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Synthesis of Poly{1-[(2-methylpropenoyl)oxy]succinimide-*co*-acrylonitrile} and the Selective Separation of a Water–Ethanol Mixture through Its Membranes

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ABSTRACT: A new polymer containing the N-substituted succinimide moiety poly{1-[(2-methylpropenoyl)oxy]succinimide-*co*-acrylonitrile} (poly(**1**-*co*-**2**)) was synthesized. The sequence distributions of the copolymers were investigated by ^{13}C NMR spectroscopy. A terminal model was used to interpret the propagation process in the copolymerization. The reactivity ratios in the solution polymerization at 60 °C were evaluated: $r_1 = 2.40$ and $r_2 = 0.42$. Radical reactivity indices and frontier electron densities were calculated. The membrane prepared from this copolymer showed a selective separation of water from a water–ethanol mixture by a pervaporation technique. The separation factor toward water reached over 2000.

Introduction

Selective separations of water from aqueous ethanol solution is of great interest in connection with the production of ethanol via fermentation of biomasses that are rich in sugar and starch.

On the basis of this point of view, we have prepared polymer membranes containing a pendant imide group,[1–3] a N-substituted imide group,[4] or a carbonyl group[5,6] that have a strong interaction with water through hydrogen bonding. Poly(maleimide-*co*-acrylonitrile)[1,2] and poly(acrylic acid-*co*-acrylonitrile)[5,6] membranes gave high separation factors, which reached over 700 for water. We concluded that high selectivity toward water through these two membranes was attained by the selective hydrogen-bonding interaction between water and maleimide or carboxylic acid in these membranes.[2,6] It was also found that not only the amount of functional groups, which interacted preferentially with water in the membrane, but also the environment (membrane polarity) around functional groups influenced the separation characterization for the water–ethanol mixture.[3]

The present paper reports the pervaporation of a novel synthetic membrane containing not only pendant a N-substituted succinimide moiety but also a pendant ester group and its use for separation of a water–ethanol mixture by pervaporation.

Experimental Section

Materials. 1-[(2-methylpropenoyl)oxy]succinimide (**1**) was synthesized from 2-methylpropenoic acid and 1-hydroxysuccinimide[7] (mp 102–105 °C). Acrylonitrile (**2**), *N,N*-dimethylformamide (DMF), and 2,2′-azobis(isobutyronitrile) (AIBN) were purified in the usual manner. Ethanol was used without further purification. The water employed was distilled once.

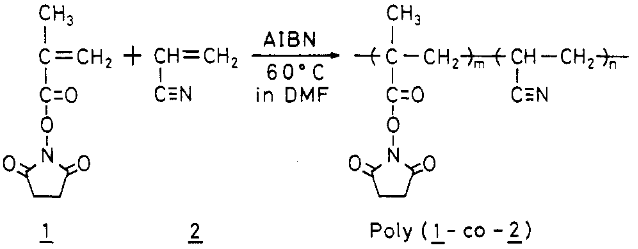
Copolymerization. Compounds **1** and **2** of various molar ratios were placed in an ampule with 0.5 mol % AIBN, which was sealed under a nitrogen atmosphere. The copolymerization was carried out at 60 °C with stirring by oscillation. The mixture was poured into benzene and filtered. No residual product was found in the filtrate.

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

Viscosity Measurement. The viscosity of the copolymer was measured with a 1.0 g dm^{-3} DMF solution at 30 °C.

Spectroscopic Measurement. ^{13}C NMR spectra were obtained with JEOL FX 200 (50.1 MHz) instruments. Typical conditions for ^{13}C NMR measurement were as follows: spectral width, 10 kHz; acquisition time, 0.819 s; data points, 16 384; pulse width, 5.3 μs (41.5°); pulse delay, 2.2 s; number of transients, 2500 for **1** and 20 000 for copolymers.

Scheme I



The spectrum of **1** was measured at 30 °C, using a 200 g dm^{-3} dimethyl-d_6 sulfoxide (Me$_2$SO-d_6) solution with hexamethyldisiloxane (HMDS) as an internal standard, and the spectra of copolymers were measured at 100 °C, using a 50 or 25 g dm^{-3} Me$_2$SO-d_6 solution with HMDS as an internal standard. The ^{13}C chemical shift of HMDS was 2.00 ppm downfield from tetramethylsilane.

IR spectra were taken at ca. 20 °C on a Hitachi 260-50 infrared spectrophotometer.

