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Preparation and Polymerization of Benzaldehyde Formaldehyde Azine (1-Phenyl-2,3-diaza-1,3-butadiene)

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ABSTRACT: Benzaldehyde formaldehyde azine (BzFAz) was prepared as a new monomer having C═N bonds, and its polymerizability was investigated by using several initiators. Polymers were obtained from BzFAz by polymerizations initiated by trifluoroacetic acid (CF_3COOH), butyllithium (n-C_4H_9Li), and methylmagnesium iodide (CH_3MgI). The structures of these polymers were investigated by elemental analysis, IR, Raman, and ^1H NMR spectroscopies. The polymers obtained by CF_3COOH and by n-C_4H_9Li consisted of 3,4-units, whereas that obtained by CH_3MgI consisted of both 1,4- and 3,4-units. In the polymerization initiated by CH_3MgI, the content of 1,4-unit increased as an increase in the dielectric constant of the solvent used. Powder X-ray diffraction of the polymers revealed that the polymer obtained by n-C_4H_9Li was highly crystalline. In addition, the thermogravimetric analyses showed these polymers were fully decomposed below 300 °C.

Introduction

There are many papers on the addition polymerization through C═C or C═O bonds, and thus the properties of these polymerizations are well-known. To our knowledge, however, there are few papers on addition polymerization of compounds containing C═N bonds, except for isocyanates,[1−3] carbodiimide,[4−6] imines,[7] 1-azabutadienes,[7] azines,[8−16] and *N*-methyleneaniline.[17] We have paid attention to the polymerization through the C═N bond.

Formaldehyde azine (CH_2═N−N═CH_2, FAz), which is the simplest azine, was synthesized by Neureiter[8] in 1959. Although Neureiter[8] reported that FAz was spontaneously polymerized above its melting point, he did not describe the type of polymerization and the structural units of the polymer. Kamachi et al.[9] succeeded in the storage of FAz without polymer formation as a THF solution even at room temperature. Thus, Kamachi et al.[10] investigated the polymerizability of FAz and found that FAz was easily polymerized by ionic initiators to form polymer composed of 1,2- and 1,4-units. Furthermore, Kamachi et al.[11−13] investigated the polymerizability of azines in order to clarify the polymerizability of C═N bonds and obtain new polymers. We have previously synthesized *trans*-1,4-polymers from alkyl azines (R^1CH═N−N═CHR^2, $R^1 = R^2 = CH_3$, C_2H_5, n-C_3H_7) with Grignard reagents[14,15] and a 1,2-polymer from trifluoroacetaldehyde azine ($R^1 = R^2 = CF_3$, TFAcAz) with triethylamine.[16] These results reveal that the structure of polymer of azines depends on the substituent of azines.

In the extension of our systematic study on the polymerizability of azines, we have focused on benzaldehyde formaldehyde azine (R^1 = H, $R^2 = C_6H_5$, BzFAz), an unsymmetric azine. Although Bestmann et al.[18] reported BzFAz in 1961, they did not describe its identification in detail. Recently, we perceived that the compound which Bestmann et al.[18] reported was not BzFAz but its polymeric product. In the present paper, we describe the synthesis and the polymerizability of BzFAz and the structures of the polymers obtained.

Experimental Section

Materials. Dichloromethane was purified by distillation over calcium hydride under an argon atmosphere. Tetrahydrofuran (THF), toluene, and hexane were purified by distillation over sodium benzophenone ketyl under an argon atmosphere. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization in methanol. Commercially available butyllithium (n-C_4H_9Li) (1.5 M hexane solution) and methylmagnesium iodide (CH_3MgI) (2.0 M diethyl ether solution) were transferred to ampules using syringes under an argon atmosphere. The concentrations of n-C_4H_9Li and CH_3MgI were determined by double titration.[19] Other reagents were used without further purification.

Preparation of Poly(BzFAz) (Prepolymer). An aqueous solution of formaldehyde (38 wt %, 19 mL, 0.25 mol) was added to a suspension of anhydrous sodium sulfate (200 g) in dichloromethane (100 mL). The mixture was stirred for 30 min at 20 °C. Benzaldehyde hydrazone[20] (30 g, 0.25 mol) was added to the mixture with stirring, and stirring was continued for 1 h at 20 °C. Sodium sulfate was removed by filtration. After evaporation of the solvent, a pale yellow residue was obtained. After washing the pale yellow residue with hexane (7 × 50 mL) and THF (7 × 50 mL), prepolymer was obtained as a pale yellow powder. Prepolymer was only slightly soluble in organic solvents, such as acetone, toluene, benzene, chloroform, dichloromethane, *N*,*N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, THF, and diethyl ether: yield 18.4 g, 56.3%; mp 130−135 °C (decomposition). IR (KBr): 1594 (aromatic C═C and C═N), 1568 (aromatic C═C), 1493 (aromatic C═C), 1449 (aromatic C═C), 1236 (C−N), 1203 (C−N), 755 (aromatic C−H), 693 cm^{-1} (aromatic C−H). ^{13}C NMR (CPMAS): δ 73.0, 128.8, 136.6. Anal. Calcd for $(C_8H_8N_2)_n$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.50; H, 6.17; N, 21.23.

