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Spontaneous Alternating Copolymerization of Methoxyallene with *N*-Phenylmaleimide

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ABSTRACT: Spontaneous copolymerization of methoxyallene (**1**) with *N*-phenylmaleimide (**2**) was carried out. In the absence of a solvent, the copolymerization proceeded via a diradical intermediate to afford the corresponding alternating copolymer, along with an adduct of **1** with **2**. The polymerization in aprotic solvents such as DMSO yielded a polymer larger than that from the bulk polymerization. The copolymer obtained in the solution polymerization contained a homopolymer of **2**. When benzyl alcohol was added to the polymerization mixture of **1** and **2** in DMSO, an adduct of all three compounds was isolated from the mixture, suggesting the formation of a zwitterion of **1** and **2**.

Introduction

Some vinyl monomers having electron-donating substituents undergo alternating copolymerization with some electron-accepting vinyl monomers spontaneously. In some systems the copolymerization proceeds via a radical mechanism, whereas in others a zwitterion is involved as illustrated in Scheme 1. This copolymerization has been extensively researched by Saegusa[1] and Hall.[2] The mechanism has been mainly examined by substituent effect on the copolymerization. The effects of electron-donating and withdrawing substituents can be arranged according to ref 2, wherein the areas of mechanistic change clearly emerge and provide predictive capability. We have previously reported the spontaneous copolymerization of methoxyallene with cyanoallene via a zwitterion process, resulting in the alternating copolymer.[3] Wan et al. have also reported that ethyl α-phenyl acrylate undergoes alternating copolymerization with *N*-phenylmaleimide spontaneously to afford the corresponding copolymer.[4] Polymers of *N*-substituted maleimide derivatives represent a class of highly stable polymers, due to the rigid imide rings in the backbone. This provides the polymers with superior mechanical and thermal properties. Recently, alternating copolymers based on *N*-substituted maleimides are intensively investigated in the field of electrooptical materials such as positive photo resists and nonlinear optical (NLO) chromophore-functionalized polymers.[5] This paper deals with the copolymerization behavior of methoxyallene with *N*-phenylmaleimide and mechanistic aspects of the copolymerization.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda-500 spectrometer, using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$). IR spectra were recorded on a Jasco FT/IR-5300 spectrometer. UV−vis spectra were recorded on a Jasco U-best 50 spectrometer. Number-average molecular weights (M_n) and polydispersity ratios (M_w/M_n) of polymers were estimated by gel permeation chromatography (GPC) on a Tosoh 8120 system equipped with two consecutive polystyrene gel columns (G4000 and G2500), using THF as an eluent at a flow rate of 1.0 mL/min, polystyrene calibration, refractive index, and ultraviolet (254 nm) detectors. Preparative high-pressure liquid chromatography (HPLC) was performed with a Japan Analytical Industry LC-908 equipped with two consecutive gel columns, JAIGELs 1H and 2H eluted with $CHCl_3$ at a flow rate of 3.8 mL/min, and refractive index and ultraviolet (254 nm) detectors. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A mass spectrometer. High-resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer.

Reagents. Unless stated otherwise, all the chemicals and reagents were obtained commercially and used without further purification. *N*-Phenylmaleimide (**2**) was purified by recrystallization from cyclohexane. Dimethyl sulfoxide, dimethylformamide, dimethylacetoamide, and acetonitrile were distilled over CaH_2. Methanol and benzyl alcohol were distilled over magnesium and $CaSO_4$, respectively. Methoxyallene (**1**) was prepared according to the previous paper.[6]

Copolymerization. The typical procedure is as follows: To a glass tube were introduced 0.140 g (2 mmol) of **1**, 0.346 g (2 mmol) of **2**, and 0.4 mL of DMSO. After five freeze−pump−thaw cycles, the glass tube was sealed under vacuum, and the reaction mixture was heated at 40, 60, 80, 100, and 120 °C for 1, 3, 6, and 12 h, respectively. The reaction mixture was dissolved in dichloromethane and poured into a large amount of ether to precipitate a polymer, which was collected by filtration and dried in vacuo: ^{1}H NMR ($CDCl_3$): δ 2.25−4.20 (br, $-CH_2$-, $>$CH- and $-OCH_3$), 5.20−5.45 (br, $CH_2=$), 6.10−6.75 (br, $=CH-$), 6.90−8.50 (br, Ar−H) ppm. ^{13}C NMR ($CDCl_3$): δ 29.6 ($-CH_2-$), 44.1 ($>CH-$), 57.9, 60.8 ($-$OMe), 78.2 ($>CH-O$), 109.0 ($=CH-O$), 114.3 ($CH_2=$), 126.0, 126.5, 127.8, 129.1, 134.1 (phenyl), 143.4, 149.8 ($=C<$), 169.5, 176.1 (C=O) ppm. IR (KBr): 1707 (imide), 1498 (phenyl), 1390 (C=C), 1192 ($-$OMe) cm^{-1}.

