Polymerization of Azastyrene Derivatives. 3.† Preparation and Polymerization of *N*-Methyleneaniline

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Although numerous papers have been published on the addition polymerization through C=C or C=O double bonds, there have been few papers on the addition polymerization through the C=N double bond except for isocyanates,[1] carbodiimides,[2] imines,[3] 1-azabutadienes,[3] and azines.[4−7] Kamachi et al.[4,5] have systematically investigated the polymerizabilities of azine compounds in order to understand the polymerizabilities of the C=N double bond and to obtain new polymers. Consequently, we have synthesized *trans*-1,4-polymers from alkyl azine compounds (RCH=NN=CHR, R=CH_3, C_2H_5, *n*-C_3H_7)[6] and a 1,2-polymer from trifluoroacetaldehyde azine (R = CF_3).[7] As an extension of the research on the polymerization of the C=N double bond, we have focused on azastyrene derivatives.[8] Since *N*-methyleneaniline (CH_2=NC_6H_5, MeAn) is one of the simplest azastyrene derivatives, the chemical reaction and the polymerization of MeAn have attracted much attention.[9] Although MeAn has been found in the gas phase,[10] MeAn is too unstable to be isolated in its condensed phase. This is because MeAn is immediately converted into a cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine.[11] Therefore, MeAn has been considered as an intermediate in some reactions,[12] because the presence of MeAn has not been confirmed in the reactions. To our knowledge, there are no papers concerning the chemical reactivity and polymerizability of MeAn. Recently, we found that MeAn could be stored without formation of cyclic trimer in THF, and we then investigated its polymerizability. In this paper, we will describe the preparation and polymerizability of MeAn and the characterization of the obtained polymer.

Kamachi et al.[5] found that formaldehyde azine, which had been considered to be unstable in its liquid phase, was stable in THF under water-free conditions. Thus, we focused on the storage of MeAn as a solution. In order to confirm the existence of MeAn in solution, NMR measurements were carried out by using THF-d_8 as a solvent. Hexahydro-1,3,5-triphenyl-1,3,5-triazine, the cyclic trimer of MeAn, was pyrolyzed with an electric furnace at 300 °C under high vacuum to form MeAn, which was collected in an NMR tube with liquid nitrogen. After THF-d_8 dried with sodium was distilled into the NMR tube, the NMR tube was sealed under high vacuum. Figure 1 shows the 67.9-MHz ^{13}C NMR spectrum of MeAn in THF-d_8 at −80 °C. The absorption bands due to the meta-, para-, ortho-, ipso-, and methylene carbons are observed at 121.3, 127.0, 129.9, 153.9, and 154.9 ppm, respectively.[13] In the 270-MHz ^{1}H NMR spectrum of MeAn, the AB type of absorption bands assignable to the methylene protons of the CH_2=N are observed at 7.31 and 7.57 ppm.[13] The ratio of the integrals of the signals is consistent with the structure of MeAn. These results show that MeAn is isolated as a solution in THF at −80 °C. In order to investigate the stability of MeAn in THF, ^{1}H NMR spectra of MeAn were measured with an increase in temperature from −80 to +30 °C. The concentration of MeAn did not change at temperatures lower than −40 °C, indicating that the cyclic trimerization did not take place.[14] The result shows that MeAn can be stored as a solution in THF-d_8.

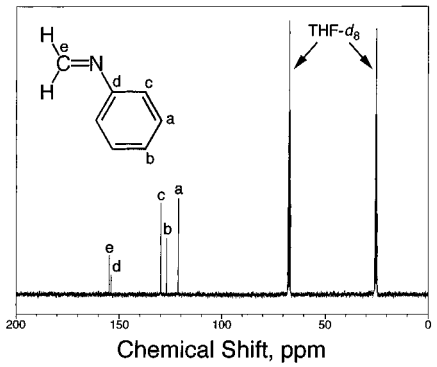

Figure 1. 67.9-MHz ^{13}C NMR spectrum of MeAn (THF-d_8, −80 °C, 0.20 mol/L).