Calculations. In this study, an ab initio molecular orbital method was used. All of the ab initio calculations were done by using STO-3G[8] basis sets. The radical reactivity index (RRI),[9–11] which is a measure of the reactivity of the monomer toward the radical, is defined by

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

where $C_r^{(i)}$ and $C_r^{(j)}$ are the coefficients of the *r*th 2pπ 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.

Preparation of Membranes. The membrane was obtained by casting from DMF solution (37.5 g dm^{-3}). The solution was poured onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at 40 °C for 3 h. The tough membrane was obtained. The thickness of the membrane was 10–12 μm.

Pervaporation. Permeation of the water–ethanol mixture was carried out through the membrane as described previously.[1–6] The membrane area in contact with liquid was 12.6 cm^2. The downstream pressure was maintained from 333 to 400 Pa (2.5–3.0 torr). Pervaporation experiments were carried out at a constant temperature of +30, +15, 0, or −9 °C. The steady state of permeation was reached within 1 h after the start of pervaporation experiment.

The separation analysis was carried out on a Hitachi 023 gas chromatograph equipped with a 1-m-long column packed with Porapak Q.

The separation factor, α, is defined as

$$\alpha = (Y_{\mathrm{H_2O}}/Y_{\mathrm{EtOH}})/(X_{\mathrm{H_2O}}/X_{\mathrm{EtOH}})$$

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Table I
Results for the Copolymerization of 1-[(2-Methylpropenoyl)oxy]succinimide (1) and Acrylonitrile (2)[a]

	monom					mol fract of 1 in		
expt no.	1/g	2/g	DMF/cm^3	time/min	yield/mg	monom	polym	$(\eta_{sp}/C)/(\mathrm{dm}^3\ \mathrm{g}^{-1})$
1	0.366	0.955	8.0	1440	196	0.100	0.152	0.088
2[b]	0.733	0.849	8.0	110	236	0.200	0.378	0.037
3[b]	1.099	0.743	8.0	195	451	0.300	0.539	0.089
4[b]	1.099	0.478	6.0	90	125	0.400	0.641	0.096
5	1.099	0.318	4.8	20	63.5	0.500	0.699	0.069
6	1.099	0.212	4.0	22	218	0.600	0.678	0.063
7	1.026	0.074	2.8	25	107	0.800	0.957	0.084
8[c]	0.733	4.033		1440	3.62[d]	0.050	0.066	0.580

[a] Polymerization temperature, 60 °C; (AIBN)/(monomer) = 1/200 (mol/mol). Reduced viscosity was measured at C = 1.0 g dm^{-3} (DMF, 30 °C). [b] ^{13}C NMR spectra were obtained for the calculation of the triad fractions. [c] This polymer was prepared for the pervaporation experiment. [d] Yield/g.

Table II
Experimental and Theoretical Triad Fractions

sample	M_1/M_2		F_{212}	$F_{112} + F_{211}$	F_{111}	F_{121}	$F_{221} + F_{122}$	F_{222}
2	2/8	obsd	0.31	0.50	0.19	0.19	0.47	0.34
		calcd[a]	0.39	0.47	0.14	0.14	0.47	0.39
3	3/7	obsd	0.23	0.51	0.26	0.26	0.51	0.23
		calcd[a]	0.24	0.50	0.26	0.26	0.50	0.24
4	4/6	obsd	0.17	0.50	0.33	0.36	0.44	0.20
		calcd[a]	0.15	0.47	0.38	0.38	0.47	0.15

[a] Calculation by terminal model with r_1 = 2.40 and r_2 = 0.42.

where Y_i's are the weight fractions of permeates and X_i's are those of the feeds, respectively.

Results and Discussion

Characterization of the Polymer Poly(1-*co*-2). Copolymerizations were achieved in high yield when the reaction time was prolonged. Table I shows the results of the copolymerization.

The infrared spectrum (KBr) of the copolymer (experiment 2) showed bands at 1820 and 1795 cm^{-1} (C=O, succinimide), 1755 cm^{-1} (C=O, ester), and 2255 cm^{-1} (C≡N), indicating that the copolymers had expected structures.

Figure 1 shows one of the ^{13}C NMR spectra of the copolymer. The signals of the nitrile carbon (b, ~121 ppm) and the methyl carbon (g, ~21 ppm), which were sensitive to the microconformation of the polymer chains, split in the range of about 5 ppm, reflecting the triads. Figure 2 shows the ^{13}C NMR spectra of the copolymer whose monomer ratio (1 and 2) was 2:8 (experiment 2), 3:7 (experiment 3), and 4:6 (experiment 4). The six kinds of signals split in these spectra were assigned as follows: for the nitrile carbon (b) of the 2 unit, 222, 221 and 122, 121; for the methyl carbon (f) of the 1 unit, 111, 112 and 211, 212 (from higher field to lower 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 assigned to the chemically equivalent carbons except for stereochemical configurations even for ^{13}C{^{1}H} resonance, the fraction of traids was calculated from the areas obtained by integration of the signals, as shown in Table II.