Preparation of BzFAz by Pyrolysis of Prepolymer. Prepolymer (300 mg, 2.3 mmol BzFAz) was placed in a bulb-to-bulb distillation apparatus and pyrolyzed gradually under reduced pressure (ca. 0.3 mmHg) at 140 °C in an electric

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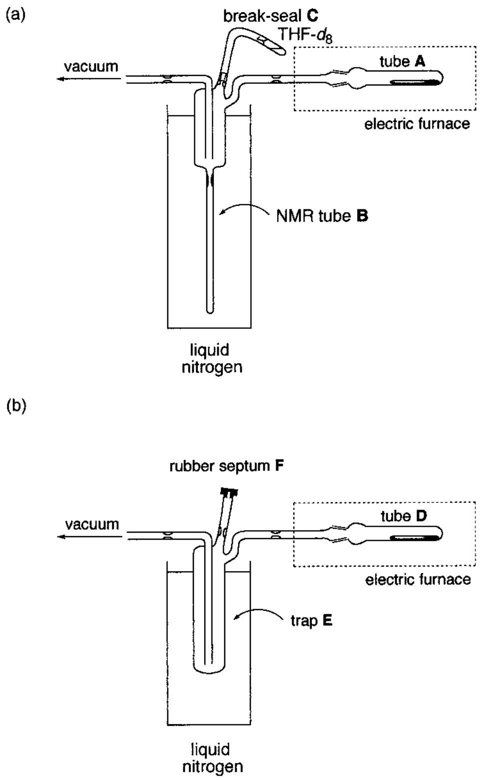


Figure 1. Apparatus for the preparation of a solution of BzFAz in THF-d_8 for NMR measurements (a) and the reaction and polymerization of BzFAz (b).

furnace. Although a pale yellow oil was obtained, this oil converted to a pale yellow powder within several minutes. The pale yellow oil: yield 15 mg, 5.0%. IR (NaCl): 1629 (C=N), 1596 (aromatic C=C), 1571 (aromatic C=C), 1493 (aromatic C=C), 1449 (aromatic C=C), 1402 (in-plane deformation of CH_2=), 1006 (out-of-plane deformation of CH_2=), 1203 (C−N), 755 (aromatic C−H), 693 cm^{-1} (aromatic C−H).

Preparation of a Solution of BzFAz in THF-d_8 for NMR Measurements. An apparatus used for preparation of a solution for NMR measurements is shown in Figure 1a. Prepolymer (300 mg, 2.3 mmol) was placed in a tube (A) and pyrolyzed gradually to BzFAz under reduced pressure (ca. 0.3 mmHg) at 140 °C in an electric furnace. The formed BzFAz was collected in an NMR tube (B) with liquid nitrogen. After breaking a break-seal (C), THF-d_8 (0.4 mL) dried with sodium was distilled into the NMR tube (B) under reduced pressure. The NMR tube (B) was sealed under reduced pressure. The solution was warmed to −20 °C to be made homogeneous, and then it was maintained at −78 °C until the measurements. NMR measurements were carried out at −80, −50, −20, 0, +20, and +30 °C: yield 183 mg, 61.0%. ^{1}H NMR (270 MHz, THF-d_8, +20 °C): δ 7.02 (d, 1H, J = 13.9 Hz, *trans*-methylene), 7.37 (m, 3H, para and meta), 7.50 (d, 1H, J = 13.9 Hz, *cis*-methylene), 7.81 (m, 2H, ortho), 8.48 (s, 1H, methine). ^{13}C NMR (67.9 MHz, THF-d_8, +20 °C): δ 129.3 (meta), 129.5 (ortho), 132.0 (para), 135.0 (ipso), 151.1 (methylene), 162.0 (methine).

Polymerization of BzFAz. A typical polymerization of BzFAz is described below.