Table 1. Polymerization of MeAn in THF[a]

MeAn, mg (mmol)	THF, mL (M)	initiator	mol %	yield,[b] %
320 (3.0)	1.0 (3.0)	*n*-BuLi	2.6	86.9
176 (1.6)	10.0 (0.16)	*n*-BuLi	4.7	31.2
237 (2.3)	1.0 (2.3)	CH_3COOH	3.9	89.0
241 (2.3)	10.0 (0.23)	CH_3COOH	3.7	30.0

[a] At 20 °C under high vacuum for 24 h. [b] THF-insoluble fraction.

As described above, the storage of MeAn in THF without cyclic trimerization was successful. Thus, the polymerizations of MeAn were carried out in THF under high vacuum with two kinds of initiators. When polymerization was carried out at −40 °C, the yield of polymer was quite low. It is ascribable to slow propagation in the polymerization at −40 °C. Thus, polymerizations were carried out at 20 °C, although it was possible that the cyclic trimerization occurred. The results are listed in Table 1. When the polymerizations were carried out in concentrated solutions (∼2−3 M), THF-insoluble fractions were obtained in high yields (>85%). Since the cyclic trimer is soluble in THF, the THF-insoluble fraction may be poly(MeAn) obtained by the polymerization through the C=N double bond. Although the THF-insoluble fraction was insoluble in most organic solvents, such as toluene, diethyl ether, 1,4-dioxane, benzene, hexane, methanol, ethanol, chloroform, dimethyl sulfoxide, *N*,*N*-dimethylformamide, and *N*-methylpyrollidone, it is soluble in acids, such as acetic acid and hydrochloric acid. Thus, the ^{1}H NMR spectrum of the THF-insoluble fraction, obtained by polymerization initiated with *n*-BuLi, was obtained by using 35% DCl−D_2O solution as a solvent, as shown in Figure 2. In the spectrum, the absorption bands due to the phenyl protons are observed in the region of 7.1−7.4 ppm. The weak absorption band at 0.7 ppm is due

† Part 2 in this series is ref 8b and part 1, ref 8a.

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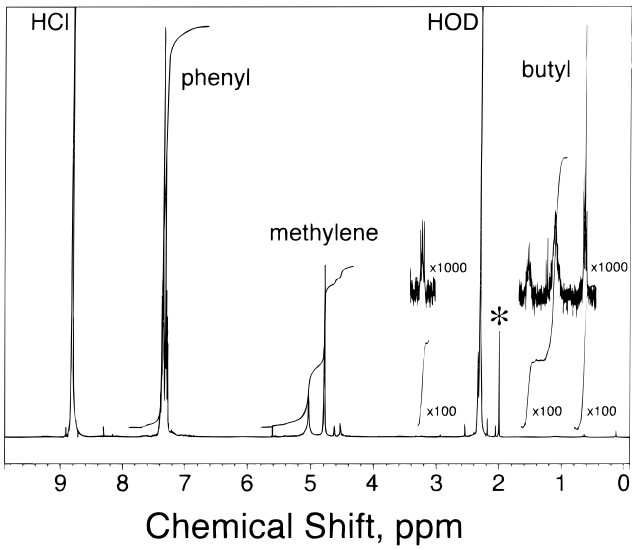
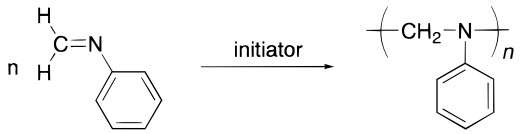


Figure 2. 270-MHz ^{1}H NMR spectrum of the polymer produced by *n*-BuLi (35% DCl-D_2O solution, 30 °C).

Scheme 1. Polymerization of MeAn



to the methyl proton of the butyl group at the chain end. From the ratio of the integrals of these absorption bands, the molecular weight of the polymer is estimated to be 1.8×10^4, assuming that no chain-transfer reaction takes place. The result shows that the THF-insoluble fraction is poly(MeAn). In addition, when the polymerization of MeAn was carried out in a dilute solution (0.16−0.29 M), the yield of the polymer was much lower (∼30%). The results show that a high concentration of MeAn (2.0−3.0 M) is required for a high yield of the polymer, suggesting that propagation competes with cyclization in the polymerization of MeAn. In other words, propagation may be predominant over cyclization at a high concentration (2.0−3.0 M).

