Novel Spontaneous Polymer Formation from Acetaldehyde Azine and Maleic Anhydride via Radical Mechanism

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ABSTRACT: A THF-insoluble polymeric product was obtained by the reaction between acetaldehyde azine (AcAz) and maleic anhydride (MAnh) without any initiator. The reduced viscosity values for this product indicate polymer formation from AcAz and MAnh. Results of the reactions between AcAz and MAnh at varying feed ratios of AcAz indicate that the polymer is formed mainly by reaction between equimolar amounts of AcAz and MAnh. (2*Z*)-4-{1-(5-Methyl-2-pyrazolinyl)}-4-oxo-2-butenoic acid (compound **1**), a one-to-one adduct of AcAz with MAnh, was isolated as a crystalline compound from the THF-soluble fraction of the reaction mixture. Comparing the spectroscopic results for the polymer with those for compound **1** and 4-{1-(5-methyl-2-pyrazolinyl)}-4-oxobutanoic acid (compound **2**), a one-to-one adduct of AcAz with SAnh, the polymer from AcAz and MAnh was found to be formed mainly by polymerization of compound **1** through the C═C bond. Results of the polymerizations of compound **1** using typical initiators show compound **1** can be polymerized by radical initiators, indicating that the polymer from AcAz and MAnh is formed by a radical mechanism. On the basis of the electron-donating property of 5-methyl-2-pyrazoline (compound **3**) formed by isomerization of AcAz in the presence of compound **1**, the spontaneous polymer formation from AcAz and MAnh was inferred to be initiated by electron transfer from compound **3** to compound **1**.

Introduction

Although there are many publications on the addition polymerization through C═C or C═O bonds, there are only a few papers on addition polymerization of compounds containing C═N bonds.[1−8] Thus, we have systematically investigated the polymerizability of azines[9−13] and synthesized crystalline *trans*-1,4-polymers from alkyl azines (RCH═N−N═CHR, R = CH_3, C_2H_5, *n*-C_3H_7)[14−16] and a crystalline 1,2-polymer from trifluoroacetaldehyde azine (R = CF_3).[16,17]

In the course of the study on the polymerizability of azines, Kamachi[18] found that acetaldehyde azine (R = CH_3, AcAz) reacted with maleic anhydride (MAnh) without any initiator to form polymeric products. Four possibilities will be considered for this polymer formation: (1) spontaneous alternating copolymerization of electron-donating and electron-accepting monomers, in which copolymer is formed by coupling of a zwitterionic one-to-one adduct of comonomers;[19,20] (2) ring-opening polymerization of MAnh initiated by organic bases;[21] (3) 1,3-dipolar addition of benzaldehyde azine or its derivatives with dienophiles leading to one-to-two adducts;[22] and (4) isomerization of alkyl azines to 2-pyrazoline derivatives in the presence of carboxylic acids.[23] However, our preliminary study suggested that the present system containing AcAz and MAnh is not consistent with any of those four possibilities. Thus, we have performed detailed studies of the spontaneous polymer formation from AcAz and MAnh. The present article describes the structure of the polymer and the mechanism for the spontaneous polymer formation from AcAz and MAnh.

Experimental Section

Materials. Acetaldehyde azine (AcAz) was prepared from acetaldehyde (Nacalai Tesque) and hydrazine monohydrate (Nacalai Tesque) according to the procedure of Curtius et al.[23] Maleic anhydride (MAnh) (Nacalai Tesque) and succinic anhydride (SAnh) (Nacalai Tesque) were recrystallized from chloroform and dried in vacuo. Tetrahydrofuran (THF) (Wako) was distilled over sodium benzophenone ketyl and stored under an argon atmosphere. (2*Z*)-4-{1-(5-Methyl-2-pyrazolinyl)}-4-oxo-2-butenoic acid (compound **1**) was prepared from AcAz and MAnh, as reported previously.[24] Triethylamine (Et_3N) (Nacalai Tesque) and *N*,*N*-dimethylaniline (DMA) (Nacalai Tesque) were distilled over calcium hydride under reduced pressure and stored under an argon atmosphere. 2,2′-Azobis(isobutyronitrile) (AIBN) (Wako) was recrystallized from methanol. Dimethyl 2,2′-azobis(isobutyrate) (MAIB) (Wako) was recrystallized from ethanol. Butyllithium (*n*-C_4H_9Li) (1.6 M hexane solution, Aldrich) and methylmagnesium iodide (CH_3MgI) (2.0 M diethyl ether solution, TCI) 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.[25] Tetracyanoethylene (TCNE) (Nacalai Tesque) was purified by sublimation. Other reagents were used as received without further purification.

Measurements. IR spectra were recorded on a JASCO FT/IR-3 spectrometer. Raman spectra were obtained on a JASCO R-800 spectrometer by using an argon ion laser 5145 Å excitation line. ^1H, ^{13}C, differential NOE, 2D H−H COSY, and 2D C−H COSY NMR were measured in DMSO-d_6 on a JEOL JNM-EX270 spectrometer. Chemical shifts were determined

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using tetramethylsilane as an internal standard. GPC analyses were performed at 40 °C on a TOSOH CO-8011 system equipped with TOSOH TSKgel G2000H$_{XL}$ and G3000H$_{XL}$ columns (pore size: 5 μm) connected in series. THF was used as an eluent at a flow rate of 0.8 mL/min. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Molecular weights of the oligomers were calibrated by polystyrene standards (TOSOH TSK standard polystyrene). EI-MS were recorded on a JEOL JMS SX-102 mass spectrometer. Mass was calibrated by using cesium iodide (CsI). Viscosity measurements were carried out in methanol at 35 °C using an Ubbelohde viscometer. ESR spectra were recorded on a JEOL JES RE-2X spectrometer operating in the X-band, utilizing a 100 kHz field modulation and a microwave power of 1 mW. UV−vis spectra were recorded on a Shimadzu UV-2100 UV−vis spectrophotometer at 25 °C.

