

Synthesis of poly[2-(*N,N*-dimethyl)aminoethyl methacrylate-co-acrylonitrile]

Masakazu Yoshikawa¹, Kiyoshi Fujimoto¹, Toshio Kitao¹, Masahiro Rikukawa², Naoya Ogata², Akimoto Tachibana³

¹ Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan

² Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

³ Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

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SUMMARY

Radical copolymerization of 2-(*N,N*-dimethyl)aminoethyl methacrylate (**1**) and acrylonitrile (**2**) initiated by 2,2'-azobis(2-methylpropionitrile) was carried out. The sequence distributions of the copolymers were investigated by ¹³C NMR spectroscopy. A terminal model was used to interpret the propagation process in the copolymerization. The monomer reactivity ratios in the bulk copolymerization at 45°C were evaluated as $r_1 = 1.06$ and $r_2 = 0.07$. Radical reactivity indices and frontier electron densities for **1** and **2** were calculated.

INTRODUCTION

Removal and concentration of CO₂ by synthetic polymeric membranes from the flue gas stream are an important subject in connection with the global warming and the recovery of carbon sources. The development of novel membrane materials, which efficiently separate CO₂ from the combustion gas, is indispensable to establish the membrane separation technique feasible in the industries. There have been a lot of studies on gas separation membranes.¹ On the other hand, an increasing number of papers, which dealt with studies on CO₂ separation membranes, have appeared in the literature since 1980.²⁻¹⁰ The membranes from the copolymers of 2-(*N,N*-dimethyl)aminoethyl methacrylate (**1**) and acrylonitrile (**2**) gave high permselectivity towards CO₂.¹⁰ In the present paper, the radical copolymerization of 2-(*N,N*-dimethyl)aminoethyl methacrylate (**1**) and acrylonitrile (**2**) initiated by 2,2'-azobis(2-methylpropionitrile) is described. In addition, radical reactivity indices and frontier electron densities for 2-(*N,N*-dimethyl)aminoethyl methacrylate (**1**) and acrylonitrile (**2**) are presented.

EXPERIMENTAL

Materials

2-(*N,N*-Dimethyl)aminoethyl methacrylate (**1**) was distilled at reduced pressure (bp₇ 65°C). Acrylonitrile (**2**) and 2,2'-azobis(2-methylpropionitrile) (**AIBN**) were purified by the usual manner. Hexane was used without further purification.

Copolymerization

The bulk copolymerizations of **1** and **2** were carried out in glass ampules at 45°C. The ampules containing the required amount of monomers and initiator

were degassed three times by the usual freeze-thaw cycles under high vacuum and then sealed. When the viscosity of the reaction mixture had slightly increased, the mixture was poured into hexane, which was kept around -50°C , and filtered. No residual product was found in the filtrate. The resulting precipitate was collected. The polymers thus obtained were dried *in vacuo*.

Polymer Composition

The chemical composition of the copolymer was determined by elemental analysis for carbon and nitrogen.

NMR Spectroscopy

The ^{13}C NMR spectra were recorded on the JEOL JNM-GX 270 instruments (67.6 MHz). Typical conditions for ^{13}C NMR measurement were as follows: spectral width, 20 kHz; acquisition time, 0.819 s; data points, 32768; pulse width, 3.7 μs (45°); pulse delay, 2.0 s; number of transients, 20000. The spectra of copolymers were measured at 100°C , using a 50 - 100 g dm^{-3} dimethylformamide- d_7 solution with hexamethyldisiloxane (**HMDS**) as an internal standard. The ^{13}C chemical shift of **HMDS** was 2.0 ppm downfield from tetramethylsilane.

Calculations

In this study, an ab initio molecular orbital method was used. All of the ab initio calculations were done by using STO-3G¹¹ basis sets. The radical reactivity index (RRI),¹²⁻¹⁶ which is a measure of the reactivity of the monomers toward the radical is defined by

$$\text{RRI} = \sum_i^{\text{occ}} \frac{(C_r^{(i)})^2}{\lambda - \epsilon_i} + \sum_j^{\text{unocc}} \frac{(C_r^{(j)})^2}{\epsilon_j - \lambda}$$

where $C_r^{(i)}$ and $C_r^{(j)}$ are the coefficients of the r th $2p\pi$ atomic orbitals in the i th and j th MO's, respectively, whose energies are ϵ_i and ϵ_j , and λ denotes the energy of the singly occupied MO of the attacking radical.

RESULTS AND DISCUSSION

Copolymerizations were achieved in high yield when the reaction time was prolonged.¹⁰ Table 1 shows the results of the copolymerization.

