

Selective Formation of Cyclic 1,3-Phenylenenitrilomethylidyne Hexamer

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Introduction

Although fully aromatic polyazomethines formed from aromatic diamines and aromatic dialdehydes are expected to exhibit excellent properties such as electric conductivity, nonlinear optical property, light-emitting property, or many other interesting characteristics, it has been known that they fully precipitate even at the initial stage of the polymerization due to their rigid-rod chain structures [1-8]. Several approaches have been undertaken to improve the processibility of conjugated polyazomethines, for example by introducing various substituted benzene ring such as cardo-structure and tetraphenylethene [9]. Processibility of insoluble polymers has generally approached *via* two methodologies processing into thin film form, namely (a) the use of soluble precursor polymers which are thermally converted into insoluble materials after film formation [10], 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. 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 [11]. Excellent examples of the former can be seen in the polyimide or the poly(*p*-phenylenevinylene) (PPV) synthesis [10]. In 1987, we synthesized a conjugated polyazomethine, poly(1,4-phenylenemethylidynenitrilo-1,3-phenylenenitrilomethylidyne) (*p,m*-polyazomethine, *pmPAM*), using a soluble precursor method [12].

In the present article we report the synthesis of new AB-type monomers, *N,N*-bistrimethylsilylated *m*-aminobenzaldehyde diethyl acetal, and the selective preparation of cyclic 1,3-phenylenenitrilomethylidyne hexamer from the monomer. The structure of the oligomer and a polymerization mechanism have been investigated using matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) and NMR analysis.

Experimental Parts

Chemicals and Solvents. *m*-Bromoaniline, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS), bromoethane, magnesium, triethoxymethane, deuterated chloroform (CDCl_3), deuterated *N,N*-dimethylformamide ($\text{DMF-}d_7$), deuterated tetrahydrofuran ($\text{THF-}d_8$), deuterated *N*-methyl-2-pyrrolidone ($\text{NMP-}d_9$), deuterated trifluoroacetic acid ($\text{TFA-}d_1$) were used as received (Tokyo Kasei Organic Chemicals, Sigma Aldrich Chemical Co., or Cambridge Isotope Laboratories, Inc.). Tetrahydrofuran (THF) and hexane were refluxed with CaH_2 and then fractionally distilled.

Characterization. Infrared spectra were obtained with a JASCO VALOR III Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were run on solutions in CDCl_3 , $\text{DMF-}d_7$, $\text{THF-}d_8$, $\text{NMP-}d_9$, or $\text{TFA-}d_1$ and recorded using a JEOL JNM-LA 500 spectrometer. Tetramethylsilane or dichloromethane ($\delta(^1\text{H})=5.306$ ppm; $\delta(^{13}\text{C})=53.37$ ppm)

was used as the internal standard for both monomer and polymers. MALDI-TOF MS experiments were performed on a Voyager-DE PRO-T system (Applied Biosystems).

Monomer Synthesis.

***N,N*-Bistrimethylsilylated *m*-bromoaniline (**2m**):** The compound **2m** was prepared *via* two steps from *m*-bromoaniline according to our previous report [13]. Yield: 44% based on *m*-bromoaniline. Bp: 52°C/1.5mmHg.

***N,N*-Bistrimethylsilylated *m*-aminobenzaldehyde diethyl acetal (**3m**):** In a four-necked flask equipped with a mechanical stirrer was placed magnesium, then tetrahydrofuran and bromoethane were charged into the flask. The bistrimethylsilylated derivative **2m** was added to the solution and the mixture was heated at reflux temperature (ca. 12 h). To the resulting solution triethoxymethane was slowly added, and then the mixture was heated at reflux temperature for 13 h. The compound **3m** was isolated by fractional distillation; yield: 10%. Bp: 122°C (0.2 mmHg). ¹H-NMR(CDCl₃,500MHz): δ= 0.11(s,18H,Si(CH₃)₃), 1.27(t, 6H, J=7Hz, CH₂CH₃), 3.33(m, 4H, CH₂CH₃), 5.53(s, 1H, CH(OEt)₂), 6.89(sex, 1H, J=2Hz,H-4), 7.05(s, 1H, H-2), 7.23(t, 1H, J=8Hz, H-5), 7.23(s, 1H, H-6). ¹³C-NMR(CDCl₃,125MHz): δ= 2.2(Si(CH₃)₃), 15.4(CH₂CH₃), 60.7(CH₂CH₃), 101.3(CH(OEt)₂), 122.2(C-6), 128.3(C-2), 128.5(C-4), 130.1(C-5), 139.6(C-1), 148.0(C-3).