Spontaneous Polymer Formation from AcAz and MAnh. A typical procedure is described below.

When AcAz (168 mg, 2.0 mmol) was added to MAnh (196 mg, 2.0 mmol) in a sample tube, an exothermic reaction took place. The reaction mixture changed gradually to a red-brown resin. After 24 h, this resin was crushed with a microspatula washing with THF to give finally a pale yellow powder. This powder was soluble in polar solvents, such as methanol, ethanol, dimethyl sulfoxide (DMSO), and water, and insoluble in THF, acetone, chloroform, diethyl ether, and hexane: yield 206 mg, 56.6%; mp 218−223 °C. IR (KBr): 3450 (OH), 3250 (NH), 1720 (carboxylic acid C═O), 1630 (amide C═O, C═N) cm^{-1}. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 0.7−1.4, 1.5−2.3, 2.6−5.0, 6.5−7.2. Anal. Calcd for $(C_8H_{10}N_2O_3)_n$: C, 52.74; H, 5.53; N,15.38. Found: C, 53.22; H, 5.87; N, 14.56.

Preparation of 4-{1-(5-Methyl-2-pyrazolinyl)}-4-oxobutanoic Acid (Compound 2), a One-to-One Adduct of AcAz with SAnh. AcAz (0.96 mL, 10 mmol) was added to a solution of SAnh (900 mg, 10 mmol) in THF (10 mL) in a flask under an argon atmosphere. The solution was stirred at ca. 20 °C for 36 h. After evaporation of the THF, compound **2** was obtained as a pale yellow oil. IR (NaCl): 1730 (carboxylic acid C═O), 1640 (amide C═O), 1600 (C═N) cm^{-1}. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 1.23 (d, 3H, J = 6.6 Hz, pyrazoline methyl), 2.53 (t, 2H, J = 6.9 Hz, methylene), 2.54 (ddd, 1H, J = 19.3, 5.2, 2.1 Hz, pyrazoline methylene), 2.81 (t, 1H, J = 6.9 Hz, methylene), 2.82 (t, 1H, J = 6.9 Hz, methylene), 3.16 (ddd, 1H, J = 18.5, 11.0, 1.7 Hz, pyrazoline methylene), 4.37 (m, 1H, pyrazoline methine), 7.16 (t, 1H, J = 1.7 Hz, CH═N), 12.09 (s, 1H, COOH).

Polymerization of Compound 1 with Typical Initiators. (**a**) **Radical Polymerization.** A typical procedure of radical polymerization is described below.[24] MAIB (5.8 mg, 0.025 mmol) and compound **1** (91 mg, 0.50 mmol) were dissolved in THF (1.0 mL). This solution in THF was placed in an ampule. The ampule was connected to a high-vacuum system, degassed by three freeze−pump−thaw cycles with an oil rotary pump and by three freeze−pump−thaw cycles with an oil diffusion pump, and then sealed under high vacuum. This sealed ampule was kept at 80 °C for 72 h. After 72 h, the ampule was opened, THF-insoluble polymer was separated by centrifugation, washed with THF, and dried in vacuo: yield 16.7 mg, 18.3%. IR (KBr): 3450 (OH), 3250 (NH), 1720 (carboxylic acid C═O), 1630 (amide C═O, C═N) cm^{-1}. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 0.7−1.4, 1.5−2.3, 2.6−5.0, 6.5−7.2.

(b) Anionic Polymerization. A typical procedure of anionic polymerization is described below. Compound **1** (91 mg, 0.50 mmol) was dissolved in THF (0.5 mL) in an ampule under an argon atmosphere. A solution of n-C_4H_9Li in hexane (1.6 M, 0.031 mL, 0.050 mmol) was added to the solution of compound **1** at −20 °C under an argon atmosphere. The ampule was sealed under an argon atmosphere and maintained at −20 °C. After 26 h, the ampule was opened, and methanol was added.

(c) Cationic Polymerization. A typical procedure of cationic polymerization is described below. Compound **1** (91 mg, 0.50 mmol) was dissolved in dichloromethane (0.5 mL) in an ampule under an argon atmosphere. A solution of titanium tetrachloride in dichloromethane (1.0 M, 0.05 mL, 0.050 mmol) was added at 0 °C under an argon atmosphere. The ampule was sealed under an argon atmosphere and maintained at 0 °C. After 35 h, the ampule was opened, and methanol was added.

Table 1. Polymer Formation from AcAz and MAnh[a]

AcAz, mmol	MAnh, mmol	solvent	yield,[b] %	η_{sp}/C,[c] cm^3/g	M_w[d]	M_w/M_n[d]
1.2	2.8		6.7	3.17		
2.0	2.0		56.6	*e*	470	3.0
2.4	1.6		43.8	2.81		
3.2	0.8		18.7	2.79		
10.0	10.0	toluene	12.5		390	2.3
10.0	10.0	THF	17.3		520	2.7
10.0	10.0	acetonitrile	53.6		460	3.2
10.0	10.0	DMSO	61.2		680	2.2

[a] Solvent: 5 mL; at 30 °C for 24 h. [b] THF-insoluble fraction. Based on the total amount of AcAz and MAnh. [c] In methanol solution at 35 °C at a polymer concentration of 1.0 × 10^{-2} g/cm^3. [d] Determined by GPC for THF-soluble fraction. [e] This polymer was not completely soluble in methanol.