Isolation of Adduct 3. The filtrate was concentrated by rotary evaporation under a reduced pressure. The residue was purified by preparative HPLC to obtain the major product: an adduct (**3**) of **1** and **2** (0.292 g, 60%). Mp: 102−104 °C (cyclohexane). ^{1}H NMR ($CDCl_3$): δ 3.52 (s, 3H, $-OCH_3$), 3.79 (d, 2H, $J = 6.0$ Hz, $>CH-$), 4.72 (s, 1H, $>CH-O-$), 5.50 (d, 2H, $J = 22.0$ Hz, $CH_2=$), 7.28 (d, 2H, $J = 9.0$ Hz, Ar−H), 7.38 (t, 1H, $J = 4.0$ Hz, Ar−H), 7.45−7.49 (m, 2H,Ar−H) ppm. ^{13}C NMR ($CDCl_3$): δ 44.0 ($>CH-$), 57.9 ($-OCH_3$), 78.2 ($>CH-O$), 114.5 ($CH_2=$), 126.4, 127.8, 128.4, 132.0 (phenyl), 143.5 ($=C<$), 173.5, 174.4 (C=O) ppm. IR (KBr): 1712 (imide), 1458 (phenyl), 1385 (C=C), 1095 ($-$OMe), 914 (cyclobutane) cm^{-1}. MS (EI): *m/z* (M^+) 243. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.19; H, 5.80; N, 5.65.

Trap of a Zwitterion Generated from 1 and 2 with Benzyl Alcohol. To a round-bottomed flask were introduced

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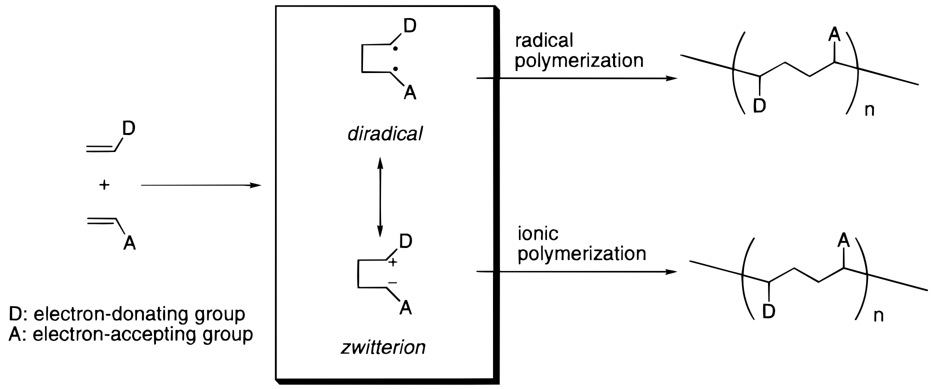
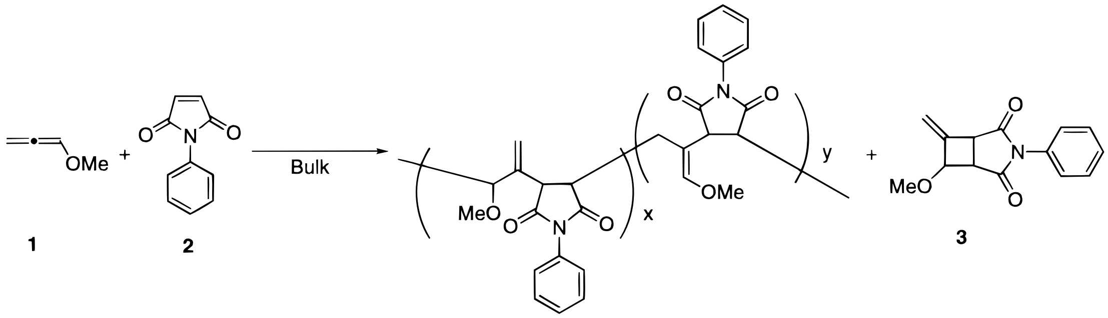
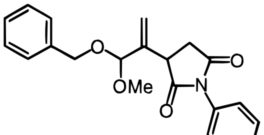
Scheme 1