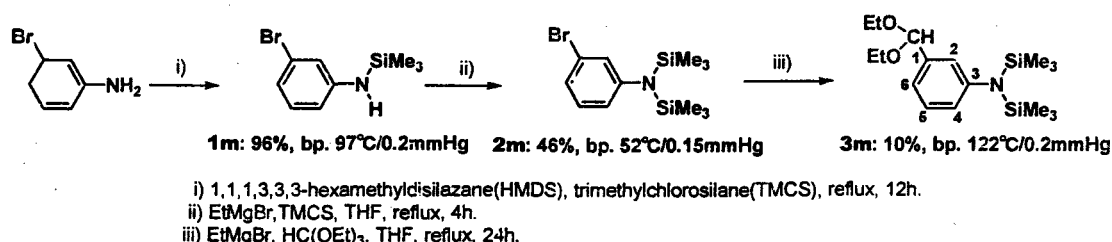
Oligomerization.

For MALDI-TOF MS analysis: In a 10-mL glass bottle with a polyethylene cap a mixture of 0.41 g (1.2 mmol) of **3m**, and 0.40 g (22 mmol) of water in 2.0 g of THF and a magnetic stirring bar were placed and stirred at room temperature for 2 weeks.

For NMR analysis: In an NMR sample tube (5 mm o.d. and 180 mm high) 0.110 g (0.323 mmol) of **3m**, 0.41 g of deuterated THF-*d*₆, and a small amount of an internal standard (CH₂Cl₂) were charged, and 0.410 g (2.27 mmol) of water was added into the tube just prior to measurement.

Results and Discussion

Monomer Synthesis. As shown in Scheme 1, a novel AB-type monomer, *N,N*-bistrimethylsilylated *m*-aminobenzaldehyde diethyl acetals (**3m**) was prepared *via* three steps from *m*-bromoanilines 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 **1m** with excess ethylmagnesium bromide in THF, followed by TMCS. The final step is formylation of triethoxymethane with Grignard reagent prepared from disilylated derivative **2m**.



Scheme 1. Synthetic route to novel AB-type monomers, *N,N*-bistrimethylsilylated *m*-aminobenzaldehyde diethyl acetal (**3m**).

Oligomerization. The oligomerization was carried out in THF in the presence of water which acts as a desilylated reagent. When the reaction was continued for 2 days, a strong peak corresponding to the linear trimer **Lm3** in Scheme 2 was observed in the MALDI-TOF mass spectrum (Figure 1(a)). At longer reaction time, more than a week, the precipitates appeared, and the MALDI-TOF spectrum (Figure 1(b)) suggested that the precipitate was a cyclic hexamer of 1,3-phenylenenitrilomethylidyne, namely 1,9,17,25,33,41-hexaaza[2.2.2.2.2.2]metacyclophanehexene **Cm6** in Scheme 2. The yield of **Cm6** based on **3m**

was as high as 82%. The melting point was observed at 204.7°C in the first scan of DSC with a heating and a cooling rates of 1K/min, and could not be found it in the second run. The T_g was recognized around 170°C in the DSC second run with a heating rate of 5K/min. The result of elemental analysis is as follows: Calculated for C₄₂H₃₀N₆+THF+2H₂O; C 76.03, H 5.79, N 11.57, Found C 75.8, H 5.66, N 12.0. In the FT-IR spectrum (KBr), the absorptions appeared at 1624(s, C=N), 1597(m, C=C), 1574(s), 1237(m), 1170(m), 791(s), 687(s), and 419(m) cm⁻¹.