Figure 1 shows one of the ^{13}C NMR spectra of the copolymer. The signal of the carbonyl carbon (a, ~ 177 ppm), which was sensitive to the microconformation of the polymer chains, split in the range of about 4 ppm, reflecting the triads. The signal of the nitrile carbon (b, ~ 123 ppm), which was also sensitive to the microconformation of the polymer chains, also split in the range of 6 ppm. However, the sequence splittings of the corresponding peaks are much complicated, and the component peaks are poorly resolved. Thus, the triad fraction sequence distributions cannot be obtained from these nitrile carbon resonances. On the other hand, the carbonyl carbon resonance are very well resolved. Figure 2 shows the ^{13}C NMR spectra of the carbonyl carbon peaks in the copolymers whose monomer ratio (**1** and **2**) was 1/9 to 9/1 (Expt. No. 1 to 9). The three kinds of signals split in these spectra were assigned as follows: **111**, **112** and **211**, **212** (from lower field to higher field). Here, **212** indicates the triad in which the monomer unit **1** is placed between two monomer units **2**, and so forth.

Since the nuclear Overhauser effect caused by the total proton decoupling does not influence the relative intensities among the peaks for stereochemical configura-

Table 1 Results for the copolymerization of **1** and **2 a**

Expt. No.	Monomer		Time min	Yield g	%	mole fraction of 1 in		T _g / °C
	1/g	2/g				Monomer	Polymer	
1	1.239	3.762	84	0.338	6.76	0.100	0.417	40
2	2.133	2.872	88	0.328	6.55	0.200	0.504	21
3	2.801	2.203	82	0.370	7.39	0.300	0.536	17
4	3.321	1.684	75	0.308	6.15	0.400	0.590	15
5	3.743	1.276	51	0.225	4.48	0.498	0.668	11
6	4.089	0.930	40	0.210	4.18	0.597	0.755	13
7	4.371	0.639	40	0.220	4.39	0.698	0.791	9
8	4.617	0.393	60	0.291	5.81	0.799	0.804	8
9	4.818	0.178	46	0.353	7.07	0.901	0.881	9

a Polymerization temperature, 45°C; (AIBN) / (monomer) = 1 / 200 (mole / mole).