Scheme 2



0.140 g (2 mmol) of **1**, 0.346 g (2 mmol) of **2**, and 0.8 mL of DMSO under a nitrogen atmosphere. The reaction mixture was stirred at 20 °C for 1 h. After that, 30 mL of benzyl alcohol was added to the mixture, resulting the disappearance of the red color. The reaction mixture was concentrated in vacuo, and the residue was purified by preparative HPLC to yield an adduct (**4**) of benzyl alcohol with a zwitterion (2 mg, 2%). ^{1}H



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NMR (CDCl$_3$): δ 2.99−3.20 (m, 2H, −CH$_2$−), 3.35 (s, 3H, −OCH$_3$), 3.74 (d, 1H, J = 4.5 Hz, >CH−), 4.48−4.69 (m, 2H, −CH$_2$−O), 5.00−5.02 (m, 1H, O−CH−O), 5.39−5.46 (m, 2H, CH$_2$=) 7.21 (dd, 2H, J = 8.5, 1.5 Hz, Ar−H) 7.28−7.32 (m, 2H, Ar−H), 7.33−7.37 (m, 3H, Ar−H), 7.38−7.39 (m, 1H, Ar−H), 7.43−7.47 (m, 2H, Ar−H). ^{13}C NMR (CDCl$_3$): δ 34.7 (−CH$_2$−), 44.4 (>CH−), 54.1 (−OCH$_3$), 68.5 (−CH$_2$−O), 103.6 (O−CH−O), 119.5 (CH$_2$=), 126.5, 127.9, 128.0, 128.1, 128.4, 128.5, 129.0, 129.1, 137.1 (phenyl), 140.9 (=C<), 175.7, 176.7 (C=O). IR (neat): 1712 (imide), 1454 (phenyl), 1387 (C=C), 1186 (acetal), 1062 (−OMe) cm^{-1}. HRMS: m/z (M$^+$) calcd for $C_{21}H_{21}NO_4$ 351.1470; found 351.4350.

Results and Discussion

Spontaneous Copolymerization in the Absence of a Solvent. First, the bulk copolymerization of methoxyallene (**1**) with *N*-phenylmaleimide (**2**) was carried out at 40−120 °C for 1−24 h (Scheme 2, Table 1). The copolymerization proceeded homogeneously in every case. At 60 °C, the conversion of **2** was nearly quantitative for 6 h, and the polymer yield was 25% (entry 4). The polymer yield little depended on the polymerization condition. The structure of the polymer was analyzed by elemental analysis and NMR spectroscopy. In every case, it was confirmed that the composition of **1** and **2** was 1:1 by elemental analysis (N). Figure 1 depicts the ^{1}H and ^{13}C NMR spectra of the polymer obtained by copolymerization at 60 °C for 6 h (entry 4 in Table 1). In the ^{1}H NMR spectrum (Figure 1a), a broad signal assignable to nonolefinic protons was observed at 2.3−4.2 ppm. Two olefinic signals were observed at 5.3 and 6.5 ppm, which were assignable to the exomethylene protons (f) and the α-methine proton (g) substituted with a methoxy group, respectively. Consequently, it might be suggested that the obtained copolymer contained two units, unit *x* (1,2-polymerization of **1**) and unit *y* (2,3-polymerization of **1**), which was similar to the radical polymerization.[7] The unit ratio of *x*:*y* was estimated to be 3:97 by the integration ratio of the signals f and g. The ^{13}C NMR spectrum (Figure 1b) might support strongly the polymer structure assumed by ^{1}H NMR spectroscopy, although the signals assignable to unit *x* could not be detected, probably due to the small content. The IR spectrum of the copolymer showed

Table 1. Copolymerization of Methoxyallene (1) with *N*-Phenylmaleimide (2)[a]

				ether-insoluble part				yield
entry	temp (°C)	time (h)	conv[b] (%)	yield (%)	M_n[c]	M_w/M_n[c]	unit ratio (x:y)[d] (%)	of **3** (%)
1	40	3	50	6	25 600	1.27	*e*	42
2	60	1	32	13	32 500	1.27	5:95	19
3	60	3	84	17	29 500	1.30	4:96	67
4	60	6	97	25	28 200	1.31	3:97	72
5	60	12	96	22	29 400	1.31	*e*	74
6	60	24	100	10	25 400	1.31	*e*	90
7	80	3	96	9	23 500	1.26	*e*	87
8	100	3	92	9	18 200	1.35	*e*	87
9	120	3	100	11	13 000	1.55	*e*	89

[a] Conditions: **1**, 2 mmol; **2**, 2 mmol. [b] Conversion of *N*-phenylmaleimide, determined by ^{1}H NMR. [c] Estimated by GPC (THF, PSt standards). [d] Determined by ^{1}H NMR, where the *x* and *y* values do not indicate the monomer composition but the different structures of the same composition. [e] Not determined.