Preparation of 5-Methyl-2-pyrazoline (Compound 3). Acetic acid (0.2 mL, 3.49 mmol) was added to AcAz (3.0 mL, 31 mmol) in a flask under an argon atmosphere. The solution was stirred at ca. 80 °C for 8 h. After 8 h, a yellow solution was obtained. The solution was distilled under reduced pressure to obtain compound **3**: yield 2.26 g, 86.7%; bp 80.1−80.2 °C (64 mmHg). ^{1}H NMR (270 MHz, DMSO-d_6): δ 1.22 (d, 3H, J = 6.27 Hz, methyl), 2.52 (ddd, 1H, J = 18.97, 3.95, 1.65 Hz, methylene), 3.12 (ddd, 1H, J = 18.64, 10.73, 1.65 Hz, methylene), 4.38 (m, 1H, methine), 7.15 (t, 1H, J = 1.65 Hz, CH═N). ^{13}C NMR (67.9 MHz, DMSO-d_6): δ 20.1 (methyl), 40.6 (methylene), 53.6 (methine), 143.2 (C═N).

Results and Discussion

Spontaneous Polymer Formation from AcAz and MAnh. Results of the spontaneous polymer formation from AcAz and MAnh are listed in Table 1. The reaction of AcAz with MAnh gave a red-brown resin. After washing with THF, a polymeric compound was obtained as a THF-insoluble powder, which was soluble only in polar solvents. To obtain information about molecular weight of this compound, viscosity measurements were carried out in methanol at 35 °C at a polymer concentration of 1.0 × 10^{-2} g/cm^3 using an Ubbelohde viscometer. The reduced viscosity values ($\eta_{sp}/C = 2.8-3.2$ cm^3/g) correspond to molecular weights of 1600−2000 based on the results of viscosity for poly(vinylpyrrolidone) in methanol at 35 °C,[26] indicative of polymer formation. The THF-soluble fraction obtained from the THF solution was considered to contain oligomer whose molecular weight is lower than that of the THF-insoluble fraction, because the IR spectrum of the THF-soluble fraction was similar to that of the THF-insoluble fraction. The C, H, and N contents (C, 53.22; H, 5.87; N, 14.56) indicate that the polymer is composed of both AcAz and MAnh units.

We carried out this polymerization in solution. These results are also listed in Table 1. The yield of the THF-insoluble fraction and the M_w of the THF-soluble fraction increase with increasing solvent polarity. When toluene, THF, or acetonitrile was used as a solvent, precipitation was formed. Thus, the dependence of the yield and the molecular weight on the solvent may be due to the solubility of the polymer in the solvent used.

The polymer formation from AcAz and MAnh were carried out at varying feed ratios of AcAz (total amount of AcAz and MAnh was fixed to be 10 mmol). Figure 1 shows the relationship between the yield of the THF-insoluble polymer and the mole fraction of AcAz in the

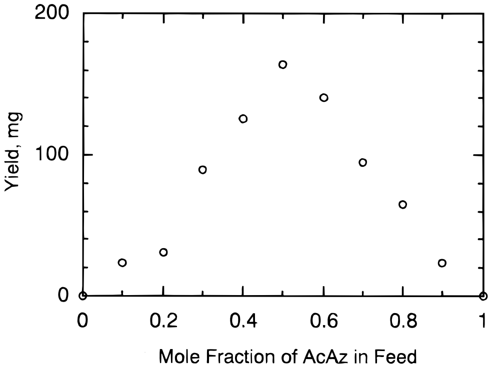


Figure 1. Continuous variation plots for the polymer formation from AcAz with MAnh at 20 °C for 24 h.

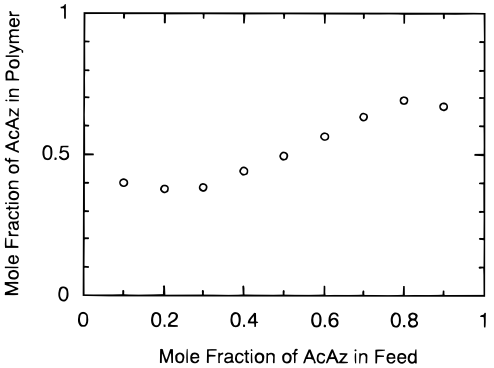


Figure 2. Dependence of the mole fraction of AcAz in the polymer on the mole fraction of AcAz in the feed.

feed. The polymer yield is maximum at mole fraction of AcAz of 0.5, suggesting that the polymer was formed by reaction between equimolar amounts of AcAz and MAnh. Furthermore, the dependence of the mole fraction of AcAz in polymer on that in the feed is shown in Figure 2. If AcAz reacts with an equimolar amount of MAnh, the mole fractions of AcAz in the polymers should be 0.5. However, Figure 2 shows that the mole fraction of AcAz in the polymers ranges from 0.38 to 0.69. In this case, the chain end may be important, because the molecular weights of the polymers are low (ca. 2000). These results indicate that the polymer is formed mainly by reaction between equimolar amounts of AcAz and MAnh.