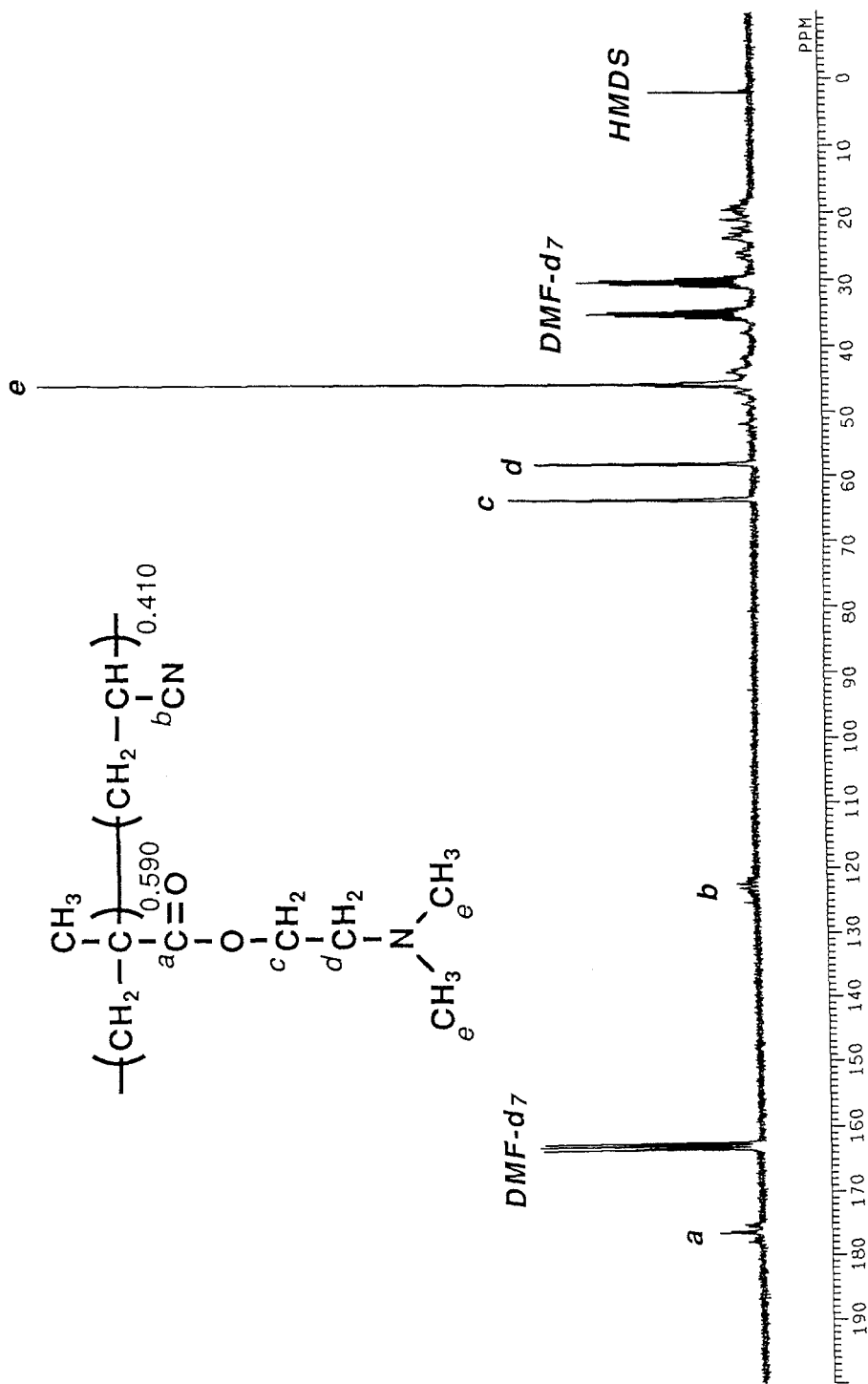


Figure 1 67.6-MHz ^{13}C NMR spectrum of a DMF- d_7 solution of poly(1-co-2) (containing 0.590 mole fraction 1) at 100°C.

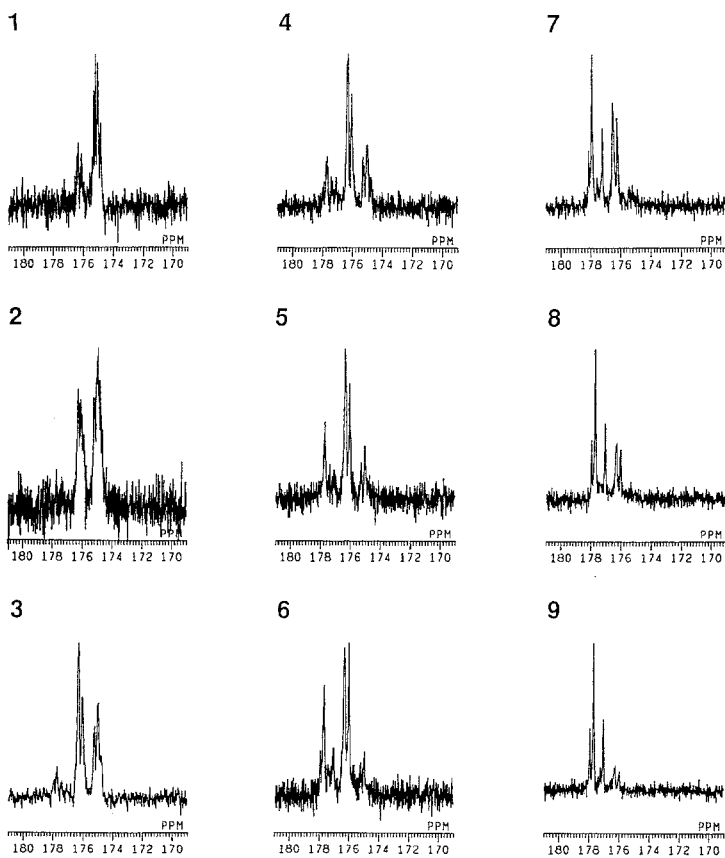


Figure 2 67.6-MHz ^{13}C NMR spectra of a DMF- d_7 solution of poly(1-co-2) at 100°C .

Table 2 Experimental and theoretical triad fractions

Sample	M ₁ / M ₂		F ₁₁₁	F ₁₁₂ + F ₂₁₁	F ₂₁₂
1	1 / 9	obsd	0.00	0.18	0.82
		calcd ^a	0.01	0.19	0.80
2	2 / 8	obsd	0.10	0.35	0.55
		calcd ^a	0.05	0.33	0.62
3	3 / 7	obsd	0.13	0.47	0.40
		calcd ^a	0.10	0.43	0.47
4	4 / 6	obsd	0.20	0.53	0.27
		calcd ^a	0.17	0.49	0.34
5	5 / 5	obsd	0.23	0.54	0.23
		calcd ^a	0.26	0.50	0.24
6	6 / 4	obsd	0.37	0.53	0.10
		calcd ^a	0.37	0.48	0.15
7	7 / 3	obsd	0.53	0.40	0.07
		calcd ^a	0.51	0.41	0.08
8	8 / 2	obsd	0.68	0.30	0.02
		calcd ^a	0.65	0.31	0.04
9	9 / 1	obsd	0.85	0.15	0.00
		calcd ^a	0.82	0.17	0.00

a Calculation by terminal model with $r_1 = 1.06$ and $r_2 = 0.07$.

