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Radical Homo- and Copolymerization of (2*Z*)-4-{1-(5-Methyl-2-pyrazolinyl)}-4-oxo-2-butenoic Acid, an Acyclic *Z*-1,2-Disubstituted Vinyl Compound

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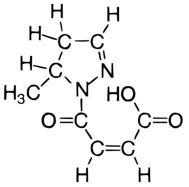
Since there are only a few papers concerning the polymerization of the C═N double bond, we have been investigating the polymerization of 2,3-diaza-1,3-butadiene derivatives (azine compounds).[1] In the course of the study on the polymerizability of azines, Kamachi[2a] found that acetaldehyde azine ($CH_3CH{=}N{-}N{=}CHCH_3$, AcAz) was spontaneously copolymerized with maleic anhydride (MAnh) without any initiators. To clarify a mechanism, we have been studying the copolymerization in detail.[2b] In this study, we succeeded in the isolation of a one-to-one adduct of AcAz and MAnh as a precursor for the copolymerization. The one-to-one adduct was confirmed to be (2*Z*)-4-{1-(5-methyl-2-pyrazolinyl)}-4-oxo-2-butenoic acid (**1**), an acyclic *Z*-1,2-disubstituted vinyl compound, which was polymerizable in the presence of radical initiators without *Z*−*E* (cis−trans) isomerization. In this communication, we report the radical homo- and copolymerization of **1**.



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When AcAz was added to a solution of MAnh in THF, the reaction mixture changed immediately to pale yellow. Then, the color gradually changed to orange, and THF-insoluble powder, which was homopolymer of **1**, deposited.[2b] The THF solution was separated from the THF-insoluble powder by filtration. A colorless crystalline product was isolated from the THF-soluble fraction by recrystallization in toluene−hexane.[3] The chemical structure of the crystalline product was investigated by elemental analysis, EI-mass, IR, Raman, ^{1}H NMR, ^{13}C NMR, 2D H−H COSY, and 2D C−H COSY.[3] These spectroscopic data revealed that the product is a one-to-one adduct of AcAz with MAnh (**1**).

The results of the radical polymerization of **1** are listed in Table 1. When 2,2′-azobis(isobutyronitrile) (AIBN) was used as an initiator, a THF-insoluble polymer was not formed. However, when dimethyl 2,2′-azobis(isobutyrate) (MAIB) was used, a THF-insoluble polymer was obtained. The M_w of the THF-soluble polymer was determined to be 5.0 × 10^3 by GPC. The M_w of the THF-insoluble polymer should be higher than 5.0 × 10^3, because the IR spectra of THF-insoluble and THF-soluble polymers were almost the same. The result that MAIB gave a higher yield and a higher molecular weight of polymer than AIBN is similar to the case of the polymerization of dialkyl fumarates.[4] Furthermore, polymer formation was remarkably retarded upon addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), indicative of a free radical mechanism.

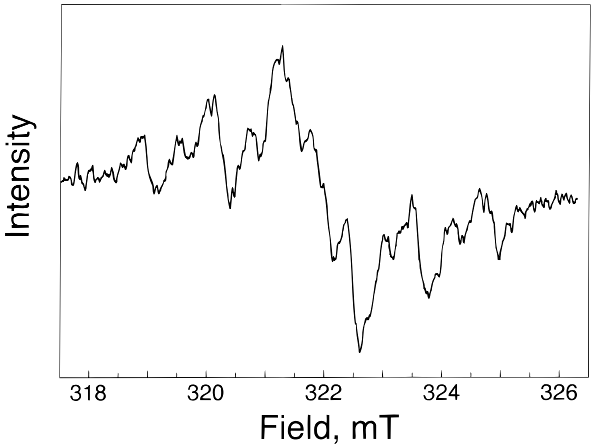

Figure 1. ESR spectrum of the propagating radical for **1** initiated by MAIB in benzene at 60 °C under photoirradiation: [**1**] = 27 mM; [MAIB] = 2.7 mM; modulation width = 0.20 mT; modulation frequency = 100 kHz.

To obtain information on the propagating radical in the polymerization of **1**, we measured ESR spectra of the radical polymerization system. Figure 1 shows the ESR spectrum of the propagating radical for **1** initiated by MAIB under photoirradiation. This result indicates that the spectrum is similar to that of dialkyl fumarates observed by Otsu et al.[5] Thus, we concluded that the propagating radical of **1** has a structure similar to that of dialkyl fumarates.