Because the IR and NMR spectra of the polymer consist only of several broad absorption bands as shown in Figures 3b and 4a, respectively, these spectra give few clues for the structure of polymer. Thus, we focused on the THF-soluble fraction as described below.

Characterization of a Crystalline Compound Isolated from the THF-Soluble Fraction. A colorless crystalline compound was isolated from the THF-soluble fraction, which consists mainly of soluble oligomers, in low yield (5.5%). This crystalline compound was also obtained by the reaction between AcAz and MAnh in THF at ca. 18 °C in a higher yield (12.2%). The structure of this compound was investigated by elemental analysis, EI-MS, IR, and ^{1}H, ^{13}C, differential NOE, 2D H−H COSY, and 2D C−H COSY NMR.

The C, H, and N contents of this crystalline compound (C, 52.80; H, 5.43; N, 15.33%) agree with those of a one-to-one adduct of AcAz with MAnh (C, 52.74; H, 5.53; N, 15.38%).

The EI-MS for this crystalline compound showed a signal at $m/z = 182$ as a molecular ion peak. This result also supports that the compound is a one-to-one adduct of AcAz (MW = 84) with MAnh (MW = 98).

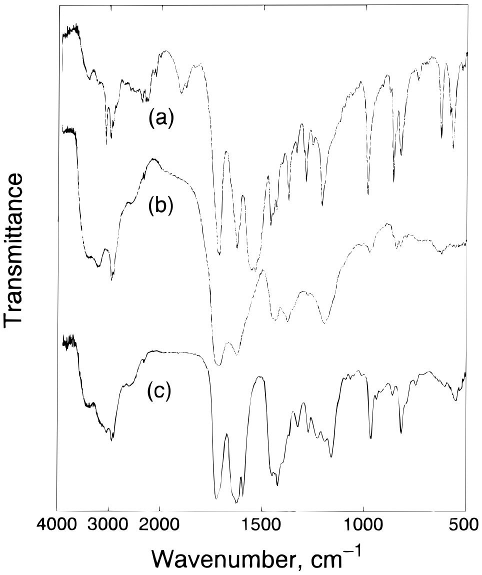


Figure 3. IR spectra of compound **1** (a), the polymer from AcAz and MAnh (b), and compound **2** (c).

In the IR spectrum of the crystalline compound (Figure 3a), there are the absorption bands due to the stretching vibrations of the C═O bonds of the carboxylic acid and amide at 1705 and 1623 cm^{-1}, respectively.[27] Furthermore, the absorption bands due to the C═N and C═C bonds are observed at 1623 and 1550 cm^{-1}, respectively.[27] In the Raman spectrum of the crystalline compound (not shown), there is only very weak band due to the C═C bond at ca. 1550 cm^{-1}. These results demonstrate that the C═C bond of this compound takes *Z*-configuration, because the stretching vibration of the C═C bond is IR-active and Raman-inactive.[28]

In the 270 MHz ^{1}H NMR of the compound shown in Figure 4b, there are the AB type of resonances due to the protons of the CH═CH at 6.15 and 6.78 ppm,[29] indicating that the C═C bond of MAnh is not consumed and that ring opening takes place on MAnh during the formation of the crystalline compound. In the spectrum, there are the resonances due to the methyl and methine protons at 1.22 and 4.38 ppm, respectively. Furthermore, the methylene protons bound to the sp^{3} carbon are observed 2.52 and 3.12 ppm. Because these methylene protons are not magnetically equivalent, this compound may have a ring structure containing this methylene. The resonances due to the CH═N and the carboxylic acid are observed at 7.15 and 12.81 ppm, respectively,[29] indicating that the compound contains a C═N bond and a carboxylic acid.

In the 67.9 MHz ^{13}C NMR spectrum of this compound (not shown), there were the resonances due to the methyl, methylene, and methine carbons at 19.0, 41.2, and 50.1 ppm, respectively. In the spectrum, the resonances due to the carbons of the C═C bond were observed at 128.0 and 131.9 ppm. Furthermore, there are the resonances due to the carbon of the C═N and two carbonyl carbons at 149.3, 162.6, and 166.4 ppm, respectively.

The differential NOE NMR spectrum of the compound revealed an increase in the intensity of the resonance at 6.78 ppm under irradiation of the resonance at 6.15 ppm. This result shows that the compound takes *Z*-configuration around this C═C bond.

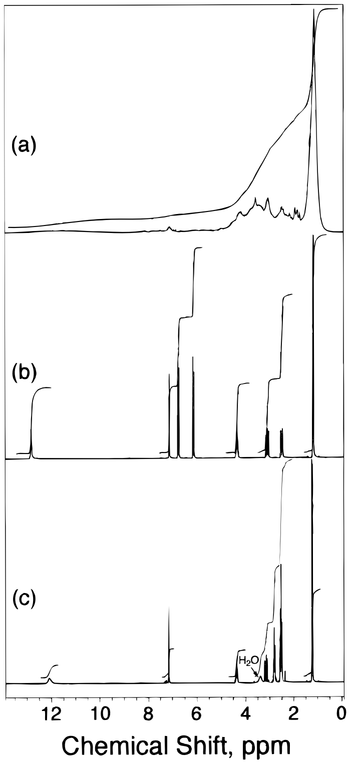
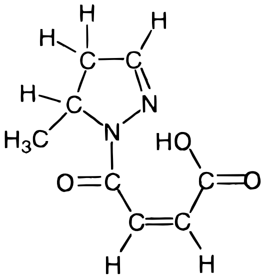


Figure 4. The 270 MHz ^1H NMR spectra of the polymer (a), compound **1** (b), and compound **2** (c) (DMSO-d_6).

