as described above, then 300 mL of tetrahydrofuran and 1.1 g (0.01 mol)) of bromoethane to activate the magnesium were charged into the flask. The bistrimethylsilylated derivative **2** (79.1 g, 0.25 mol) was added to the solution through the dropping funnel and the mixture was heated at reflux temperature until the magnesium solid disappeared (ca. 12 h). To the resulting solution 37.1g (0.25 mol) of triethoxymethane was slowly added through the dropping funnel, and then the mixture was heated at reflux temperature for 13 h. The reaction mixture was treated as described above, and the compound **3** was isolated by fractional distillation; yield: 22%. Bp: 96°C (0.2 mmHg). ^{1}H NMR ($CDCl_3$, 500MHz): δ= 0.09 (18H, s, $Si(C\underline{H}_3)_3$), 1.26 (6H, t, J=7Hz, $CH_2C\underline{H}_3$), 3.58 (2H, qd, $C\underline{H}_2CH_3$), 3.63 (2H, qd, $C\underline{H}_2CH_3$), 5.54 (1H, s, $C\underline{H}(OEt)_2$), 6.90 (2H, d, H^2 and H^6, $J_{2,3}$=$J_{6,5}$=8Hz), 7.34 (2H, d, H^3 and H^5, $J_{3,2}$=$J_{5,6}$=8Hz). ^{13}C NMR ($CDCl_3$, 125MHz): δ= 2.0 ($Si(CH_3)_3$), 15.2 ($OCH_2\underline{C}H_3$), 60.6 ($O\underline{C}H_2CH_3$), 101.3 ($\underline{C}H(OEt)_2$), 119.7 (C^4), 126.7 (C^3 and C^5), 129.7 (C^2 and C^6), 147.9 (C^1). $(C_{17}H_{33}NO_2Si_2)_n$: Calcd. C 60.12 H 9.80 N 4.12; Found C 60.29 H 9.61 N 4.51.

Polymer Synthesis for MALDI-TOF MS Analysis and Film Preparation

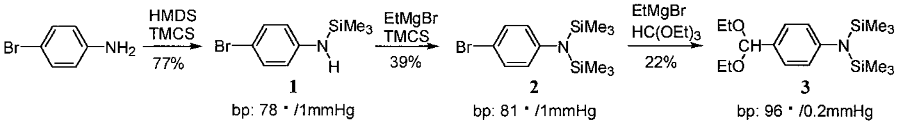
In a 10-mL glass bottle with a polyethylene cap a mixture of 0.41 g (1.2 mmol) of **3** and 0.40 g (22 mmol) of water in 2.0 g of THF or HMPA and a magnetic stirring bar were placed and stirred under a nitrogen atmosphere at room temperature for 2 weeks. The solution given by polymerization in HMPA was cast on a glass plate, and the glass plate was heated over 300 °C for 30 min.

Polymer Preparation for NMR Analysis

In an NMR sample tube (5 mm o.d. and 180 mm high) 0.0545 g (0.147 mmol) of **3**, 1.0 g of deuterated DMF-d_7), and a small amount of an internal standard (CH_2Cl_2) were charged, and 5.4 mg (0.294 mmol) of water was added into the tube using a micro-syringe just prior to measurement.