The monomer reactivity ratios r_1 = 2.40 and r_2 = 0.42 were obtained[12] on the basis of the chemical composition and the triad fractions of the copolymers. As shown in Table II and Figure 3, the triad fraction and the chemical composition diagram calculated from these monomer reactivity ratios coincided with those of experiments.

Table III 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.

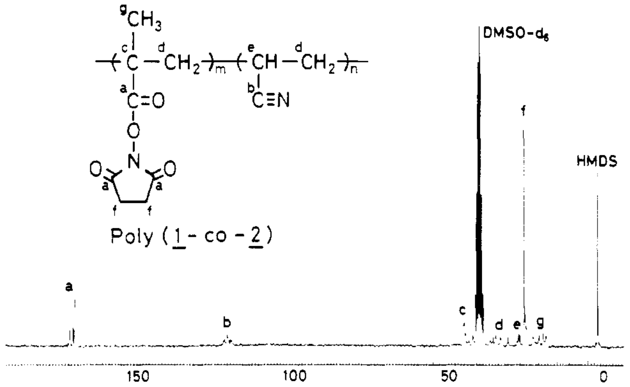


Figure 1. 50.1-MHz ^{13}C NMR spectrum of a Me$_2$SO-d_6 solution of poly(1-*co*-2) (containing 0.378 mole fraction 1) at 100 °C.

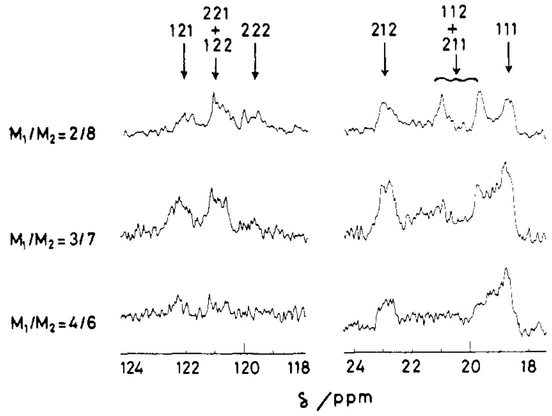


Figure 2. 50.1-MHz ^{13}C NMR spectra of a Me$_2$SO-d_6 solution of poly(1-*co*-2) at 100 °C.

As for $f_r^{(R)}$ of 2, $f_r^{(R)}$ was calculated by using the coefficients of the vinyl carbon 2pπ atomic orbitals in the highest occupied and lowest unoccupied MOs. But, in the case of 1, the coefficients of the vinyl 2pπ atomic orbitals

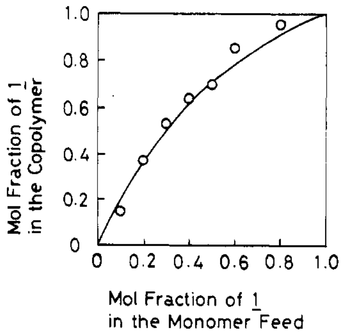
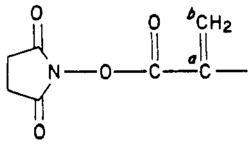
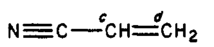


Figure 3. Polymer vs. monomer composition in the copolymerization of 1-[(2-methylpropenoyl)oxy]succinimide (1) and acrylonitrile (2) (polymerization temperature, 60 °C).

Table III
Radical Reactivity Indices (RRI) and Frontier Electron Densities ($f_r^{(R)}$) for Monomers



1



$N\equiv C-CH=CH_2$

2

position	RRI[a]	$f_r^{(R)}$
a	3.78	
b	6.09	
c	3.45	0.624
d	3.59	0.870

[a] RRI was calculated, taking the value $\lambda = -0.15$ au.

were so dispersed that the evaluation of $f_r^{(R)}$ was impossible.

RRI (and $f_r^{(R)}$) values indicate that the reacting position of these two monomers toward the growing chain radical is situated mostly at the β carbon of the vinyl group. Accordingly, the polymerization proceeded via a head-to-tail mechanism.

From RRI values at the b carbon in 1 and at the d 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 the addition of monomer 1 and monomer 2 to the growing chain (r_1 and $1/r_2$) are above unity.