These results demonstrate that the crystalline compound is (2*Z*)-4-{1-(5-methyl-2-pyrazolinyl)}-4-oxo-2-butenoic acid (compound **1**), a one-to-one adduct of AcAz with MAnh. In addition, the 2D H−H and C−H COSY NMR support this structure.



Compound 1

Reactions of Compound 1 with Several Types of Reagents. To clarify the role of compound **1** in the polymer formation from AcAz and MAnh, the reactions of compound **1** were carried out. These results are listed in Table 2.

In THF, compound **1** itself was stable even at 60 °C. It was also stable against protic compounds, such as acetic acid and methanol, at 30 °C. Although compound **1** did not react with MAnh, compound **1** reacted with AcAz to form THF-insoluble polymer. In addition, compound **1** was also polymerized with Et_3N and DMA, organic bases.

The IR and 270 MHz ^1H NMR spectra of the polymer given by reaction of compound **1** with AcAz were almost the same as those of the polymer obtained from the mixture of AcAz with MAnh, respectively. These results suggest that compound **1** is a precursor of the spontaneous polymer formation from AcAz and MAnh.

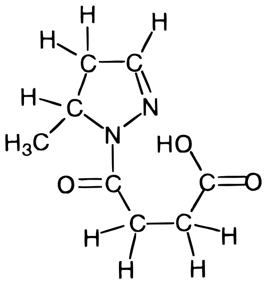
Table 2. Reaction of Compound 1 with Several Types of Reagents in THF

compd **1**, mg (mmol)	concn, M	initiator (mol %)	temp, °C	time, h	conv, %
91 (0.50)	0.5		80	48	0[a]
55 (0.30)	1.0	MAnh (50)	30	72	0[a]
18 (0.10)	0.5	AcAz (17)	60	24	23.6[c]
18 (0.10)	0.5	AcAz (17)[b]	60	24	5.5[c]
18 (0.10)	0.5	CH_3OH (50)	30	72	0[a]
18 (0.10)	0.5	CH_3COOH (50)	30	72	0[a]
18 (0.10)	0.5	Et_3N (17)	60	24	11.5[c]
18 (0.10)	0.5	DMA (17)	60	24	8.2[c]

[a] Determined by GPC. [b] In the presence of TEMPO (0.25 M). [c] THF-insoluble fraction, whose M_w values were not determined.

Reaction of AcAz with SAnh. To obtain information about the polymer formation from AcAz and MAnh, the reaction of AcAz with SAnh, which has no C=C bond, was carried out. Although no resin was obtained, an oily compound was formed.

The structure of this compound was investigated by IR and ^1H NMR spectroscopies. In the IR spectrum for this compound shown in Figure 3c, there are the absorption bands due to the stretching vibration of the carboxylic acid C=O, amide C=O, and C=N bonds at 1730, 1640, and 1600 cm^{-1}, respectively.[27] Naturally, there are no absorption bands due to the stretching vibration of the C=C bond around 1550 cm^{-1}. In the ^1H NMR spectrum for the compound shown in Figure 4c, there are the resonances due to the 5-methyl-2-pyrazoline ring at 1.23, 2.54, 3.16, 4.37, and 7.16 ppm. Furthermore, the resonances due to the CH_2CH_2 are observed at 2.53, 2.81, and 2.82 ppm.[29] In addition, there is the resonance due to the COOH at 12.09 ppm.[29] These results show that the compound is 4-{1-(5-methyl-2-pyrazolinyl)}-4-oxobutanoic acid (compound **2**), a one-to-one adduct of AcAz with SAnh.



Compound 2

Structure of the Polymer Formed from AcAz and MAnh. The structure of the polymer was investigated by comparing the IR and ^1H NMR spectra of the polymer with those of compounds **1** and **2**, respectively.

In the IR spectrum of the polymer from the mixture of AcAz and MAnh (Figure 3b), the absorption band due to the stretching vibration of the C=C bond disappeared, although the other characteristic bands observed in the spectrum of compound **1** remained (Figure 3a). This result suggests that the C=C bond of compound **1** was consumed during polymer formation. Furthermore, the IR spectrum for compound **2** (Figure 3c) resembles that for the polymer (Figure 3b).

In the ^1H NMR spectrum of compound **1** (Figure 4b), there are the AB type of the absorption bands due to the protons of the CH=CH at 6.15 and 6.78 ppm,[29] while the signals due to the protons of the CH=CH almost disappeared in the spectrum of the polymer (Figure 4a).