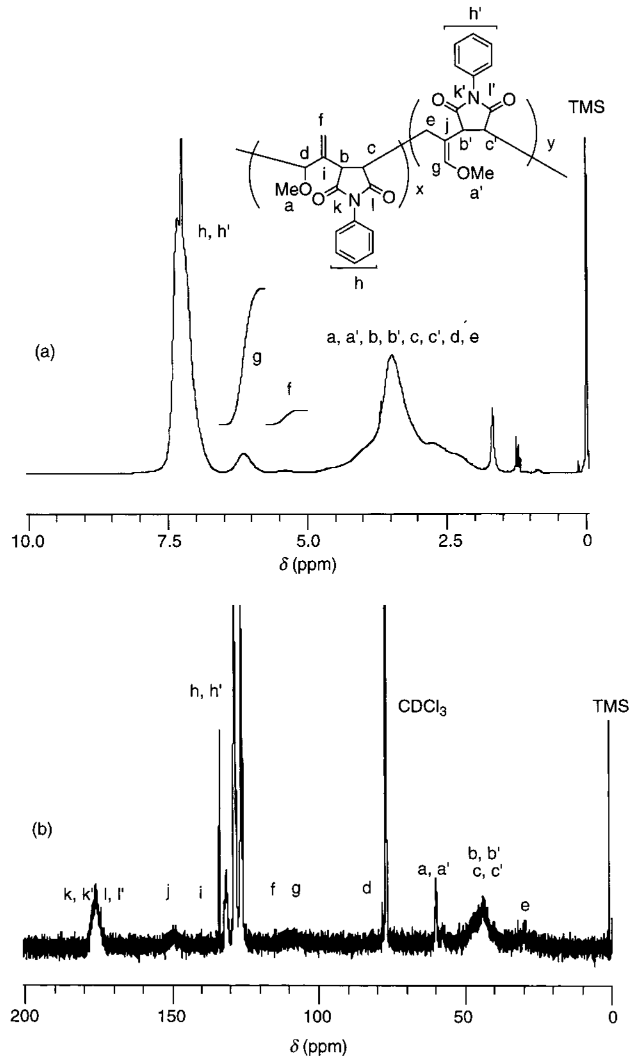


Figure 1. ^{1}H (a) and ^{13}C (b) NMR spectra (CDCl$_3$, 500 and 125 MHz) of the copolymer obtained by the copolymerization of **1** with **2** at 60 °C for 6 h (entry 4 in Table 1).

an absorption peak assignable to an imide group at 1707 cm^{-1}.

The ether-soluble part was fractionated by preparative HPLC, because the yield of the ether-insoluble polymer was low (<25%) in every case. The major product was identified as a 1:1 adduct (**3**) of **1** with **2** consisting of a cyclobutane ring by ^{1}H and ^{13}C NMR spectroscopy (Figure 2) besides elemental analysis.

The effect of monomer feed ratio on the copolymerization was examined. When the reaction was carried out in various feed ratios of **1** to **2**, the copolymers was constantly composed of a ratio of 1:1 irrespective of the monomer feed ratio, and their yields attained the maximum value possible for a monomer feed ratio of 1:1 (Figure 3). These results strongly suggest that alternating copolymerization of **1** and **2** took place.

Spontaneous Copolymerization in Solvents. Furthermore, the copolymerization was attempted in a number of solvents (Scheme 3, Table 2). When polar aprotic solvents such as DMSO, DMF and DMAc were employed, the reaction mixture was colored to deep red (entries 1–11), although this color could not be observed in the polymerization in MeOH and MeCN (entries 12 and 13). It might be assumed that this red color was derived from zwitterions, and the copolymerization mechanism in the first three solvents was different from