The structure of the polymer obtained was investigated with elemental analysis and ^{1}H NMR and IR spectroscopies. The C, H, and N contents of the polymer (C, 79.69; H, 6.67; N, 13.27) agreed with those of MeAn (C, 79.97; H, 6.71; N, 13.32). This result shows that the polymer was formed by addition polymerization. In the ^{1}H NMR spectrum of poly(MeAn) produced by *n*-BuLi (Figure 2), the absorption bands due to methylene and phenyl protons are observed in the regions 4.5−5.2 and 7.1−7.4 ppm, respectively. The ratio of the integrals of these bands agrees with the structure of poly(MeAn) shown in Scheme 1. Two strong absorption bands due to the methylene proton are observed at 4.8 and 5.1 ppm. The band at lower field may be due to the protons of the methylene bound to the deuteronated nitrogen.[13] In addition, the weak absorption band due to the methylene bound to the butyl group is observed at 3.2 ppm. The IR spectra of the cyclic trimer and the polymer produced by *n*-BuLi are shown in Figure 3. In both spectra, the absorption bands due to the out-of-plane deformation vibration of the C−H bond of the monosubstituted benzene are observed at about 690 and 750 cm^{-1}.[15] The result shows that the polymer contains monosubstituted benzenes, similar to the cyclic trimer.

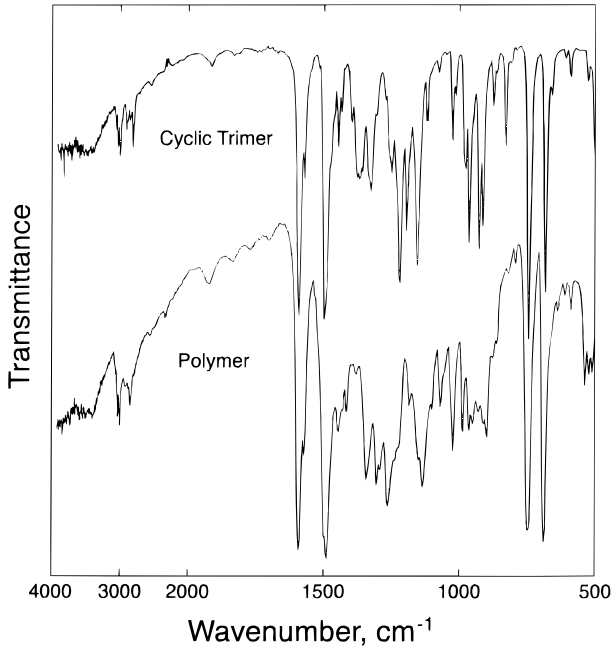


Figure 3. IR spectra of the polymer produced by *n*-BuLi and the cyclic trimer (KBr).

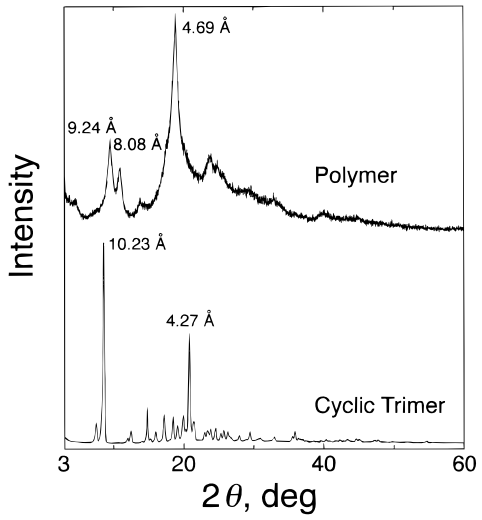


Figure 4. Powder X-ray diffraction patterns of the polymer produced by *n*-BuLi and cyclic trimer by using nickel-filtered Cu Kα radiation (voltage, 4.0 kV; current, 100 mA; scanning rate, 3 °C/min).