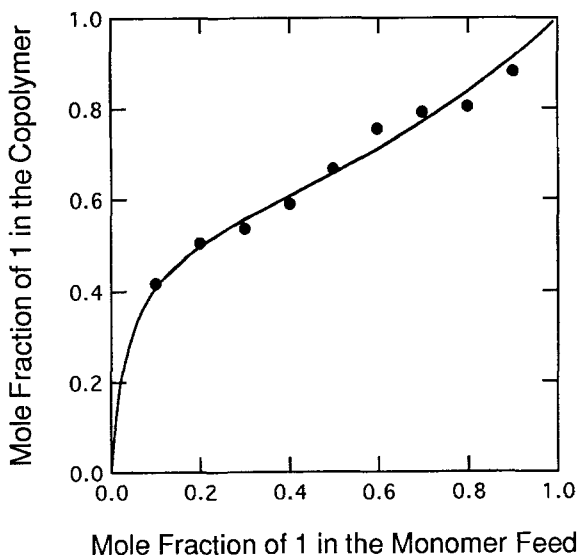


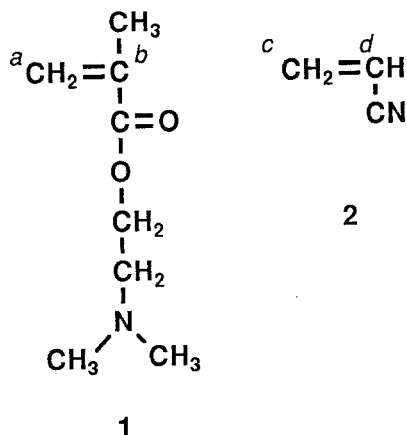
Figure 3 Polymer vs. monomer composition in the copolymerization of 2-(N,N-dimethyl)aminoethyl methacrylate (1) and acrylonitrile (2) (polymerization temperature, 45°C).

Table 3 Radical reactivity indices (RRI) and frontier electron densities ($f_r^{(R)}$) for monomers

position	RRI*	$f_r^{(R)}$
a	5.75	
b	3.02	
c	3.59	0.870**
d	3.45	0.624**

* RRI was calculated, taking the value $\lambda = -0.15$ au.

** Cited from Table III in ref. 16.

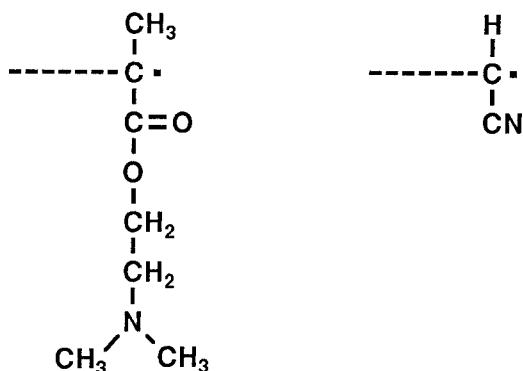


tions even for $^{13}\text{C}\{^1\text{H}\}$ resonance, the fraction of triads was calculated from the areas obtained by integration of the signals, as shown in Table 2. The monomer reactivity ratios $r_1 = 1.06$ and $r_2 = 0.07$ were obtained on the basis of the chemical composition¹⁷ and the triad fraction¹⁸ of the copolymers. As shown in Table 2 and Figure 3, the triad fraction and the chemical composition diagram calculated from these monomer reactivity ratios coincided with those of experiments.

Table 3 shows the radical reactivity indices (RRI) and the frontier electron densities ($f_r^{(R)}$), where the orbital energy of the radical, λ , which attacks the monomer is assumed to be -0.15 au.

As for $f_r^{(R)}$ of **2**, $f_r^{(R)}$ was calculated by using the coefficients of the vinyl carbon $2p\pi$ atomic orbitals in the highest occupied and lowest unoccupied MOs. But in the case of **1**, the coefficients of the vinyl $2p\pi$ atomic orbitals were so dispersed that the evaluation of $f_r^{(R)}$ was impossible.

From RRI (and $f_r^{(R)}$) values at the a carbon in **1** and at the c carbon in **2**, monomer **1** is more reactive than monomer **2**. The obtained monomer reactivity ratios reflect this result; that is, relative rate ratios of addition of monomer **1** and **2** to the growing chain (r_1 and $1/r_2$) are over unity. RRI also indicates that the reacting position of the monomer towards the growing chain radical is mostly often at the a carbon in **1** and the c carbon in **2**. Accordingly, the polymer structure is to be a head-to-tail one and the growing chain terminals are to be



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