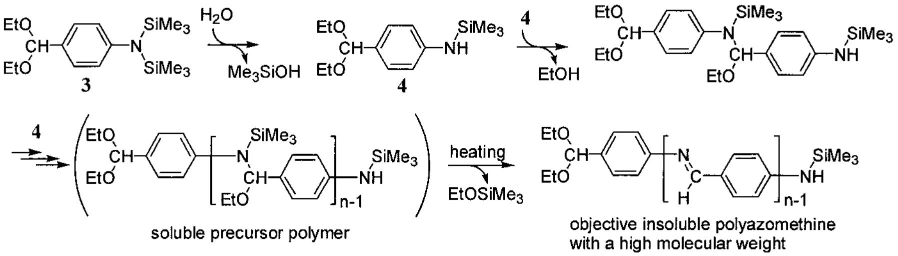
Results and Discussion

As shown in Scheme 2, a novel AB-type monomer, *N,N*-bistrimethylsilylated *p*-amino-benzaldehyde diethyl acetal (**3**) was prepared *via* three steps from *p*-bromoaniline as a starting material. The first step is an ordinary mono-trimethylsilylation of the amino group using excess HMDS with 10 mol-% TMCS present at a reflux temperature without solvent for 12 h. The second step involves reaction of the monosilylated derivative **1** with excess ethylmagnesium bromide in THF, followed by TMCS.[23] The final step is formylation reaction of triethoxymethane with Grignard reagent prepared from disilylated derivative **2**.[25] The usual precautions for protecting the reaction from moisture were taken through the whole process for preparation of the monomer. All moisture-sensitive substances (**1**, **2**, and **3**) were handled in a dry box, and all the glass apparatus was flame-dried thoroughly using a gas burner, nitrogen being flowed. The monomer **3** is stable when a deprotecting reagent such as water is absent, and it can be stored for a long time in a refrigerator. The stability is explained by the steric hindrance between the diethoxymethyl and the *N,N*-bistrimethylsilylated amino groups and/or by an electronic effect of the two groups, that is a push-pull effect of them through a benzene ring.



Scheme 2. Synthetic route to a novel AB-type monomer, *N,N*-bistrimethylsilylated *p*-aminobenzaldehyde diethyl acetal (**3**).

We attempted to synthesize the polyazomethine, poly(1,4-phenylenenitrilomethylidyne) using two-stage method, that is, through a soluble precursor polymer. The expected synthetic route is illustrated in Scheme 3. The first stage polymerization is initiated with *N*-trimethylsilylated *p*-aminobenzaldehyde diethyl acetal **4** which is generated by removal of a trimethysilyl group with water. We have reported that the condensation of *N*-trimethylsilylated amino group with diethyl acetal group underwent to form polyazomethine with a high molecular weight *via* a precursor polymer, although the precursor has not been isolated and characterized yet.[21] In the second stage, the precursor polymer, if produced, is thermally converted into the corresponding polyazomethine. In the present study, the first stage polycondensation was carried out in THF or HMPA containing 15-16 wt-% of water. MALDI-TOF MS was a useful tool in the structural characterization of the precursor and the final form of these polyazomethines.[26] The result of products obtained in THF solvent using dithranol as the matrix is displayed in Figure 2. No cationization salt such as silver (I) trifluoroacetate was used, as it might oxidize the polymer. The correct repeat unit mass difference (103.12 amu) is observed between peaks, which is caused by the phenylene azomethine unit, -C_6H_5-N=CH-. The spectrum shows peaks belonging to more than four series, and that the products consist of polyazomethine oligomers terminated with different end groups. The most intense peak series, at m/z = 267.44 + 103.12(n-1) + 1, is due to the protonated ions of oligomer chains terminated with diethyl acetal group at one end and monosilylated amino group at the other end (species **Bn**), where n is equal to the number of monomer units. A second series of peaks at m/z = 195.26 + 103.12(n-1) + 1 can be assigned to the protonated ions of oligomer chains terminated with diethyl acetal group at one end and free amino group at the other end (species **An**). A third series of peaks appearing with low intensity at m/z = 399.62 + 103.12(n-1) + 1 corresponds to protonated ions of oligomer chains terminated with diethyl acetal group at one end and disilylated amino group at the other end (species **Cn**).



Scheme 3. Expected synthetic route to polyazomethine from *N*,*N*-bistrimethysilylated *p*-aminobenzaldehyde diethyl acetal (**3**) using soluble precursor method.

The large amount of oligomer chains containing free or monosilylated amino groups as end groups (series **An** or **Bn**) indicates that an extensive hydrolysis reaction of disilylated amino groups occurred, either due to the water added at initial stage of the polymerization or to the atomospheric air moisture when preparing the samples for MALDI-TOF MS analysis. The last series of peaks appearing with relatively high intensity at m/z = 432.70 + 103.12(n-2) + 1 is due to protonated ions of oligomer chains (species **Dn**). Although the structures corresponding to the mass peak series **Dn** are unknown, we propose some possible ones which may contain a azomethine precursor unit such as -C_6H_5-N($SiMe_3$)-CH(OEt)- (see Figure 3). The precursor polymers are thought to be very unstable, and once formed they may be quickly converted into polyazomethines. The azomethine oligomers having monomer units in a range from 4 to 11 were observed. At longer reaction time (after 1 week) the sample showed precipitate formation and was subjected to extraction with THF, to have a soluble portion suitable to MALDI-TOF MS analysis. As the precipitated polymers have higher molecular weights than those in the soluble portion, polymerization degrees of the polymers produced indeed may be more than 11.