The apparatus for polymerization is shown in Figure 1b. Prepolymer (500 mg, 3.8 mmol) was placed in a tube (D) and gradually pyrolyzed to BzFAz at 140 °C under reduced pressure (ca. 0.3 mmHg). The formed BzFAz (ca. 300 mg, 2.3 mmol) was collected in a trap (E) with liquid nitrogen. After pyrolysis, the trap was warmed to −78 °C and filled with argon. THF (1.1 mL) was immediately added to the BzFAz through a rubber septum (F) by a syringe. The mixture was warmed to −20 °C to be made homogeneous. CH_3MgI (0.01 mL, 2.0 M diethyl ether solution) was added to the solution of BzFAz in THF using a syringe under an argon atmosphere. The trap (E) was sealed and maintained at −20 °C. After 6 h, the trap (E) was opened, and the reaction mixture was poured into excess methanol to terminate polymerization. Polymer was obtained as a pale yellow powder and purified by reprecipitation with THF−methanol: yield 72 mg, 24%. IR (KBr): 1593 (aromatic C=C), 1567 (aromatic C=C), 1239 (C−N), 1201 (C−N), 755 (aromatic C−H), 695 cm^{-1} (aromatic C−H). Raman: 1597 (aromatic C=C), 1570 (aromatic C=C), 1225 (C−N), 1209 cm^{-1} (C−N). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.7−4.6 (methine and methylene), 4.6−5.2 (methylene), 7.0−7.4 (ortho and meta), 7.4−7.6 (para), 7.6−7.8 (methine). Anal. Calcd for $(C_8H_8N_2)_n$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.36; H, 6.11; N, 21.41.

Measurements. Infrared spectra were recorded on a Jasco FT/IR-410 spectrometer. Raman spectra were obtained on a BIO RAD FT Raman spectrometer by using a Nd:YAG laser 1064 nm excitation line. ^{1}H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270 spectrometer using $CDCl_3$ or THF-d_8 as a solvent. The ^{13}C CPMAS NMR spectrum was measured at 75.6 MHz on a Chemagnetics CMX300W spectrometer at room temperature (25 °C). Gel permeation chromatography (GPC) analyses were performed in THF with a TOSOH CCP & 8010 system by using TSK columns at 40 °C. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. The molecular weights were calibrated by polystyrene standards (TOSOH TSK polystyrene standard). Powder X-ray diffraction patterns were taken using nickel-filtered Cu Kα radiation with a Rigaku Rotaflex diffractometer. Thermogravimetric analyses (TGA) were carried out with a Seiko Instruments TG/DTA6200 under a slow stream of nitrogen (20 mL/min) at a heating rate of 10 °C/min.

Results and Discussion

Synthesis and Identification of BzFAz. We attempted to prepare BzFAz from benzaldehyde hydrazone and formaldehyde according to the procedure of Shaw et al.,[21,22] who synthesized several metal complexes containing unsymmetric azines as ligands. As a result, we obtained a pale yellow powder which was only slightly soluble in organic solvents (see Experimental Section). As described later, because oligomers and cyclic trimer of BzFAz are easily soluble in organic solvents, this powder is found to be polymer of BzFAz. This polymer is called prepolymer for the sake of convenience in this paper. The structure of the prepolymer is described later in detail.

We tried to prepare BzFAz by pyrolysis of prepolymer under reduced pressure (ca. 0.3 mmHg) at 140 °C and obtained a pale yellow oil. The IR spectrum of this pale yellow oil is shown in Figure 2a. In this spectrum, the absorption band due to the out-of-phase stretching vibration of the C=N−N=C bond is observed at 1629 cm^{-1}.[23] The absorption bands due to the stretching vibrations due to the aromatic C=C bonds are observed in the region of 1449−1596 cm^{-1}.[24] Furthermore, the IR spectrum reveals that the pale yellow oil has a CH_2= bond. These results show that this pale yellow oil is BzFAz. However, BzFAz was so unstable that it was converted to a pale yellow powder, which is prepolymer, in several minutes.

According to the procedure of Kamachi et al.,[9,10,17] we prepared a solution of BzFAz in THF-d_8. Figure 3 shows the 67.9 MHz ^{13}C NMR spectrum of BzFAz. In Figure 3, the absorption bands due to the methylene and methine carbons are observed at 151.1 and 162.0 ppm, respectively.[25] In this spectrum, the peaks due to the phenyl carbons are also observed in the region of 129.3−135.0 ppm.[25] This result indicates that BzFAz is obtained as a THF-d_8 solution. In the 270 MHz ^{1}H NMR