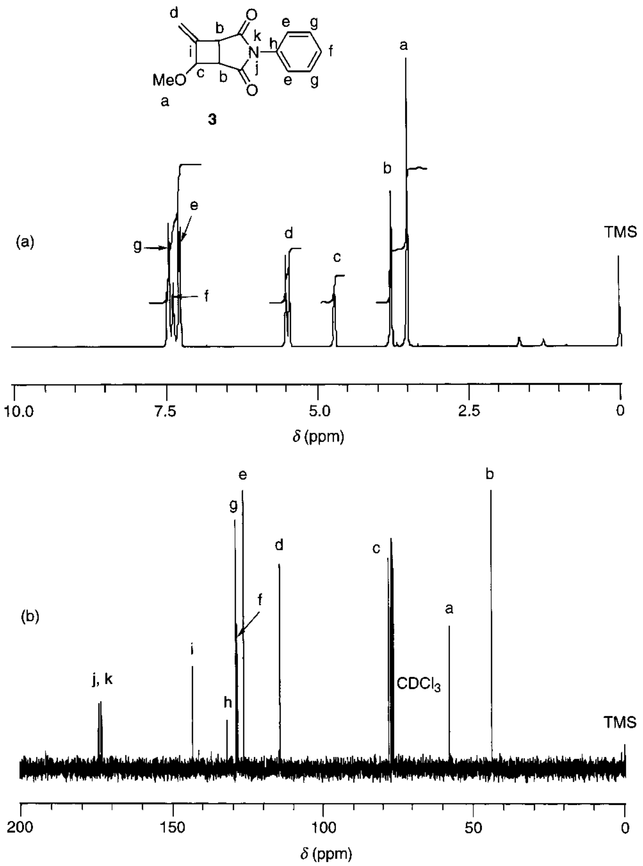


Figure 2. ^{1}H (a) and ^{13}C (b) NMR spectra (CDCl$_3$, 500 and 125 MHz) of adduct **3** obtained by the copolymerization of **1** with **2** at 60 °C for 3 h (entry 3 in Table 1).

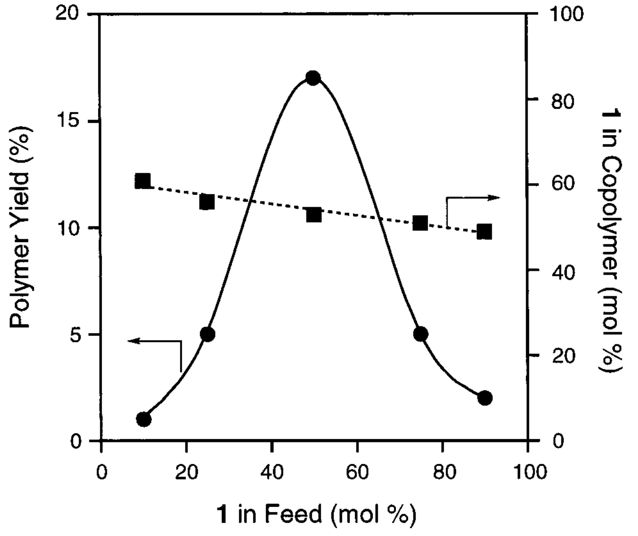


Figure 3. Effect of monomer feed ratio on the polymer yield (●) and the copolymer composition (■) in the copolymerization of **1** with **2** in bulk at 60 °C for 3 h, estimated by elemental analysis.

that without solvent. Therefore, we investigated the copolymerization in DMSO in detail.

In the polymerization in DMSO at 20 °C, the conversion and polymer yield increased, while the M_n of the obtained polymer rather decreased according to the time progress (entries 1–5). At 40 and 60 °C, the conversion was observed to be quantitative after 1 h (entries 6 and 8), which indicated the larger polymerization rate in DMSO compared with that in the bulk (Table 1, entry

Scheme 3

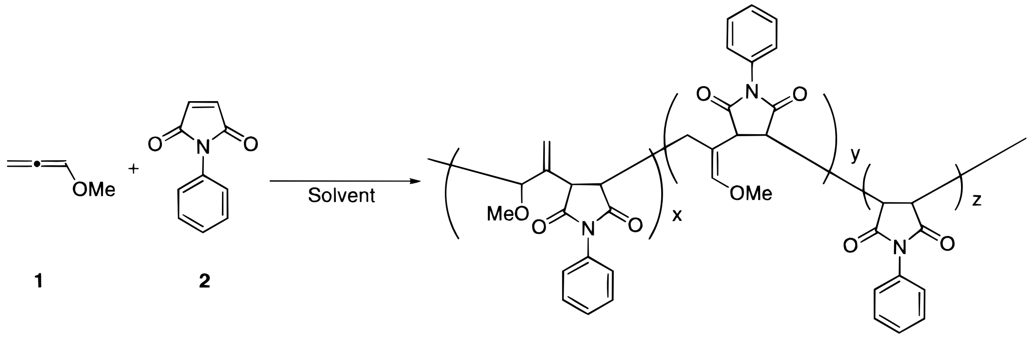


Table 2. Copolymerization of Methoxyallene (1) with *N*-Phenylmaleimide (2) in Solvents[a]