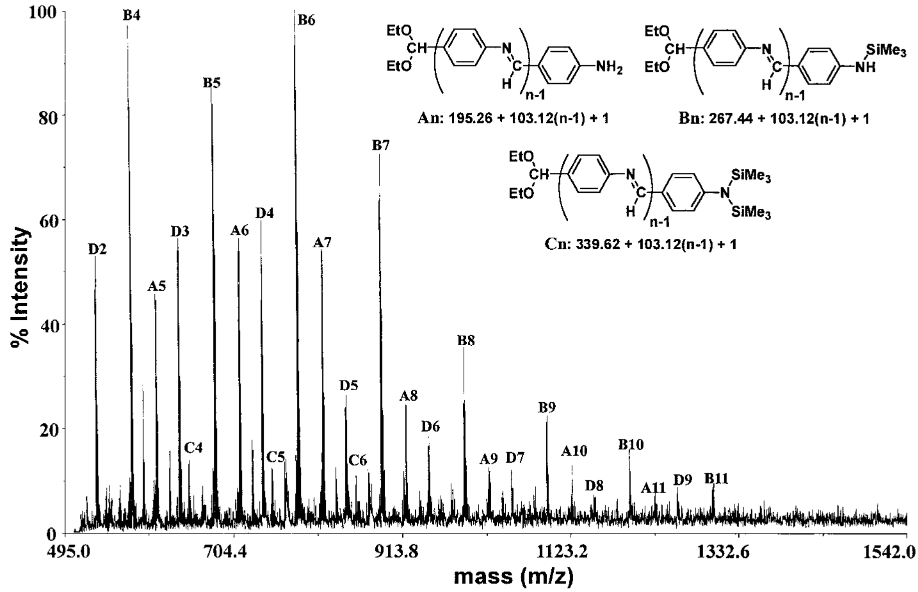


Fig. 2. MALDI-TOF mass spectrum, in the range 500-1500 g/mol, of the products obtained by reaction of **3** with water in THF at room temperature for 2 weeks. Species exist with an attached proton.

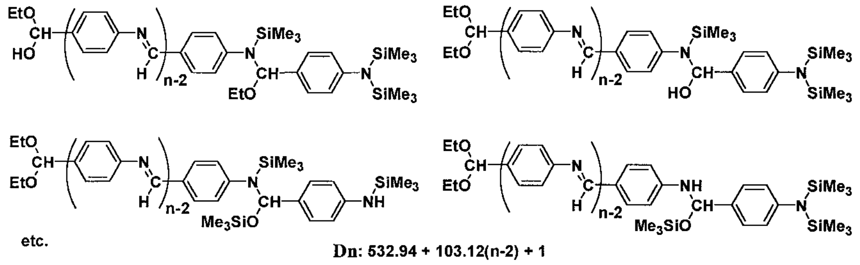


Fig. 3. Possible structures corresponding to the mass peak series **Dn**.