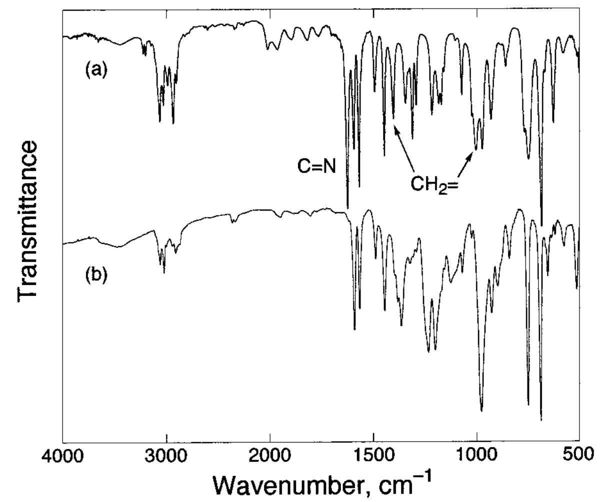


Figure 2. IR spectra of BzFAz (NaCl) (a) and prepolymer (KBr) (b).

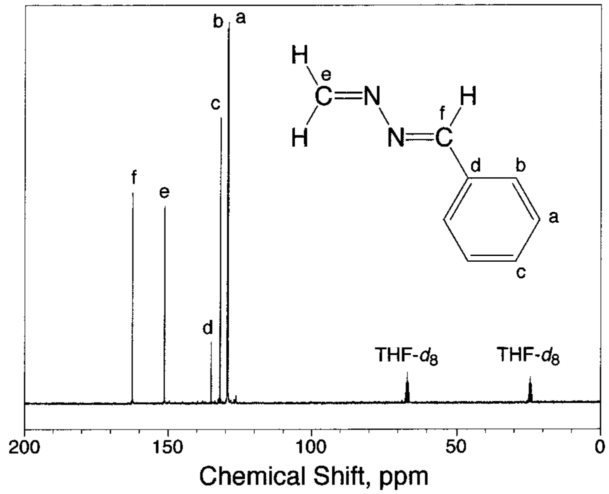


Figure 3. The 67.9 MHz ^{13}C NMR spectrum of BzFAz (THF-d_8, 20 °C).

spectrum for BzFAz (not shown), the AB type of signals due to the methylene protons of the $CH_2{=}N$ was observed at 7.02 and 7.50 ppm.[25] The absorption bands due to the benzyl and phenyl protons of the $C_6H_5CH{=}N$ were also observed in the region of 7.4−8.5 ppm.[25] The ratio of the integration for the absorption bands agrees with the structure of BzFAz. This result of ^{1}H NMR spectroscopy supports that BzFAz is obtained as a solution in THF-d_8. To clarify the stability of BzFAz in THF, ^{1}H NMR spectra for BzFAz were recorded increasing the measurement temperature from −80 to +30 °C. The intensities of the signals due to BzFAz did not decrease at a temperature lower than −20 °C, indicating that the BzFAz was stable in THF below −20 °C. Furthermore, BzFAz was stable in THF-d_8 for 30 min at ca. 3 M even at +30 °C.

Polymerization of BzFAz. (a) Seeking Initiators for Polymer Formation from BzFAz. Because BzFAz can be stored as a THF solution without polymer formation, the polymerizations of BzFAz were performed using several typical initiators at −20 °C under an argon atmosphere. The results are listed in Table 1. No polymer was obtained by polymerization of BzFAz initiated by AIBN under photoirradiation, indicative of the poor radical polymerizability of BzFAz. When trifluoroacetic acid (CF_3COOH) was used as a cationic initiator, methanol-insoluble polymer was formed in a relatively high yield (81%). Anionic polymerizability of BzFAz was investigated with two types of initiators. Methanol-insoluble polymer was obtained by polymerization initiated by n-C_4H_9Li in a relatively high yield (77%). A high molecular weight polymer (M_w = 53 000) was given by polymerization initiated by CH_3MgI. These results show that BzFAz is polymerized with cationic and anionic initiators.

Table 1. Polymerization of BzFAz Using Typical Initiators[a]

initiator (mol %)	solvent	concn, M	yield,[b] %	M_w[c]	$M_\mathrm{w}/M_\mathrm{n}$[c]
AIBN (10)[d]	THF	2.0	0		
CF_3COOH (1.0)	CH_2Cl_2	1.2	81 (60[e])	1600 [f]	1.9 [f]
C_4H_9Li (1.0)	THF	2.0	77 (58[e])	4100 [f]	1.9 [f]
CH_3MgI (1.0)	THF	2.0	24	53000	2.2

[a] At −20 °C under an argon atmosphere. Polymerization time = 6 h. [b] Methanol-insoluble fraction. [c] Determined by GPC. [d] Under photoirradiation. [e] THF-insoluble fraction. [f] THF-soluble fraction.