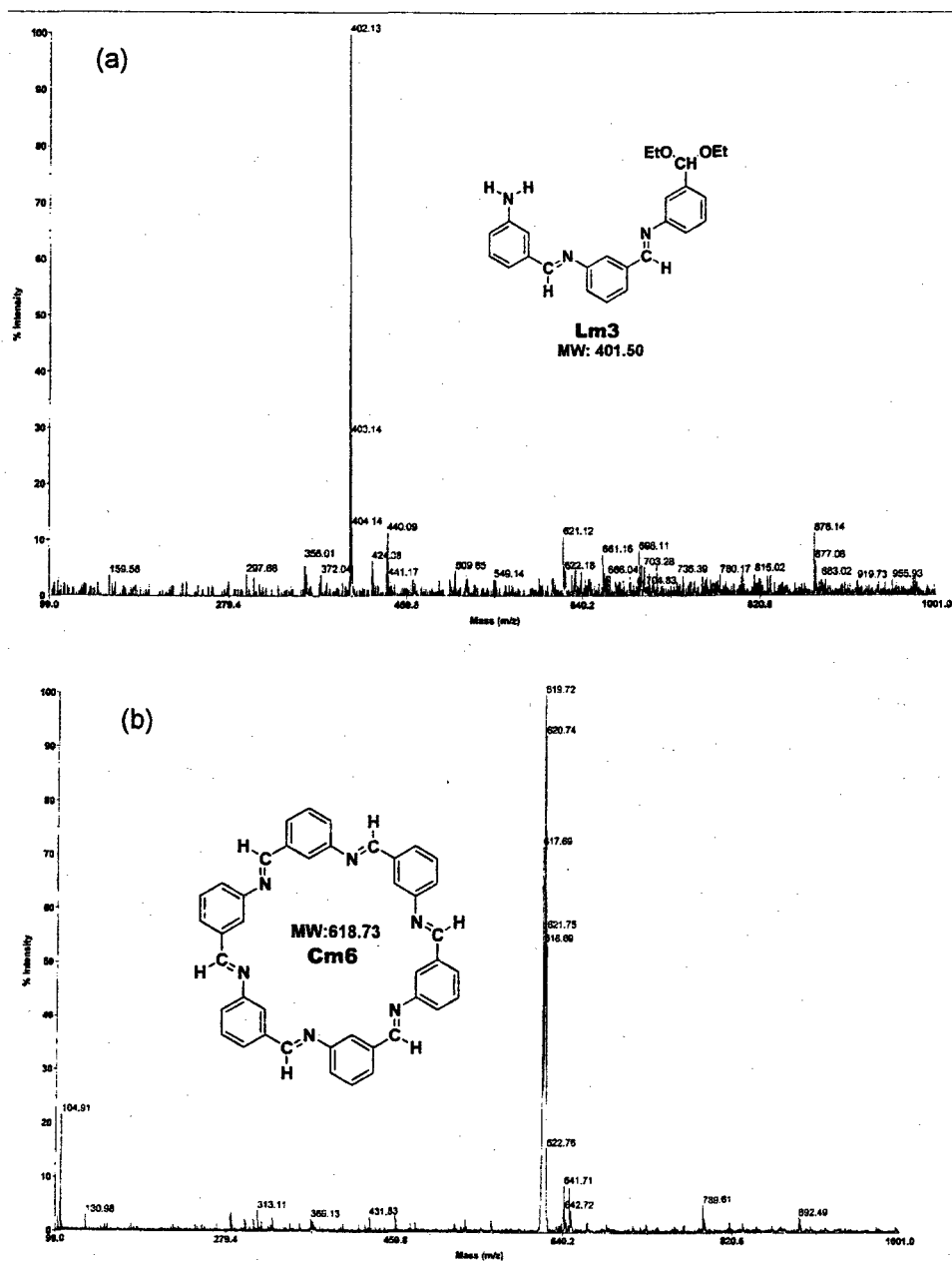


Figure 1. MALDI-TOF mass spectra of the products obtained by the oligomerization of **3m** in THF in the presence of water at room temperature for (a) 2 days and (b) 2 weeks.

The precipitate was hardly soluble in common organic solvents except for *N*-methyl-2-pyrrolidone (NMP) or trifluoroacetic acid (TFA). The ¹H-NMR spectrum measured in NMP-*d*₉ spectrum is shown in **Figure 2**. The

azomethine hydrogen $-\text{CH}=\text{N}-$ is observed at 8.49(s, 1H) ppm and the hydrogens attached to benzene ring appeared at 7.12(d, 2H), 7.40(t, 1H), and 7.63(s, 1H) ppm. It is interesting that the $^1\text{H-NMR}$ spectrum measured in $\text{TFA-}d_1$ became complicated because of collapse of the symmetry caused by partial protonation of azomethine nitrogen.