A model reaction, which was carried out in an NMR tube containing a DMF-d_7 solution of **3** and two times molecular amount of water, was studied by ^{1}H NMR spectroscopy in order to estimate the polymerization mechanism. At each interval after adding water to the DMF-d_7 solution of **3**, ^{1}H NMR spectrum was determined. The aromatic proton region is expanded and displayed in Figure 4. The signal intensities of aromatic protons corresponding to **3** (signals α and β) were decreased gradually. Proton signals due to the desilylated compound (signals A and B), appeared just after adding water and were increased gradually as shown in Figure 4(a). The signals had the maximum intensity after several hours. It is noteworthy that no signals corresponding to the monosilylated derivative (compound **4** in Scheme 3) were observed at any time in DMF-d_7. The result indicates that the two trimethylsilyl groups were removed almost at the same time and that a life-time of the monosilylated derivative may be very short. It is also supported by the fact that a signal due to trimethylsilanol methyl proton ($(C\underline{H}_3)_3SiOH$) appeared at -0.43 ppm just after adding water and that no signal corresponding to monotrimehylsilylated compound ($(CH_3)_3Si$-NH-) was detected over the whole time. After approximately 30 min, aromatic proton signals assigned to the first formed azomethine (signals 1-4), which is a dimer terminated with an acetal group at one end and a free amino group at the other end, appeared with very low intensity. Judging from the spectral change, the dimerization rate is estimated to be slow, although the signal intensities became higher with an increase of time. After 14 days, the signals due to a trimer (signals 1'-6') are observed and those to the higher molecular weight products than a trimer appear with low intensity as shown in Figure 4(b). In ^{1}H-NMR spectrum, an azomethin proton signal, -C$\underline{H}$=N-, is observed in the range of 7.9-8.3 ppm. The azomethine proton region is expanded and displayed in Figure 5. At one hour after adding water, only a signal assigned to the first produced azomethine (a dimer) was observed at 7.92 ppm. The signal intensity became higher with an increase of time, and had a maximum intensity after several days. In the spectrum after 4 hours (Figure 5(a)), two azomethine proton signals, x and y, corresponding to a trimer can be also observed at 7.98 and 8.18 ppm, respectively. After 14 days, the signals assigned to high molecular weight azomethine oligomers such as a tetramer, a pentamer, etc., appear (signals z') other than those to a dimer and a trimer (Figure 5(b)). After several hours, a signal due to hexamethyldisiloxane ($[(CH_3)_3Si]_2O$) appeared at -0.39 ppm with very low intensity. The intensity of the signal increased with an increase in time, whereas that due to trimethylsilanol methyl proton at -0.43 ppm degreased. Signals corresponding to ethanol, which was produced by

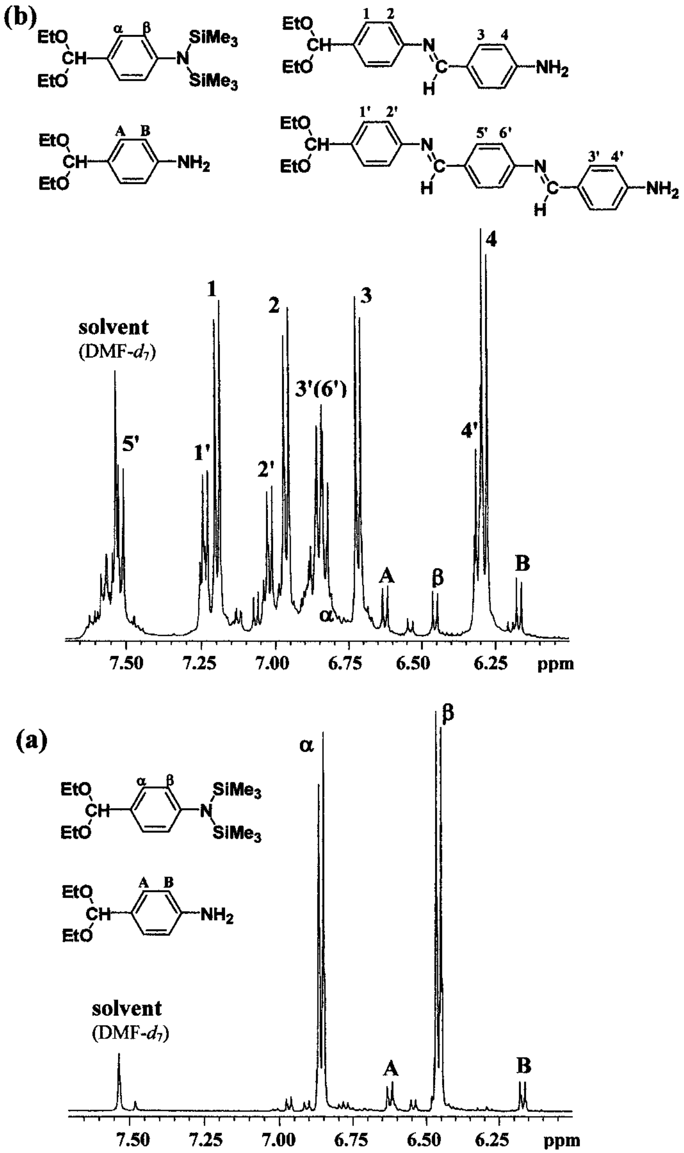


Fig. 4. Expanded ^{1}H NMR spectra (aromatic proton region, 6.0-7.7 ppm) of the mixture of **3** and water in DMF-d_7: (a) 0 h; (b) 14 days after adding water.