(b) Polymerization and Reaction of BzFAz with Cationic Initiators. When CF_3COOH was added to a solution of BzFAz in dichloromethane as an initiator, the reaction mixture changed from pale yellow to colorless. After 1 h, precipitate, which was insoluble in THF, was formed. The THF-soluble fraction contained oligomer with M_w of 1600. Because the IR spectrum of the THF-insoluble fraction was almost the same as that of the THF-soluble oligomer, the THF-insoluble fraction was concluded to be polymers with M_w higher than 1600.

When a cationic polymerization of BzFAz was attempted using titanium tetrachloride ($TiCl_4$), one of the typical cationic initiators, a pale yellow crystalline compound, and a colorless precipitate were obtained. The structures of these products were investigated by elemental analysis and ^{1}H NMR and IR spectroscopies,[26] indicating that the crystalline compound and the precipitate were benzaldehyde azine (BzAz) and polymer of formaldehyde azine (FAz), respectively. From this result, we conclude that BzFAz was rearranged to the corresponding symmetric azines, BzAz and FAz, in the presence of $TiCl_4$ and that FAz was immediately converted to its polymer.[10]

(c) Polymerizations of BzFAz with Anionic Initiators. When n-C_4H_9Li was added to a solution of BzFAz in THF, the reaction mixture changed immediately from pale yellow to brown. After 15 min, precipitate was formed. The THF-soluble fraction contained an oligomer with M_w of 4100. The THF-insoluble powders are considered to be polymers with M_w higher than 4100, because the IR spectra for the THF-insoluble and THF-soluble fractions were almost the same.

To obtain high molecular weight polymer, anionic polymerizations initiated by CH_3MgI were performed in a few solvents. These results are shown in Table 2. When CH_3MgI was used as an initiator, the reaction mixture changed from pale yellow to pale brown. Contrary to the case of the polymerization initiated by n-C_4H_9Li, little precipitate was formed in THF and toluene. However, precipitate was formed upon the polymerization in hexane. Thus, the low M_w (2000) is due to the poor solubility of poly(BzFAz) in hexane. On the basis of the results of the polymerizations in THF and toluene, M_w of the polymer obtained might depend on the dielectric constant of solvent used.[27]

Table 2. Anionic Polymerization of BzFAz[a]

initiator (mol %)	solvent	yield,[b] %	M_w[c]	M_w/M_n[c]	1,4-unit,[d] %
CH_3MgI (1.0)	THF	24	53 000	2.2	35
CH_3MgI (1.0)	toluene	44	13 000	1.7	24
CH_3MgI (1.0)	hexane	49	2 000	1.5	15

[a] At −20 °C under an argon atmosphere. [BzFAz] = 2.0 M. Polymerization time = 6 h. [b] Methanol-insoluble fraction. [c] Determined by GPC. [d] Determined by ^{1}H NMR.

Structure of Poly(BzFAz). The C, H, and N contents of prepolymer and the polymers obtained agreed with those of the monomer. This result shows that these polymers were formed by addition polymerization of BzFAz. The structures of these polymers were investigated by several spectroscopies.

(a) Structure of Prepolymer. The structure of prepolymer was investigated by IR, Raman, and solid-state CPMAS ^{13}C NMR spectroscopies.

In the IR spectrum of prepolymer shown in Figure 2b, the absorption band due to the out-of-phase stretching vibration of the C═N−N═C bond disappears, although this absorption band is clearly observed at 1629 cm^{-1} in that of BzFAz.[23] Furthermore, in the spectrum of prepolymer, the absorption bands due to the in-plane and out-of-plane deformations of the CH_2═ , which are observed in that of BzFAz, disappear. On the basis of these results, we consider that prepolymer is formed by 1,4- or 3,4-addition of BzFAz, because the absorption band due to the stretching vibration of the C═N double bond conjugated with the aromatic ring can be observed at ca. 1590 cm^{-1}.

To decide whether prepolymer is formed by 1,4- or 3,4-addition, we investigated whether the signal due to the stretching vibration of the N═N bond is observed in the IR or Raman spectrum for prepolymer or not. However, it was quite difficult to see whether the absorption band due to the N═N bond is there or not, because the strong signal due to the stretching vibration of the aromatic C═C bond is observed at ca. 1570 cm^{-1} in the IR and Raman spectra of prepolymer.[24]

In the solid-state CPMAS ^{13}C NMR spectrum of prepolymer (not shown), an absorption band at 73.0 ppm was clearly seen. On the basis of the spectroscopic results for a cyclic trimer of BzFAz as described below,[28] we conclude that this absorption band at 73.0 ppm is due to the methylene carbon of the N−CH_2−N. From these results, it is found that prepolymer is formed by 3,4-addition of BzFAz.