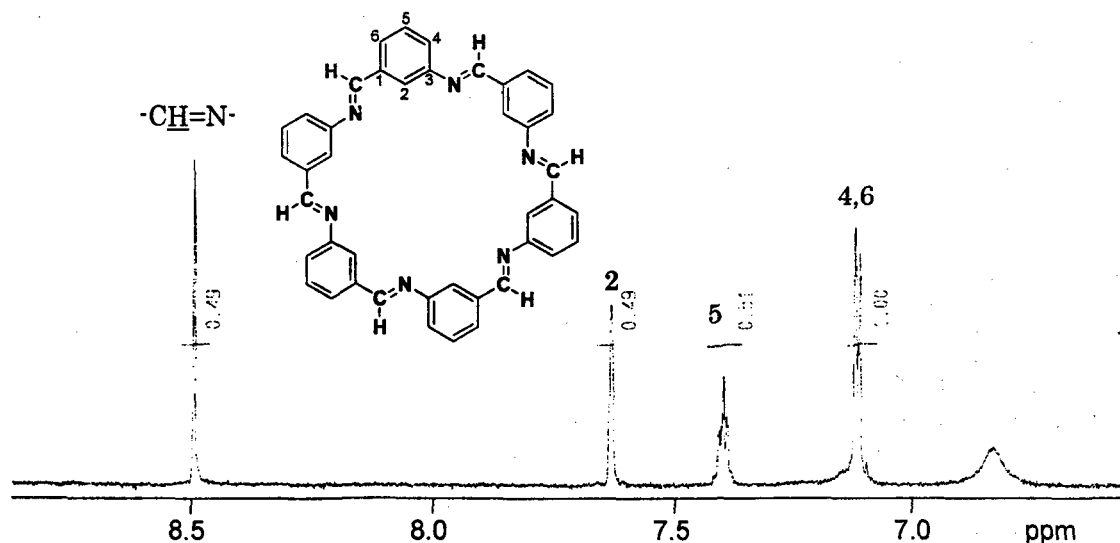
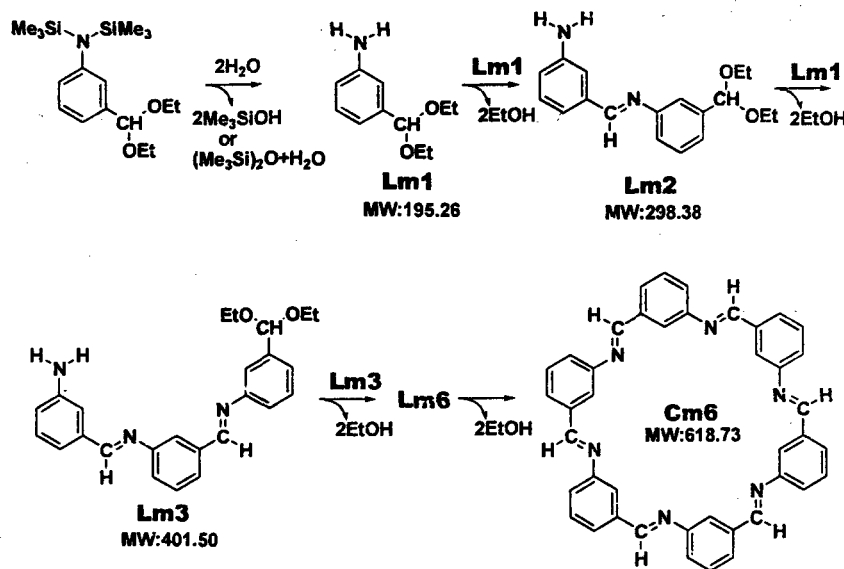


Figure 2. $^1\text{H-NMR}$ spectrum of **Cm6** measured in $\text{NMP-}d_9$.

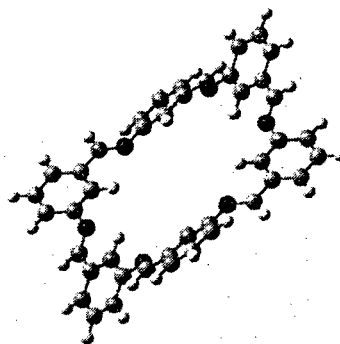
A possible mechanism for the selective formation of 1,9,17,25,33,41-hexaaza[2.2.2.2.2.2]-metacyclophanehexene (**Cm6**) is illustrated in Scheme 2.

The conformation was geometrically optimized using an *ab initio* MO calculation (*Gaussian98*, B3LYP/321G*) and the result is displayed in Figure 3. The exact structure analysis and further characterization of the product are currently under way.



Scheme 2. A possible mechanism for the selective formation of 1,9,17,25,33,41-hexaaza[2.2.2.2.2.2]metacyclophanehexene **Cm6**.

Figure 3. A calculated and geometrically optimized structure of 1,9,17,25,33,41-hexaaza[2.2.2.2.2.2]metacyclophanehexene (**Cm6**). Calculations: Gaussian 98, B3LYP/3-21G*.



Conclusions

A new AB-type monomer, *N,N*-bistrimethylsilylated *m*-aminobenzaldehyde diethyl acetal (**3m**) was prepared via three steps from *m*-bromoaniline. The oligomerization initiated with water gave selectively a cyclic 1,3-phenylenenitrilomethylidyne hexamer, 1,9,17,25,33,41-hexaaza[2.2.2.2.2.2]metacyclophanehexene (**Cm6**). The investigation of the oligomerization process by means of MALDI-TOF MS proved that the linear trimer **Lm3** at first, then the cyclic hexamer **Cm6** were formed in THF containing water.

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