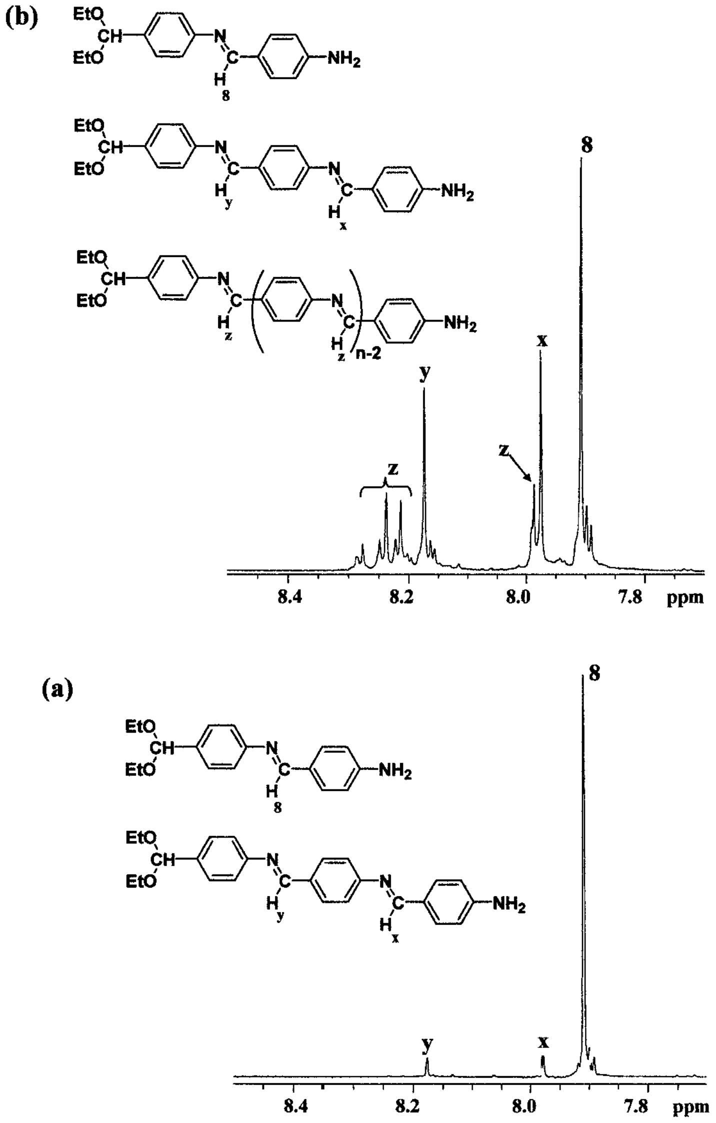
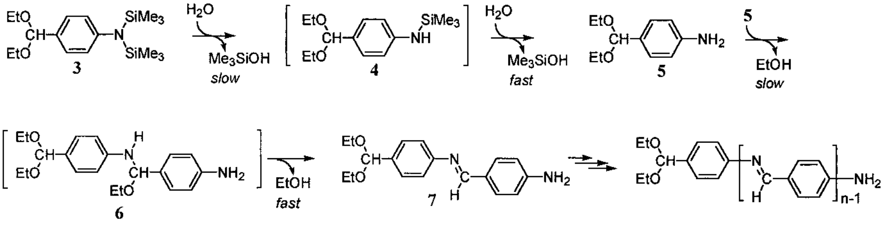


Fig. 5. Expanded ^{1}H NMR spectra (azomethine proton region, 7.7-8.5 ppm) of the mixture of **3** and water in DMF-d_7: (a) 4 h; (b) 14 days after adding water.