The result of the elemental analysis of the polymer shows that the polymer was formed by addition polymerization (Anal. Calcd for $(C_8H_{10}N_2O_3)_n$: C,52.74; H, 5.53; N, 15.38. Found: C, 52.80; H, 5.49; N, 14.96). Figure 2 shows the IR spectra of the polymer and **1**. In the spectrum of **1**, the absorption bands due to the C═O of the carboxylic acid and the amide are observed at 1705 and 1623 cm^{-1}, respectively.[6] Furthermore, in the spectrum of **1**, the absorption bands due to the C═N and C═C bonds are observed at 1623 and 1550 cm^{-1}, respectively.[6] In the spectrum of the polymer, the absorption band due to the C═C double bond disappeared, although the absorption bands due to the C═O and C═N double bonds are observed. These results indicate that the polymerization of **1** proceeds through the C═C double bond (Scheme 1).

Otsu et al.[7] reported that dialkyl maleates were polymerized by a radical initiator after the isomerization from cis to trans around the C═C double bond by a reagent, such as morpholine. To confirm whether *Z*−*E* isomerization occurs around the C═C double bond of **1** during the polymerization, we measured ^{1}H NMR spectrum of **1** after heating it in THF at 60 °C for 6 h. The spectrum showed that no isomerization occurred.

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Table 1. Polymerization of 1 with Azo Initiators

1, mg (mmol)	solvent	concentration, M	initiator (mol %)	temperature, °C	time, h	yield,^{a} %	M_w^{b}	M_w/M_n^{b}
91 (0.50)	THF	0.5	AIBN (9.1)	80	48	*c*	1200	2.67
91 (0.50)	THF	1.0	MAIB (4.8)	80	24	18.3	5000^d	1.14^d

[a] THF-insoluble fraction. [b] Determined by GPC. [c] Although a THF-insoluble polymer was not formed, a GPC elution diagram showed that the THF-soluble oligomer was formed in a low yield (~10%). [d] THF-soluble fraction.

Table 2. Radical Copolymerization of 1 and Vinyl Monomers^a

comonomer	initiator (mol %)	yield,^{b} %	M_w^{c} × 10^{-3}	M_w/M_n^{c}	content of **1** in copolymer,^{d} mol %
styrene	AIBN (2.0)	30.0	3.0	1.14	45.2
	AIBN (2.0)	43.1	8.3	1.32	45.9
	BPO (2.0)	2.8	4.9	1.23	45.7
	MAIB (2.0)	35.9	3.7	1.16	44.4
N-vinylcarbazole	AIBN (1.0)	51.2	15.0	1.29	54.1
n-butyl vinyl ether	AIBN (1.0)	14.6	3.6	1.08	76.9
methyl acrylate	AIBN (1.0)	10.3	2.6	1.27	7.9
methyl methacrylate	AIBN (1.0)	35.1	8.6	1.48	0

[a] In THF for 24 h at 60 °C. [**1**] = [comonomer] = 1.0 M. [b] Based on the total amount of comonomers. [c] Determined by GPC. [d] Determined by ^{1}H NMR.

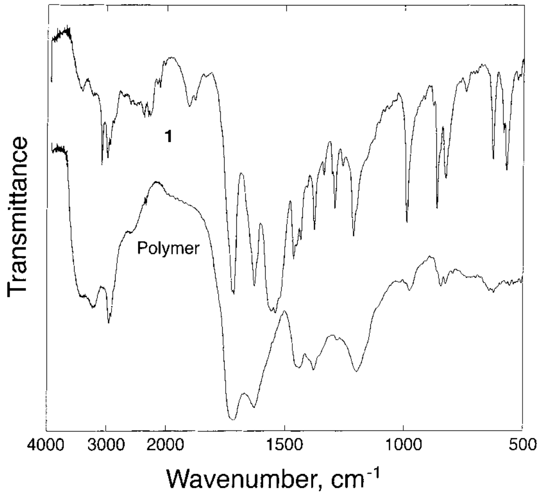

Figure 2. IR spectra of **1** and its polymer (KBr).

Scheme 1. Polymerization of 1

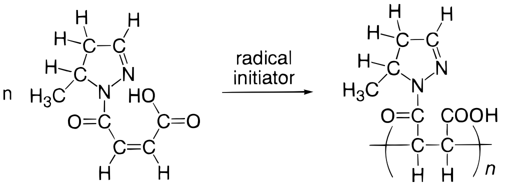

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Table 3. Results of Radical Copolymerization of 1 and Styrene^a

run	x_1 in feed^b	x_1 in copolymer^c	polymerization time, h	yield,^{d} %	M_w,^{e} × 10^3
1	0.10	0.21	4.0	3.2	3.0
2	0.20	0.39	4.0	7.4	2.7
3	0.30	0.48	3.0	4.8	3.2
4	0.40	0.51	3.0	5.6	3.6
5	0.50	0.51	2.5	6.2	3.5
6	0.60	0.55	3.0	3.9	2.6
7	0.70	0.58	3.0	3.9	3.1
8	0.80	0.62	3.5	8.0	1.9
9	0.90	0.69	3.5	9.1	2.0

[a] Initiated by AIBN in THF at 60 °C: [total comonomers] = 1.0 M; [AIBN] = 0.010 M. [b] Mole fraction of **1** in feed. [c] Mole fraction of **1** in copolymer determined by ^{1}H NMR. [d] Acetone-insoluble fraction. [e] Determined by GPC.