As described above, prepolymer is only slightly soluble in organic solvents, suggesting that the polymer is cross-linked through the pendant C═N bonds. However, no swelling of prepolymer was observed in any organic solvents. The powder X-ray diffraction pattern shown in Figure 4a reveals that prepolymer is highly crystalline. The formation of crystalline polymer could be due to the interchain regular structure. The poor solubility might be ascribed to the interchain regular structure rather than to the cross-linking.

(b) Structure of Poly(BzFAz) Obtained by Polymerization with CF_3COOH. To obtain information about the structure of the THF-insoluble fraction, we tried to isolate a reaction product from the THF-soluble fraction. As a result, a crystalline compound was isolated. The structure of this product was investigated by elemental analysis and EI-mass, ^{1}H NMR, and ^{13}C NMR spectroscopies.[28] The C, H, and N contents of the product agree with those of BzFAz, indicating that the product is an oligomer of BzFAz. The EI-mass spectrum of this product showed a peak at m/z = 396 as a molecular ion peak, indicating a trimer of BzFAz. In the ^{1}H NMR spectrum for this product (Figure 5a), the singlet signals observed at 5.12 and 7.71 ppm are due to the methylene proton of the N−CH_2−N and the methine proton of the C_6H_5CH═N, respectively.[25] The absorption bands due to the phenyl protons are observed in the region of 7.2−7.7 ppm.[25] In the ^{13}C NMR spectrum for this product (not shown), the absorption bands due to the methylene and methine carbons were observed at 68.8 and 136.1 ppm, respectively.[25] In the ^{13}C NMR spectrum, the absorption bands due to the

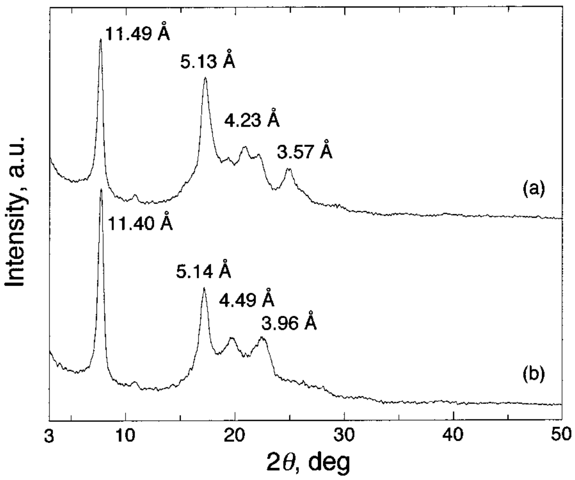


Figure 4. Powder X-ray diffraction patterns of prepolymer (a) and the poly(BzFAz) formed by n-C_4H_9Li (b) by using nickel-filtered Cu Kα radiation (voltage, 4.0 kV; current, 100 mA; scanning rate, 3°/min).

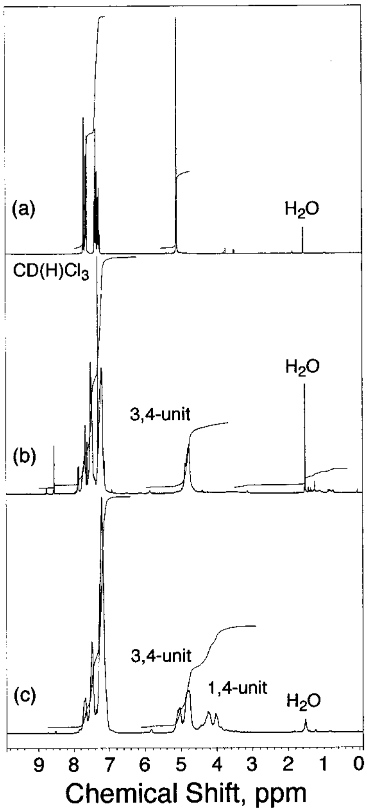
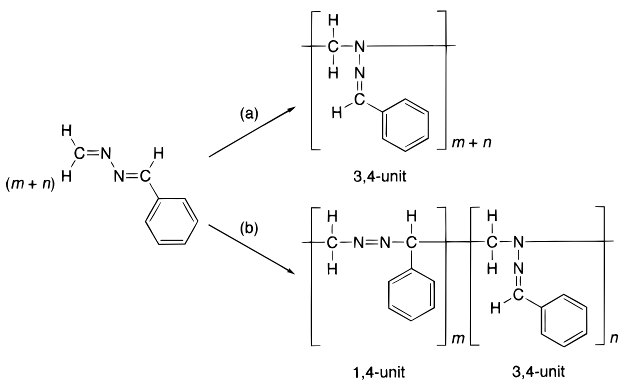


Figure 5. The 270 MHz ^{1}H NMR spectra of the cyclic trimer of BzFAz (a) and poly(BzFAz) formed by n-C_4H_9Li (b) by CH_3MgI in THF (c) ($CDCl_3$, 30 °C).