Scheme 1. Tentative Mechanism for the Spontaneous Polymer Formation from AcAz and MAnh

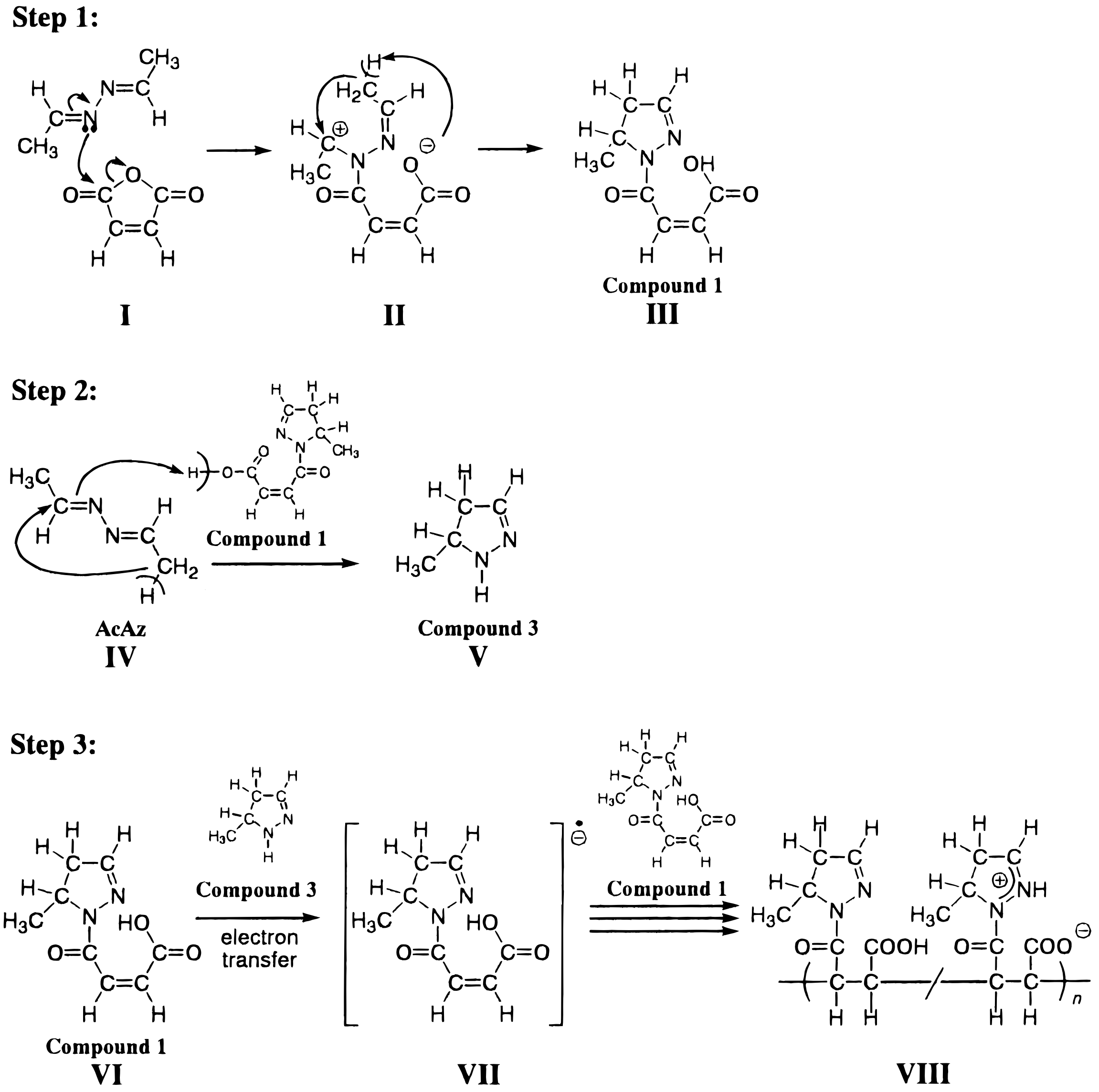


Table 3. Polymerization of Compound 1 with Various Initiators

compd **1**, mg (mmol)	solvent	concn, M	initiator (mol %)	temp, °C	time, h	conversion,[a] %	M_w[b]	M_w/M_n[b]
91 (0.50)	THF	0.5	AIBN (9.1)	80	48	8.4	1200	1.8
91 (0.50)	THF	1.0	MAIB (4.8)	80	24	41.2	5000	1.2
91 (0.50)	CH_2Cl_2	0.5	$TiCl_4$ (9.1)	0	35	0		
91 (0.50)	CH_2Cl_2	0.5	CF_3COOH (9.1)	0	35	0		
91 (0.50)	THF	0.5	*n*-C_4H_9Li (9.1)	−20	26	0		
91 (0.50)	THF	0.5	DBU[c] (9.1)	−20	26	0		

[a] Determined by GPC. [b] Determined by GPC for the THF-soluble fraction. [c] 1,8-Diazabicyclo[5.4.0]-7-undecene.

These results support that the polymerization proceeds mainly through the C=C bond. In addition, a decrease in the signal intensity for the proton of the CH=N suggests intramolecular salt formation between parts of the carboxylic acid and the C=N bond of the 2-pyrazolinyl group. This proposition is supported by the fact that the polymer is soluble in only polar solvents.

These spectroscopic results indicate that the polymer is mainly composed of **VIII**, as shown in Scheme 1.

Active Species in the Spontaneous Polymer Formation from AcAz and MAnh. To clarify the active species in the spontaneous polymer formation from AcAz and MAnh, polymerizations of compound **1** were carried out using typical radical, anionic, and cationic initiators. These results are listed in Table 3. A polymer of compound **1** was obtained by radical initiators, although no polymer was formed by either cationic or anionic initiators. These results show that compound **1** is polymerized by radical initiator,[24] indicating that the polymer from AcAz and MAnh is formed by a radical mechanism.