entry	solvent	temp (°C)	time (h)	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	unit ratio[e] (%) $x{:}y{:}z$
1	DMSO	20	1	45	28	5400	1.61	0:19:81
2	DMSO	20	3	79	47	4400	1.67	0:14:86
3	DMSO	20	6	95	60	3700	1.89	0:19:81
4	DMSO	20	12	100	63	3900	1.81	0:22:78
5	DMSO	20	24	100	70	3500	1.66	1:20:79
6	DMSO	40	1	96	48	4200	1.82	0:10:90
7	DMSO	40	12	100	57	5300	1.59	0:20:80
8	DMSO	60	1	98	55	3700	3.41	0:10:90
9	DMSO	60	24	100	63	4200	4.60	0:17:83
10	DMF	60	24	100	27	4700	2.55	1:11:88
11	DMAc	60	24	100	26	2500	3.40	1:10:89
12	MeCN	60	24	100	7	1800	4.16	1:42:53
13	MeOH	60	24	100	2	17500	2.65	32:68:3

[a] **1**, 2 mmol; **2**, 2 mmol; solvent, 0.4 mL. [b] Conversion of **2**, determined by GC. [c] Ether-insoluble part. [d] Estimated by GPC (THF, PSt standards). [e] Determined by ^{1}H NMR, where the *x* and *y* values do not indicate the monomer composition but the different structures of the same composition.

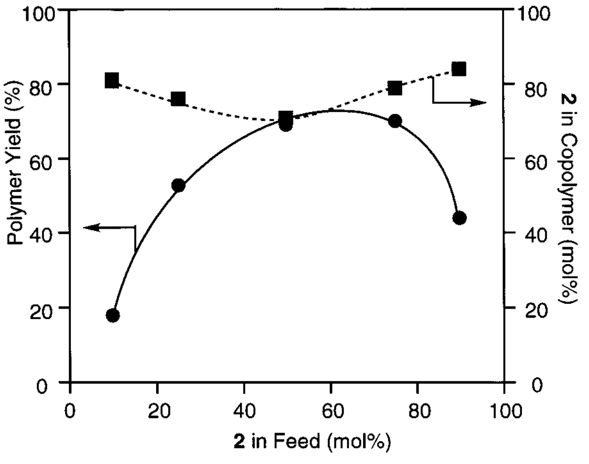


Figure 4. Effect of monomer feed ratio on the polymer yield (●) and the copolymer composition (■) in the copolymerization of **1** with **2** in DMSO at 20 °C for 6 h, estimated by elemental analysis. Total monomer, 4 mmol; DMSO, 0.8 mL.

1). The structure of the obtained polymer was analyzed by ^{1}H NMR spectroscopy to find a larger incorporation of unit **2** than unit **1**, which was different from the bulk copolymerization. The yield of **3** was markedly lower (ca. 5%) compared with the bulk polymerization. Figure 4 depicts the relationships between the monomer feed ratio, polymer yield, and unit ratio in the copolymer. The yield increased in proportion to the feed ratio of **2** to the total monomers up to 50 mol %, but decreased above 60 mol %. The unit ratio of **2** in the copolymer was ca. 80% independent of the monomer feed ratio. These results may suggest that the copolymerization not only proceeded via an alternating mechanism but also accompanied the homopolymerization of **2**. The polymer product may contain a 1:1 copolymer of **1** and **2**, and a homopolymer of **2**, because the GPC traces showed bimodal peaks. The product could not be fractionated by reprecipitation or preparative HPLC. The product showed no clear T_g up to 200 °C.

The copolymerization was carried out in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical inhibitor to clear the mechanism (Table 3). No polymer was obtained in the presence of TEMPO (2 mol %) in bulk (entry 2), suggesting that this polymerization proceeded via a radical process along with the fact that the yield and M_n of the polymer little depended on the temperature and time as summarized in Table 1.[8] In the copolymerization in DMSO, the presence of 25 mol % of TEMPO little decreased the polymer yield (entries 3 and 4). When the feed ratio of TEMPO was increased to as large as 100 mol %, the yield decreased to 25% (entry 6). Furthermore, the composition of **2** in the copolymer increased in proportion to the feed of TEMPO. It might be assumed that the copolymerization in DMSO proceeded ionically to some extent in addition to a radical process. A zwitterion consisting of **1** and **2** might be plausible as the active ionic species. Thus, trapping of the zwitterionic intermediate from the reaction mixture was attempted in the early stages of the copolymerization.