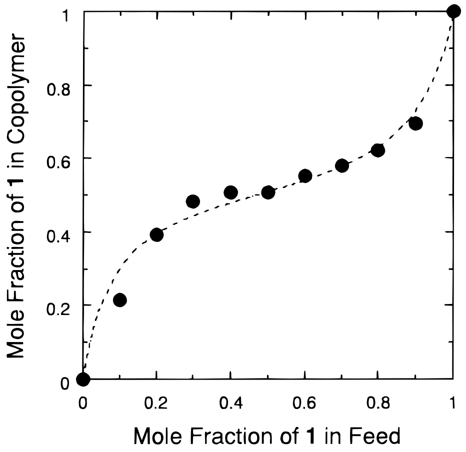

Figure 3. Copolymer composition plots for the copolymerization of **1** and styrene initiated by AIBN in THF at 60 °C: [total comonomers] = 1.0 M; [AIBN] = 0.010 M (a broken line represents the best-fitted curve.)

Therefore, to our knowledge, this is the first example of the radical polymerization of acyclic *Z*-1,2-disubstituted vinyl monomers.

The results of the copolymerization of **1** and vinyl monomers are listed in Table 2. Copolymers with relative high contents of **1** (44.4−45.9, 54.1, and 76.9 mol %, respectively) were produced by copolymerizations of **1** with styrene, *N*-vinylcarbazole, and butyl vinyl ether. However, a copolymer with a low content of **1** (7.9 mol %) was obtained by copolymerization of **1** and methyl acrylate. The *e*-values of styrene, *N*-vinylcarbazole, and butyl vinyl ether are negative (−0.80, −1.29, and −1.50, respectively).[8] However, the *e*-value of methyl acrylate is positive (0.64).[8] These results show that negative *e*-values of comonomers are required for formation of copolymers with high content of **1**. Furthermore, when copolymerization of **1** and methyl methacrylate (MMA) was tried, only the homopolymer of MMA was formed. Since MMA is a 1,1-disubstituted vinyl monomer, the propagating radical of MMA may be too sterically hindered to react with **1**.

Copolymerization of **1** and styrene was carried out to estimate the reactivity ratios for **1** and styrene. The results of copolymerization are listed in Table 3. Copolymer composition plot and the best-fitted curve are shown in Figure 3. From this curve, the reactivity ratios for **1** and styrene, r_1 and r_{styrene}, were estimated to be 0.20 ± 0.01 and 0.14 ± 0.02, respectively, at 60 °C. In addition, the *Q*- and *e*-values were also calculated to be 1.4 and 1.1, respectively, from these reactivity ratios.

In conclusion, the radical polymerization of **1**, an acyclic *Z*-1,2-disubstituted vinyl monomer, was investigated. We found that **1** was polymerized by MAIB to form polymer without *Z*−*E* isomerization. This is the first example of homopolymerization of *Z*-1,2-disubstituted vinyl monomers. Furthermore, it was found that **1** was copolymerized with styrene, *N*-vinylcarbazole, butyl vinyl ether, or methyl acrylate by using a radical initiator. The reactivity ratios for **1** and styrene, r_1 and r_{styrene}, were estimated to be 0.20 ± 0.01 and 0.14 ± 0.02, respectively, from the results of copolymerization of **1** and styrene at 60 °C.

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(3) In this reaction, the polymer, the THF-insoluble powder, and the oligomer, contained by the THF-soluble fraction, of **1** were obtained in a relative high yield.[2b] The crystalline compound: yield 1.17 g, 12.2%; mp 108.2−109.0 °C; IR (KBr) 1705 (carboxylic acid C═O), 1623 (amide C═O, C═N), 1550 (C═C) cm^{-1}; ^{1}H NMR (DMSO-d_6, 270 MHz) δ 1.22 (d, 3H, J = 6.4 Hz), 2.52 (ddd, 1H, J = 12.5, 3.1, 1.8 Hz), 3.12 (ddd, 1H, J = 15.5, 6.2, 1.6 Hz), 4.38 (m, 1H), 6.15 (d, 1H, J = 12.1 Hz), 6.78 (d, 1H, J = 12.1 Hz), 7.15 (t, 1H, J = 1.6 Hz), 12.81 (s, 1H); ^{13}C NMR (DMSO-$d_{6,}$ 67.9 MHz) δ 19.0, 41.2, 50.1, 128.0, 131.9, 149.3 162.6, 166.4. Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.80; H, 5.43; N, 15.33. EI-MS [M$^+$]: calcd, 182; found, 182.

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