Scheme 1



phenyl carbons were also observed in the region of 125.8−133.4 ppm.[25] These NMR spectra reveal that this product is hexahydro-1,3,5-tris(2-phenyl-1-azaethenyl)-1,3,5-triazine, a cyclic trimer of BzFAz, formed by 3,4-addition and cyclization.

IR and Raman spectra for the polymer obtained using CF_3COOH were the same as those of prepolymer. From these results, we conclude that this polymer is formed by 3,4-addition (Scheme 1, path a). Furthermore, the structure of the cyclic trimer obtained supports this conclusion.

In this polymerization, the proton of CF_3COOH could attack the lone pairs of the nitrogens of BzFAz. The structure of polymer shows that polymerization proceeded through the less hindered $CH_2{=}N$ bond. This may be because the benzyl cation is too stable to attack another monomer.

(c) Structure of Poly(BzFAz) Obtained by Polymerization with n-C_4H_9Li. Because the polymer obtained by n-C_4H_9Li was insoluble in organic solvents, the structure of the soluble oligomer obtained from the THF-soluble fraction was investigated by ^1H NMR spectroscopy. In the ^1H NMR spectrum for the oligomer (Figure 5b), the broad absorption band due to the methylene proton of the $N{-}CH_2{-}N$ is observed around 4.8 ppm.[25] In the ^1H NMR spectra, the absorption bands observed in the region of 7.0−7.7 ppm are due to the phenyl and methine protons of the $C_6H_5CH{=}N$.[25] The ratio of the integrals of the absorption bands agrees with the 3,4-addition structure. These results show that the oligomer consists of 3,4-units.

The IR spectrum of the THF-insoluble polymer obtained using n-C_4H_9Li was almost the same as that of the THF-soluble oligomer (not shown). This result indicates that this polymer also consists of 3,4-units (Scheme 1, path a).

In this polymerization, n-C_4H_9Li could attack to the less hindered $CH_2{=}N$ bond, and then polymerization might proceed through 3,4-addition because of the stability of the lithium amide.

In addition, it is found that this polymer is highly crystalline on the basis of the X-ray diffraction patterns shown in Figure 4b. Because no swelling of the polymer obtained by n-C_4H_9Li was observed in any solvent, the nonsolubility of this polymer is ascribed to the formation of the crystalline polymer due to the interchain regular structure.

(d) Structure of Poly(BzFAz) Obtained by Polymerization Initiated by CH_3MgI. As an example, Figure 5c shows the 270 MHz ^1H NMR spectrum of the polymer obtained by polymerization initiated by CH_3MgI in THF. The broad absorption band due to the methylene protons of the 3,4-addition unit is observed in the region of 4.6−5.2 ppm.[25] The broad absorption bands due to the methylene and the methine protons of the 1,4-addition units are observed in the region of 3.7−4.6 ppm.[14,15] These results show that the polymer obtained by CH_3MgI in THF consists of both 1,4- and 3,4-units (Scheme 1, path b). From the ratio of the integrals for these absorption bands, the 1,4-unit content of this polymer is estimated to be 35%. The 1,4-unit contents of the polymers obtained by polymerizations initiated by CH_3MgI in three kinds of solvents are also shown in Table 2. The 1,4-unit content in the polymer increases as an increase in the dielectric constant of solvent.[27]

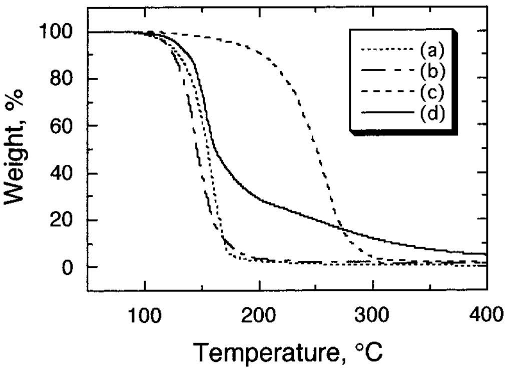


Figure 6. TGA curves of prepolymer (a) and the polymers formed by CF_3COOH (b), by n-C_4H_9Li (c), and by CH_3MgI (d) under a slow stream of nitrogen. Sample ca. 2 mg; heating rate, 10 °C/min; flow rate of nitrogen, 20 mL/min.