Selective Separation of a Water–Ethanol Binary Mixture through the Present Membrane. Figure 4 indicates results of the pervaporation experiment, where weight fractions of water in permeate, total fluxes, and separation factors (α) are plotted against weight fractions of water in the feed. These experiments were carried out at 15 °C through the poly(1-*co*-2) membrane, whose mole fraction of 1 was 0.066. Figure 4a clearly shows that the selective separation of water was attained through the present membrane. No swelling was observed during all pervaporation experiments.

Figure 4b shows the effect of feed composition on flux and separation factor, α, at 15 °C. As shown in Figure 4b, the α values were over 360 during all runs. Especially, the value of α was greater than 2000 when the weight fraction of water in the feed was 0.699. The flux increased with increasing water content in the feeds, as was expected from the fact that the present membrane permeated water with a high selectivity.

In our previous experiments, a spectroscopic approach was carried out to detect the selective hydrogen-bonding interaction between water and imide units in a poly(maleimide-*co*-acrylonitrile) membrane[2] or carboxylic acids in a poly(acrylic acid-*co*-acrylonitrile) membrane.[6] In the present paper, low solubility of 1 into water made a spectroscopic approach impossible. So an analysis was made to separate observed fluxes into those of ethanol and water, and each separated flux was plotted against its concentration in the feed. These separated fluxes are shown in Figure 5.

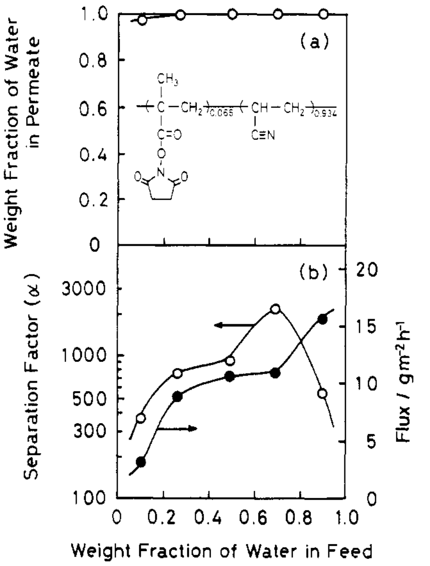


Figure 4. Effect of feed composition on the separation of water–ethanol, flux, and separation factor (α) in water–ethanol pervaporation through a poly(1-*co*-2) membrane (1 fraction, 0.066) at 15 °C.

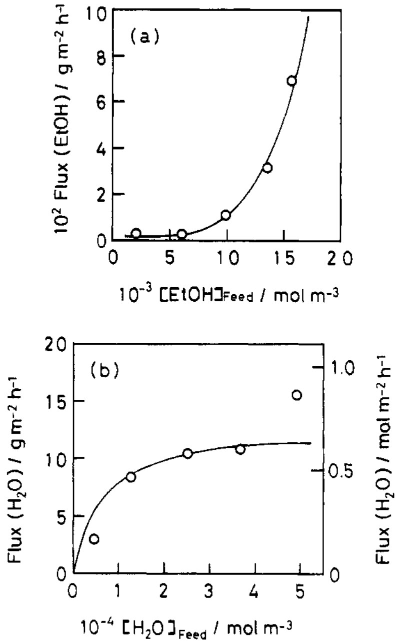


Figure 5. Effect of water and ethanol concentrations on their fluxes in water–ethanol pervaporation through a poly(1-*co*-2) membrane (1 fraction, 0.066) at 15 °C.

The relationship between the ethanol flux and ethanol concentration in the feed is shown in Figure 5a and that between the water flux and its concentration in the feed in Figure 5b.

The ethanol flux through the present membrane shows an exponential profile, while that of the poly(acrylic acid-*co*-acrylonitrile) membrane was a straight line passing through the origin.[6] This may be due to microscopic swelling, which was not detected by the changes of weight, area, and thickness of the membranes within experimental error, of the permeation path for ethanol by ethanol.

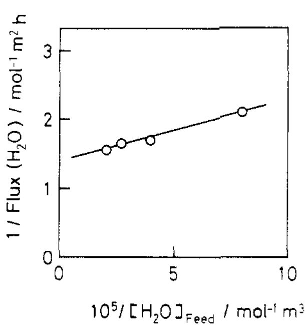


Figure 6. Relationship between reciprocal of flux of water and reciprocal of water concentration through a poly(1-*co*-2) membrane (1 fraction, 0.066).