However, in the region of 900−1400 cm^{-1}, the spectra are not the same, supporting the suggestion that the polymer is not the cyclic trimer. From these spectroscopic data, we conclude that the polymer has the structure shown in Scheme 1. In addition, the IR spectrum of the polymer produced by acetic acid was almost the same as that of the polymer obtained by *n*-BuLi, suggesting that this polymer is also linear.

The powder X-ray diffraction patterns of the polymer produced by *n*-BuLi and the cyclic trimer are shown in Figure 4. These patterns show that the THF-insoluble polymer is not the cyclic trimer. The pattern of the polymer shows that the polymer is crystalline and contains a regular structure with a distance of 4.69 Å. Assuming that the polymer takes a trans zigzag structure, two units of the monomer corresponds to ∼4.8 Å. Since the distance of the regular structure estimated from the 2θ value in the X-ray diffraction pattern (4.69

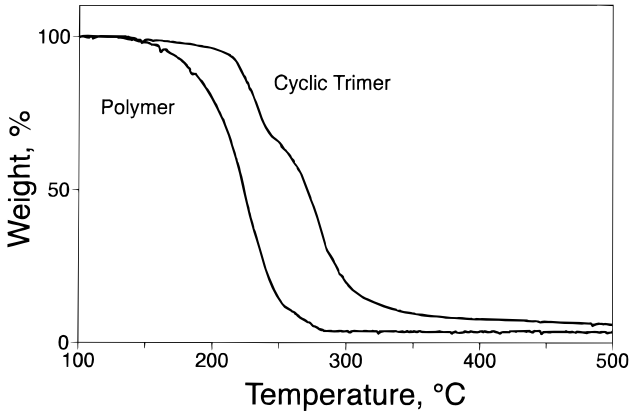


Figure 5. TGA curves of the polymer produced by *n*-BuLi and the cyclic trimer under a slow stream of nitrogen (polymer, 4.02 mg; cyclic trimer, 5.78 mg; heating rate, 10 °C/min; flow rate of nitrogen, 20 mL/min).

Å) is quite close to that estimated from the assumption (4.8 Å), it is suggested that the polymer takes a trans zigzag structure. The polymer is not soluble in organic solvents, suggesting that the polymer is cross-linked. However, the formation of crystalline polymer suggests that the insolubility may be ascribed to the interchain regular structure rather than the cross-linking. Furthermore, no swelling was observed upon the addition of organic solvents to the polymer, and the polymer was soluble in acids, such as acetic acid. These results also support that cross-linking does not occur during the polymerization.

The thermal behavior of the polymer was investigated by thermogravimetric analysis (TGA). The TGA curves of the polymer and the cyclic trimer are shown in Figure 5. The results show the polymer is less thermally stable than the cyclic trimer. In the case of the polymer, a gradual weight loss started at ∼100 °C, with full decomposition at ∼260 °C. This result shows that the polymer is a thermally degradable polymer. To obtain information on the pyrolysis, the product, produced by pyrolysis of the polymer at 200 °C, was collected under high vacuum and its structure was analyzed by ^{1}H NMR spectroscopy at −80 °C. The spectrum showed that the product was the monomer. MeAn was recovered in a high yield (∼70%).[16] These results led us to conclude that depolymerization of poly(MeAn) occurred at ∼200 °C.

In summary, MeAn was prepared by the pyrolysis of the cyclic trimer of MeAn, hexahydro-1,3,5-triphenyl-1,3,5-triazine. MeAn could be stored in THF. The polymerizability of MeAn was investigated. Polymer was obtained by the polymerization of MeAn with acetic acid or *n*-BuLi in THF. The polymer was insoluble in many organic solvents. The structure of the polymer was investigated by elemental analysis and ^{1}H NMR and IR spectroscopies. The results show that the polymer is formed by 1,2-addition of the C═N double bond. In addition, the obtained polymer is crystalline and decomposed at ∼200 °C to form the monomer.

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(16) The polymer was quantitatively decomposed to monomer. However, ∼30% of the formed monomer converted to colorless powder on the inner surface of the apparatus for recovering monomer.

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