As shown in Table 2, the yield of the THF-insoluble polymer declines remarkably for the reaction of compound **1** with AcAz in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), a typical inhibitor for radical polymerization. Furthermore, formation of radicals was confirmed by ESR signal which appeared upon mixing AcAz and MAnh. These results support that the

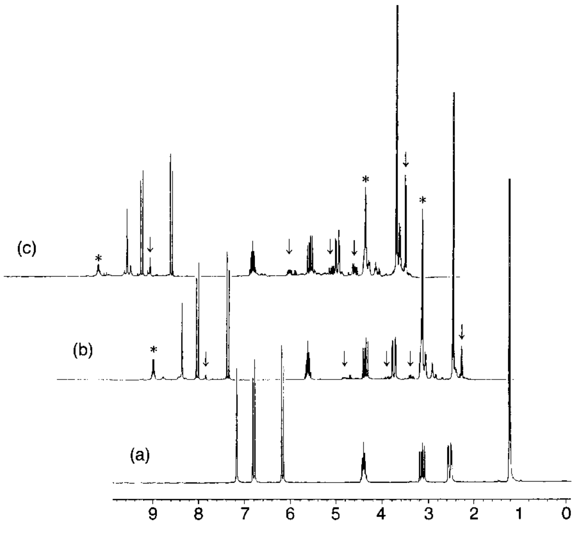
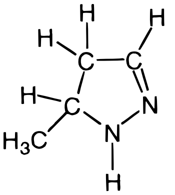


Figure 5. The 270 MHz ^{1}H NMR spectra of compound **1** (a) and the reaction mixture of compound **1** with AcAz at 80 °C after 10 min (b) and after 120 min (c) (DMSO-d_6). Asterisks and arrows mean the resonances due to AcAz and compound **2**, respectively.

polymer is formed from AcAz and MAnh by a radical mechanism.

Initiation for the Polymerization of Compound 1. (a) Detection of the Initiator for the Polymerization of Compound 1. As described above, the reaction of compound **1** with AcAz formed the polymer. To clarify how AcAz initiates the polymerization of compound **1**, we followed the reaction of AcAz with compound **1** by NMR spectroscopy (Figure 5). At 30 °C, there are no signals except for those due to compound **1** and AcAz, indicating that the concentrations of compound **1** and AcAz were too low (275 mM) to react with each other at this temperature. After the solution was kept at 80 °C for ca. 10 min, a set of new resonances appear at 1.22, 2.52, 3.12, 4.38, and 7.15 ppm. Furthermore, the intensities of these resonances increased gradually at 80 °C. These resonances are due to 5-methyl-2-pyrazoline (compound **3**), which was prepared independently by reaction of AcAz with acetic acid, according to the procedure of Curtius et al.[23] When NMR measurements for the reaction system were continued, the spectra revealed that the oligomerization occurred.



Compound 3

Because this result suggests that compound **3** initiates polymerization of compound **1**, we followed the reactions of compound **1** with compound **3** and with AcAz by GPC. Figure 6 shows the time–conversion curves for these reactions. The conversion of compound **1** was determined from the area ratio of the peaks due to compound **1** and toluene, which was added as an internal reference, monitored by UV absorption at 254 nm. When compound **3** was added to a THF solution of compound **1**, the conversion increased immediately, indicating that compound **3** initiates the polymerization of compound **1**. Whereas, in the case of the reaction of compound **1** with AcAz, there is an induction period in the earlier stage (0–20 h). The NMR spectra for the mixture of AcAz with compound **1** (Figure 5) suggest that AcAz is converted to compound **3** during this induction period. On the basis of these results, we conclude that compound **3** initiates the polymerization of compound **1**.

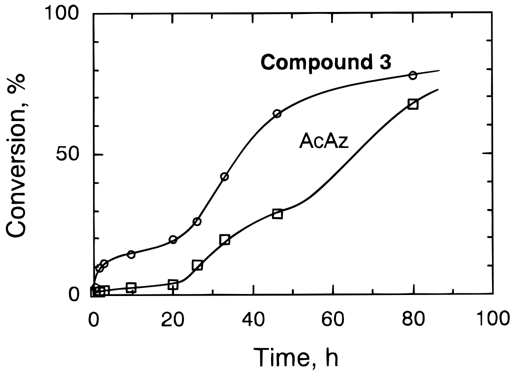


Figure 6. Time–conversion curves for polymerizations of compound **1** (18.2 mg, 0.10 M) initiated by AcAz and by compound **3** in THF at 60 °C. [Initiator] = 0.10 M.

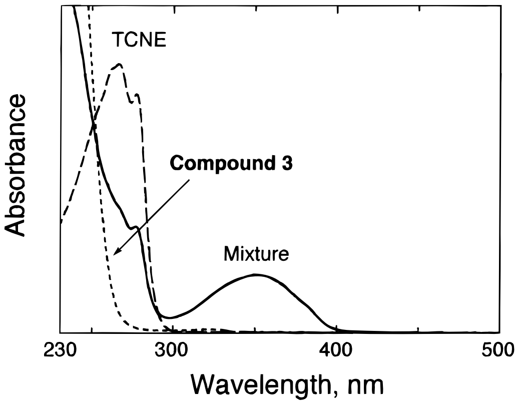


Figure 7. UV–vis spectra of compound **3**, TCNE, and a mixture of compound **3** with TCNE in dichloromethane.

The time–conversion curve for the polymerization of compound **1** initiated by compound **3** shows that the conversion of compound **1** commences again to increase rapidly at ca. 20 h. At the present time, we are not sure about this acceleration. The *Z*–*E* isomerization and the *E*-isomer of compound **1** might concern this acceleration.