Except the point where the water concentration in the feed was around 5×10^4 mol m^{-3}, the water flux approached an asymptotic limit as the water concentration in the feed increased; that is, a typical Michaelis–Menten profile was observed. Around the very point where the water concentration in the feed was about 5×10^4 mol m^{-3}, the flux gave over the limiting flux. This may be due to microscopic swelling of the neighborhood of the carrier (1 unit in the membrane) by water. It is, however, a mere speculation, and no evidence is available. Figure 5b supports a carrier-mediated mechanism for water permeation through the present membrane. In the present case, however, a carrier (the imide carbon and ester group in the 1 unit) was immobilized in the membrane. The water flux noted in Figure 5b may be represented by the following equation:

$$J = \frac{D}{l}\,\frac{K[\mathrm{C}]_0[\mathrm{H_2O}]_{\mathrm{feed}}}{1 + K[\mathrm{H_2O}]_{\mathrm{feed}}} \qquad (1)$$

In this equation, D is the diffusion coefficient in the membrane for water, l is the membrane thickness, K is the complex formation constant between the carrier (fixed carrier) and water, $[\mathrm{C}]_0$ denotes the carrier concentration in the membrane, and $[\mathrm{H_2O}]_{\mathrm{feed}}$ is the water concentration in the feed. A Lineweaver–Burk plot (Figure 6) was obtained by using the data shown in Figure 5b (one point where the water concentration in the feed was around 5×10^4 mol m^{-3} is excluded). The slope and the intercept in Figure 6 gave values of K and D. Obtained values were as follows: $K = 1.66 \times 10^{-4}$ mol^{-1} m^3; $D = 5.08 \times 10^{-9}$ m^2 h^{-1}. Such a relationship between the water flux and the water concentration in the feed was considered to be attributed principally to the hydrogen-bonding ability of the 1 unit in the membrane.

We reported[1,2,5,6] that the selectivity and the flux are affected by the operating temperature. Accordingly, the effect of the operating temperature on the permeation through the present membrane was investigated under the conditions that the weight fraction of water in the feed was fixed at around 0.21 or 0.67 and separation experiments were carried out at −9, 0, +15, or +30 °C. Figures 7 and 8 summarize the dependence of the membrane selectivity and total flux on the operating temperature. When the hydrogen-bonding interaction is a dominant factor to control the selectivity, it is in general expected that the selectivity toward water might increase on lowering the operating temperature, as was observed in the poly(maleimide-*co*-acrylonitrile) membrane.[1,2] On the other hand, both selectivities toward water and the total fluxes tended to decrease on lowering the operating temperature, as shown in Figures 7 and 8. Separation factors of the present membrane and the poly(maleimide-*co*-acrylonitrile) membrane[1,2] indicated that the hydrogen-bonding interaction between the 1 unit (carrier) in the present membrane and water might be stronger than that between the maleimide unit in a poly(maleimide-*co*-acrylonitrile) membrane and water. Such a strong interaction of the present membrane hindered the migration of water among carrier from upstream to downstream or (and) the desorption (or evaporation) of water from the membrane toward downstream. Therefore, both selectivities toward water and fluxes decreased on lowering the operating temperature, as shown in Figures 7 and 8.

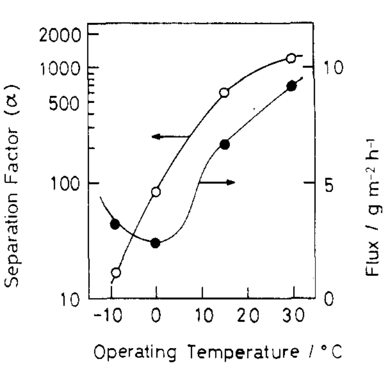


Figure 7. Effect of operating temperature on water–ethanol permeation through a poly(1-*co*-2) membrane (1 fraction, 0.066; weight fraction of water in feed, ~0.21).

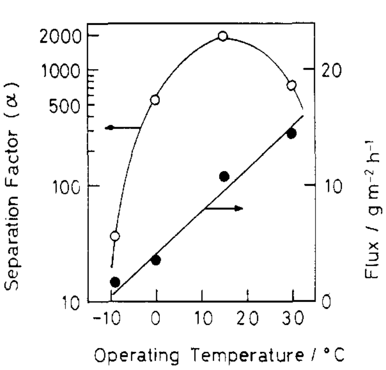


Figure 8. Effect of operating temperature on water–ethanol permeation through a poly(1-*co*-2) membrane (1 fraction, 0.066; weight fraction of water in feed, ~0.67).

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