Among several reagents reported for this purpose so far,[3,9,10] we employed benzyl alcohol as the trapping reagent because of easiness of determination by ^{1}H NMR spectroscopy. After copolymerization of **1** with **2** in DMSO at 20 °C for 1 h, a large amount of benzyl alcohol was added into the reaction mixture, resulting in the disappearance of the red color. This mixture could be separated with preparative HPLC to obtain an adduct (**4**) of the zwitterion and benzyl alcohol, although the yield was very low (2%). The ^{1}H NMR spectrum (Figure 5) showed no signals corresponding to the olefin protons of **2** at 6.9 ppm and methine proton of **1** at 6.68 ppm but showed the methylene (a) and methine (c) protons assignable to a succinimide structure and methine and methylene protons assignable to an acetal position and a benzyl position, respectively. These results may suggest strongly that the copolymerization in DMSO involves two intermediates, i.e., diradical and zwitterion.

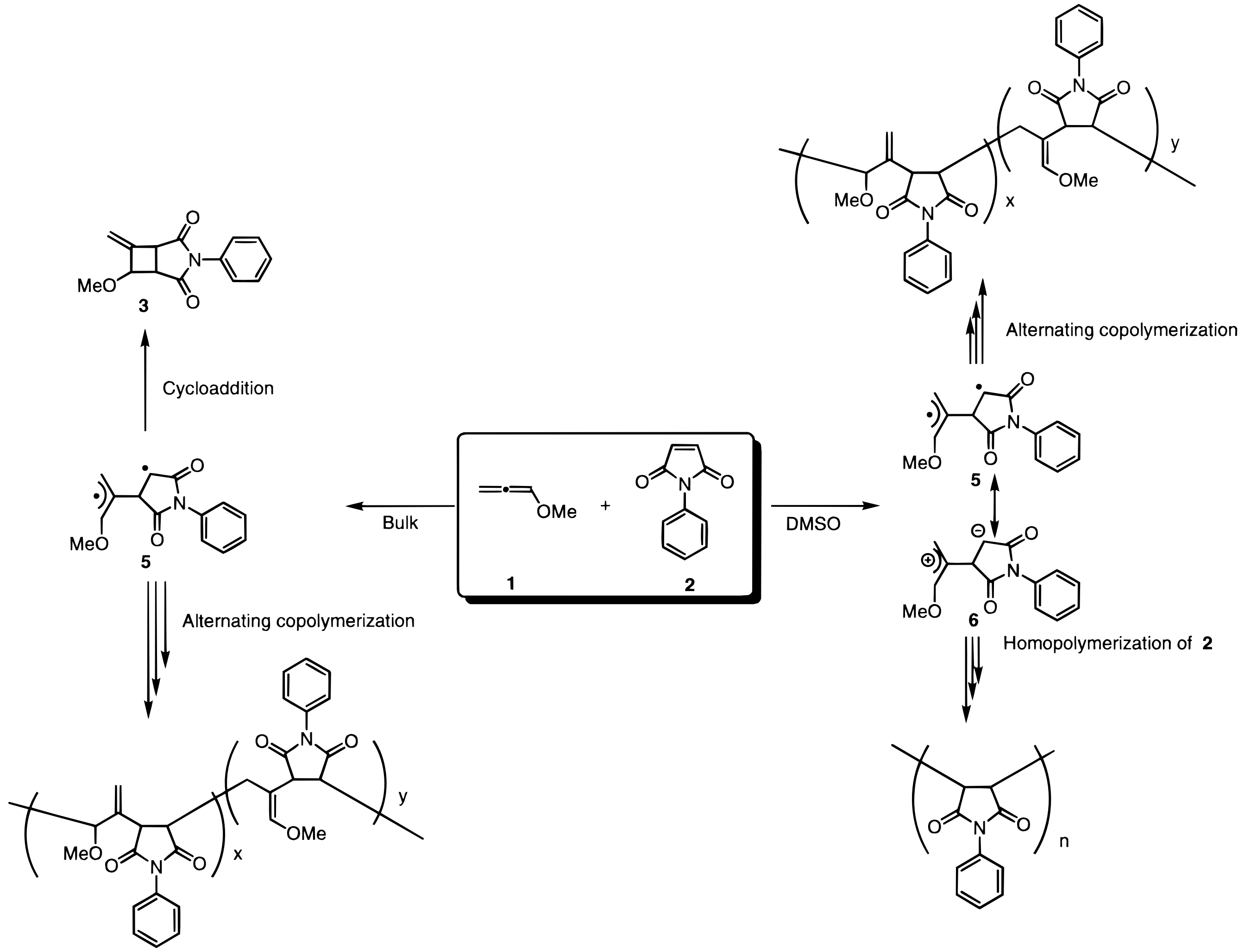
Hall et al. have reported that zwitterionic species can initiate ionic homopolymerization, while diradical species initiate alternating copolymerization.[2] Thus, it may be concluded that the copolymerization in this work