There are at least two active species in this polymerization of BzFAz initiated by CH_3MgI, whose contents depend on the polarity of the solvent used. The active species formed by Grignard reagents have been reported to be complicated in the anionic polymerization of methacrylates.[29] The active species in the polymerization of BzFAz initiated by CH_3MgI remain unsolved as further problems.

Thermal Properties of Poly(BzFAz)s. The thermal behavior of the poly(BzFAz)s was investigated by TGA. The TGA curves of prepolymer and the polymers obtained are shown in Figure 6. In the cases of poly(BzFAz)s composed of 3,4-units (Figure 6a−c), the TGA curves show single decompositions. On the basis of these TGA results, prepolymer and the poly(BzFAz) obtained by CF_3COOH commence decomposition around 100 °C with full decomposition at 180 °C (Figure 6a,b). Although the polymer obtained by n-C_4H_9Li commences decomposition around 100 °C, this polymer is much more stable than the above two polymers, suggesting that the THF-insoluble polymer obtained by n-C_4H_9Li has a much higher molecular weight. On the other hand, the TGA curve for the poly(BzFAz) formed by CH_3MgI shows multistep decomposition (Figure 6d). On the basis of the previous results of TGA for polymers of azines,[14−16] it is considered that the 3,4-units were decomposed at ca. 100 °C followed by decomposition of the 1,4-units.

Conclusion

BzFAz was prepared by pyrolysis of prepolymer of BzFAz. BzFAz was stable in solutions at −20 °C. The polymerizability of BzFAz was investigated. Polymerizations of BzFAz initiated by CF_3COOH, n-C_4H_9Li, and CH_3MgI produced polymers of BzFAz, although no polymer was obtained by polymerization initiated by

AIBN. The structures of the polymers obtained were investigated by elemental analysis and several spectroscopies. The polymers obtained by CF_3COOH and n-C_4H_9Li were found to be produced by 3,4-addition, whereas the polymer obtained by CH_3MgI consisted of both 3,4- and 1,4-units. In the polymerization initiated by CH_3MgI, the 1,4-content of the polymer obtained increased as an increase in the dielectric constant of the solvent used. Furthermore, powder X-ray diffraction analysis revealed that the polymer initiated by n-C_4H_9Li was crystalline. Thermal behavior of the polymers obtained was investigated by TGA.

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(20) Benzaldehyde hydrazone was prepared by reaction of benzaldehyde and hydrazine monohydrate in ethanol and purified by successive distillations under reduced pressure over calcium hydride: yield 88%; bp 107−110 °C (0.5 mmHg). IR (neat): 3331 (N−H), 1597 cm^{-1} (C=N). ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.62 (s, 2H, NH_2), 7.37 (m, 3H, para and meta), 7.58 (dd, 2H, J = 8.9, 1, 7 Hz, ortho), 7.69 (s, 1H, CH=N). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 125.6 (meta), 127.9 (ortho), 128.1 (para), 134.8 (ipso), 150.0 (C=N).
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(26) Pale yellow crystalline product: IR (KBr): 1650 (C=N), 1600 (aromatic C=C), 1500 (aromatic C=C), 1160 (C−N), 755 (aromatic C−H), 690 cm^{-1} (aromatic C−H). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.46 (m, 3H, ortho and para), 7.87 (dd, 2H, J = 8.0, 3.0 Hz, meta), 8.68 (s, 1H, methine). Colorless powder: IR (KBr): 1646 (C=N), 1586 (N=N), 1500 (aromatic C=C), 1194 cm^{-1} (C−N).
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(28) Cyclic trimer: mp 190−191 °C. IR (KBr): 1589 (aromatic C=C), 1563 (aromatic C=C), 1240 (C−N), 1213 (C−N), 754 (aromatic C−H), 693 cm^{-1} (aromatic C−H). ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.12 (s, 2H, methylene), 7.27 (dd, 1H, J = 8.5, 1.7 Hz, para), 7.36 (t, 2H, J = 8.5 Hz, meta), 7.62 (dd, 2H, J = 8.5, 1.7 Hz, ortho), 7.71 (s, 1H, methine). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 68.8 (methylene), 125.8 (meta), 127.8 (para), 128.5 (ortho), 133.4 (ipso), 136.1 (methine). Anal. Calcd for $(C_8H_8N_2)_3$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.50; H, 6.13; N, 21.15. EI-MS [M$^+$] Calcd 396. Found 396.
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