(b) Production of Radical Species in the Spontaneous Polymer Formation. Table 2 shows that organic bases, which can be electron donors, give the polymer of compound **1**. This result suggests that the polymerization is initiated by an electron transfer from an electron donor to compound **1**, which has a positive *e* value (+1.1).[24]

In the spontaneous polymer formation, compound **3** may donate an electron to compound **1** to initiate the polymerization. To our knowledge, however, the chemical properties of compound **3** are hardly known. This may be because compound **3** is not stable. Thus, we carried out the electron transfer of compound **3** with TCNE, a typical electron acceptor, to determine the electron-donating property of compound **3**. Figure 7 shows the UV–vis spectra of compound **3**, TCNE, and a mixture of compound **3** and TCNE in dichloromethane.

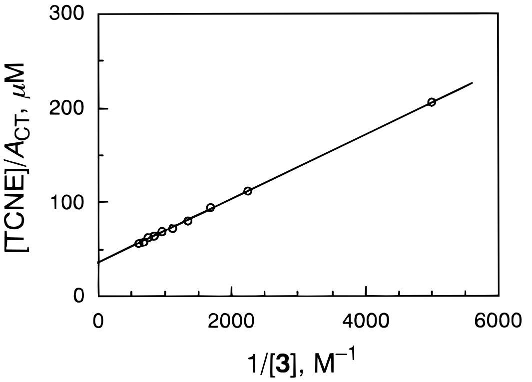


Figure 8. Benesi–Hildebrand plot for the CT complex formation between compound **3** and TCNE in dichloromethane at 25 °C. [TCNE] = 25 μM.

In the spectrum of the mixture, there is the broad absorption band due to the charge-transfer (CT) complex around 356 nm. Assuming that compound **3** and TCNE form a one-to-one CT complex, the association constant (K_{CT}) can be estimated using the Benesi–Hildebrand equation:[30]

$$\frac{[\mathrm{TCNE}]}{A_{\mathrm{CT}}} = \frac{1}{K_{\mathrm{CT}}\epsilon_{\mathrm{CT}}}\frac{1}{[\mathbf{3}]} + \frac{1}{\epsilon_{\mathrm{CT}}} \qquad (1)$$

where A_{CT} and ϵ_{CT} are the absorbance and the extinction coefficient for the CT complex, respectively, at the maximum of the absorption band due to the CT complex (356 nm, in this case), and [**3**] and [TCNE] denote the concentrations of compound **3** and TCNE, respectively. When [**3**] is much higher than [TCNE], the relationship of 1/[**3**] with [TCNE]/A_{CT} is linear. Figure 8 shows the Benesi–Hildebrand plot for the mixture of compound **3** and TCNE. From the slope and the intercept of the best-fitted line, K_{CT} and ϵ_{CT} were estimated to be 1.0×10^3 M^{-1} and 2.9×10^4 M^{-1} cm^{-1}, respectively. In addition, the ESR spectra for the mixture of compound **3** and TCNE showed the resonances due to the CT complex (data not shown). These results reveal that compound **3** is a strong electron donor, indicative of the electron transfer from compound **3** to compound **1** in the spontaneous polymer formation.

Tentative Mechanism for the Spontaneous Polymer Formation from AcAz and MAnh. On the basis of the results described above, a tentative mechanism for the spontaneous polymer formation from AcAz and MAnh is proposed in Scheme 1. The lone pair of the nitrogen of AcAz attacks the carbonyl carbon of MAnh to form a zwitterion (step 1, **I** to **II**). When ring closure takes place accompanying with shift of the proton from the α-carbon of the C═N bond to the carboxylate, compound **1** is formed (step 1, **II** to **III**). Then, AcAz is isomerized to compound **3** by the carboxylic acid of compound **1** (step 2). After compound **3** donates its electron to compound **1** to form an anion radical (step 3, **VI** to **VII**), this anion is deactivated by the proton derived from the carboxylic acid of compound **1**. Then, the polymer is formed by addition of compound **1** through the C═C bond (step 3, **VII** to **VIII**).

Because the reaction mixture contains MAnh in the spontaneous polymer formation, MAnh may participate the initiation and propagation of the polymerization. The polymer of molecular weight of 1600–2000 obtained from the mixture of AcAz and MAnh is insoluble in THF, whereas the polymer of molecular weight 5000 which was obtained by polymerization of compound **1** initiated by MAIB is soluble in THF. These results indicate that MAnh is contained in the polymer obtained from the mixture of AcAz and MAnh. In addition, a small percent of polymer may be formed by some ionic reactions, because TEMPO could not completely inhibit the polymerization of compound **1** initiated by AcAz as shown in Table 2.

Conclusions

Polymeric product was formed spontaneously by the reaction between AcAz and MAnh without any initiator. The reduced viscosity values for this product indicate polymer formation from AcAz and MAnh. Compound **1** was isolated as a crystalline compound from the THF-soluble fraction of the reaction mixture. The spectroscopic results for the polymer demonstrate that the polymer is formed mainly by polymerization of compound **1** through the C═C bond. The results of polymerizations of compound **1** using typical initiators show that compound **1** can be polymerized by radical initiators, indicating that the polymer from AcAz and MAnh is formed by a radical mechanism. On the basis of the electron-donating property of compound **3**, to which AcAz is isomerized in the presence of compound **1**, polymerization of compound **1** was found to be initiated by electron transfer from compound **3** to compound **1** in the spontaneous polymer formation.

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