Table 3. Copolymerization of Methoxyallene (1) with *N*-Phenylmaleimide (2) in the Presence of TEMPO

entry	solvent	temp (°C)	time (h)	TEMPO (mol %)	yield[c] (%)	composition[d] **1**:**2**	M_n[e]	M_w/M_n[e]
1	none[a]	60	3	0	17	54:46	29500	1.30
2	none[a]	60	3	2	0			
3	DMSO[b]	20	6	0	60	29:71	3900	1.89
4	DMSO[b]	20	6	25	50	14:86	4500	2.03
5	DMSO[b]	20	6	50	37	10:90	3500	1.80
6	DMSO[b]	20	6	100	25	7:93	3400	1.71

[a] **1**, 2 mmol; **2**, 2 mmol. [b] **1** 2 mmol; **2**, 2 mmol; DMSO, 0.4 mL. [c] Ether-insoluble part. [d] Estimated by elemental analysis. [e] Estimated by GPC (THF, PSt standards).

Scheme 4



involves the homopolymerization of **2** initiated with the zwitterion intermediate. Scheme 4 shows two plausible mechanisms of the polymerization. Without a solvent, a diradical intermediate (**5**) may initiate the alternating copolymerization via a radical process. In DMSO, the active species is considered not only to be the diradical **5** but also a zwitterion (**6**). The homopolymer of *N*-phenylmaleimide may be produced from the anionic site of **6** along with the alternating copolymer formed from **5**.

Salem and Rowland have reported that the diradical and zwitterionic intermediates are resonance forms.[11] In polar solvents such as DMSO, the radical intermediate has more polar character than the case without a solvent. In other words, the equilibrium between the diradical and zwitterion shifts to the latter with increasing the polarity of the polymerization mixture.[12,13] In methanol, the anionic polymerization from the zwitterion is inhibited by the solvent, resulting in switch back to the radical copolymerization. In acetonitrile, the polymer structure is similar to DMSO, but the red color cannot be observed. The zwitterion concentration should be lower in acetonitrile than that in DMSO, because the polarity of acetonitrile is lower than DMSO.[14] DMSO may stabilize the cationic site more sufficiently than the anionic site of the zwitterion because of the electron-donating character. This may be the reason for the occurrence of the anionic homopolymerization of **2** but no cationic homopolymerization of **1**.

Summary

In this article, we demonstrated the novel spontaneous copolymerization of methoxyallene (**1**) with *N*-phenylmaleimide (**2**). It proceeded via a diradical intermediate to afford the alternating copolymer without a solvent. When DMSO was used as the solvent, it

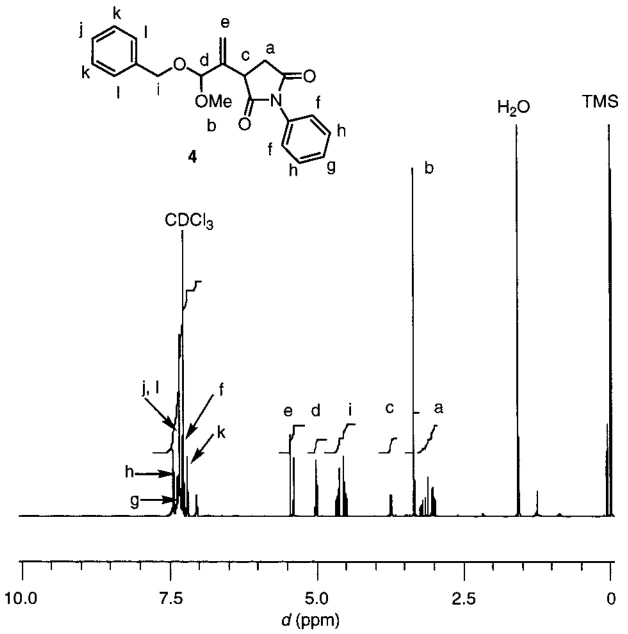


Figure 5. ^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of **4** obtained by the reaction of benzyl alcohol with the polymerization mixture of **1** and **2** in DMSO at 20 °C.

proceeded not only via the diradical but also via a zwitterion to afford the homopolymer of **2** along with the copolymer. It was considered that the alternating copolymer was formed through the diradical, while the homopolymer of **2** was obtained by anionic polymerization initiated from the anionic site of the zwitterion.

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(14) UV–vis spectra of the polymerization mixture of **1** and **2** showed absorption at 515 nm assignable to the zwitterion produced at 60 °C for 1 h, where ϵ values in DMSO, acetonitrile, and methanol were 2.147, 0.382 and 0.04, respectively. Concentration: [**1**] = [**2**] = 0.5 M.

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