reaction of a free amino group with a diethoxymethyl (diethyl acetal) group, appeared after about 30 min, and the intensity increased gradually throughout the whole time. On the basis of these results, a possible mechanism for the model reaction in DMF-d_7 is assumed as shown Scheme 4. In the first step, the monomer **3** reacts with water and generates *p*-aminobenzaldehyde diethyl acetal **5** and trimethylsilanol. As trimethysilanol is very sensitive and unstable, it undergoes condensation to form hexamehyldisiloxane and water.[27] The next step involves condensation of two molecules of **5** to give the first azomethine **6** (a dimer) and ethanol. The compound **6** reacts with **5** to form a trimer and ethanol, and condensation between two molecules of **5** gives a tetramer.

In the NMR spectral analysis of the model reaction carried out in a NMR tube using DMF-d_7 as a solvent, unfortunately we cannot find the evidence for the existence of soluble precursor polymers. On the other hand, in the MALDI-TOF MS spectrum of the polymerization products obtained in THF solution, the peak series due to the oligomers terminated with an *N*-monotrimethylsilylated or an *N*,*N*-bistrimethylsilylated amino group at the one end were observed, and it would suggest that the polymerization proceeds *via* soluble precursor polymers with a very short life-time. The difference in the polymerization mechanism may be caused by the reaction condition, such as solvent, the ratio of monomer and water, etc. The further characterization of the polymer and the study of polymerization mechanism are currently under way.



Scheme 4. A possible mechanism for the model reaction of **3** with water in DMF-d_7 to form polyazomethine oligomers.

The free-standing but somewhat brittle film was obtained by heating the polymerization solution (HMPA) on a glass plate. The film was insoluble in common organic solvents and its color was reddish brawn. Figure 6 shows the infrared spectrum of a converted polyazomethine film prepared from the precursor in HMPA with a final heat treatment of 0.5 h over 300°C. The peak at 1621 cm^{-1} is assign to a C=N streching band, and the other assignments are based on a correlation of the peaks to characteristic group frequencies which are listed in the reference.[16a]

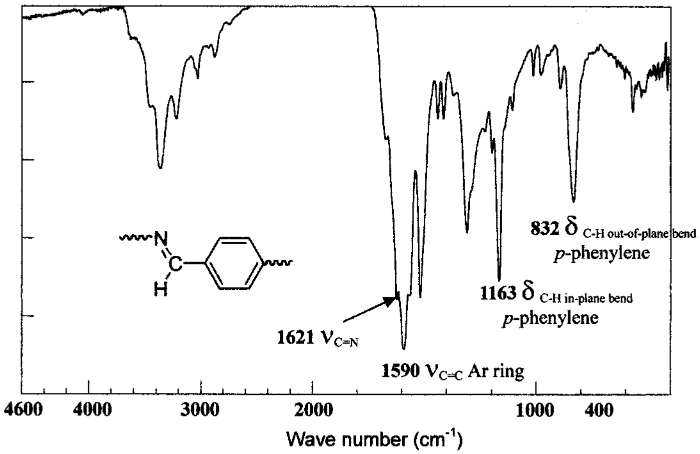


Fig. 6. FT-IR spectrum of a converted polyazomethine film prepared from the precursor in HMPA with a final heat treatment of 0.5 h over 300°C.

Conclusions

We synthesized a new AB monomer, *N*,*N*-bistrimethylsilylated *p*-aminobenzaldehyde diethyl acetal (**3**) via three steps from *p*-bromoaniline. A PPV-type polyazomethine, poly(1,4-phenylenenitrilomethylidyne), was prepared using a solution-processable precursor polymer. The first stage polymerization was carried out in THF or HMPA containing water at room temperature. In the second stage, the polymer was thermally converted into the final polyazomethine by heating over 300°C. The investigation of the first-stage products, which were THF-soluble fractions, by means of MALDI-TOF mass spectroscopy proved the oligomers with 4-11 repeating units per molecule. The ^{1}H-NMR spectral analysis of the products of the reaction in DMF-d_7 shows that the oligomers were produced by a stepwise polycondensation of 4-diethoxymethylaniline which was formed by desilylation of the monomer **3**. The final polyazometine was given as a free-standing film (somewhat brittle) with reddish brown color and insoluble in common organic solvents.

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