Synthesis of Poly{1-(2-methylpropenoxy)phthalimide-co-acrylonitrile} and the Selective Separation of Water and Ethanol through Its Membranes

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ABSTRACT: A new polymer, poly{1-(2-methylpropenoxy)phthalimide-co-acrylonitrile} (Poly(1-co-2)) was synthesized based on molecular designs for the separation of water and ethanol. The sequence distribution 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 45°C were evaluated as $r_1 = 1.90$ and $r_2 = 0.39$. Radical reactivity indices and frontier electron densities were calculated. The membrane prepared from this copolymer carried out a selective separation of water from aqueous ethanol solution by pervaporation method. The separation factor toward water was as high as 1200.

KEY WORDS Copolymerization / Monomer Reactivity Ratio / Frontier Electron Density / Radical Reactivity Index / Pervaporation / Permselectivity / Carrier Mechanism / Michaelis-Menten Profile /

It is now widely recognized that separations by membranes are one of the most promising processes as an energy-saving separation technology. Considering separations of low molecular weight organic compounds, pervaporation technique, which is a liquid phase permeation system in which the liquid feed mixture is maintained in contact with membrane, and the permeate is removed from the opposite side on membrane as a vapor, is one of the potential methods to separate specifically and selectively low molecular weight organic liquid mixtures as suggested by Binning *et al.*¹

Pervaporation technique may be classified into two ways as was observed in general membrane transport process. One way is that the permeation through the membrane is obtained by the nonmediated mechanism, while

the other way is that the permeation is attained by the mediated mechanism. So far, many works on pervaporation technique have been reported. Most of these membranes permeated organic compounds by the former mechanism. The specific separation of substrate through membranes requires to incorporate a group into membranes that may cause a strong interaction between the incorporated group and the substrate to be separated specifically. In other words, membranes having a fixed carrier makes it possible to separate organic mixtures with a high selectivity by means of pervaporation.

On the basis of this idea, we chose imide group or carbonyl moiety as a functional group in order to cause a strong hydrogen-bonding interaction among many functional

groups, and we synthesized polymer membranes containing pendant imide group,^{2,3} *N*-substituted imide group,⁴ carboxylic acid moiety,⁵ or ester and *N*-substituted imide group⁶. We investigated the ability to carry out the separation of water-ethanol mixture with these membranes, since the separation of aqueous ethanol solution draws much attention in connection with the production of ethanol *via* fermentation of biomasses. Most of these membranes permeated water preferentially, especially, poly{1-(2-methylpropenyloxy)succinimide-*co*-acrylonitrile} membrane gave a high separation factor, which reached over 2000 for water.⁶ We concluded that the high selectivity toward water through these membranes was attained by the selective hydrogen-bonding interaction between water and functional groups incorporated into these membranes.^{2,5,6}

In order to obtain a novel membrane which has a much higher selectivity toward water, a polymer having ester and *N*-substituted phthalimide as a fixed carrier in the side chain, poly{1-(2-methylpropenyloxy)phthalimide-*co*-acrylonitrile} (poly(1-*co*-2)), was synthesized by a radical copolymerization.

The propagation process in the copolymerization of 1-(2-methylpropenyloxy)phthalimide (1) and acrylonitrile (2) was found to follow a terminal model by ¹³C NMR polymer analysis. The monomer reactivity ratios were also determined. It was assumed that propagation was entirely head-to-tail.

The membrane made of the present copolymer permeated water with a high selectivity from water-ethanol mixture.

EXPERIMENTAL SECTION

Materials

1-(2-Methylpropenyloxy)phthalimide (1) was synthesized by the following procedure⁷: to a solution of 49.0 g (0.300 mol) *N*-hydroxyphthalimide in 500 cm³ of a mixture of 1,4-dioxane and DMF (4:1) cooled to 5°C

were added with stirring 25.8 g (0.300 mol) of

2-methylpropenoic acid and 62.0 g (0.300 mol) of 1,3-dicyclohexylcarbodiimide. The mixture was stirred for 2 h at 5°C, and then 0.4 g of 4-*tert*-butylcatechol was added. The mixture was allowed to warm to ambient temperature and stirred for an additional 2 h. The precipitate of 1,3-dicyclohexylurea was removed and the filtrate was evaporated to *ca.* 100 cm³ and cooled, whereupon a crude crystalline solid separated. Crystallization from heptane gave 15.4 g (0.067 mol) (22.3%) of white crystals; mp 119–121°C.

Acrylonitrile (2), 2,2'-azobis(2-methylpropionitrile) (AIBN) were purified in the usual manner. Ethanol was used without further purification. The water employed here was distilled once.

Copolymerization

Compounds 1 and 2 of various molar ratios and DMF were placed in an ampule with 0.5 mol% AIBN, which was sealed under a nitrogen atmosphere. The copolymerization was carried out at 45°C with stirring by oscillation. The mixture was poured into diethyl ether 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

^1H and ^{13}C -NMR spectra were obtained with JEOL FX200 (199.5 MHz for ^1H and 50.1 MHz for ^{13}C) instruments. Typical conditions for ^{13}C NMR measurement were as follows: spectral width, 10 kHz; acquisition time, 0.819 s; data points, 16384; pulse width, 5.3 μs (41.5°); pulse delay, 2.2 s; number of transients, 500 for **1** and 20000–40000 for copolymers.

The spectrum of **1** was measured at 30°C, using a 100 g dm^{-3} CDCl_3 solution with hexamethyldisiloxane (HMDS) as an internal standard, and the spectra of copolymers were measured at 100°C, using a 25–50 g dm^{-3} dimethyl- d_6 sulfoxide solution with HMDS as an internal standard. The ^{13}C chemical shift of HMDS was 2.0 ppm downfield from tetramethylsilane.

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

Calculations

An *ab initio* molecular orbital method was used in this study. All of the *ab initio* calculations were done by using STO-3G⁸ 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

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

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.

Preparation of Membranes

The membrane was obtained by casting from DMF solution (100 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 thickness of the membrane was *ca.* 14 μm .

Pervaporation

Permeation of water-ethanol mixture was carried out through the membranes as described previously.^{2–6} The membrane area in contact with liquid was 12.6 cm^2 . The downstream pressure was maintained from 360 to 430 Pa (2.7–3.2 torr). Pervaporation experiments were carried out at a constant temperature of 30, 15, 0 or –13°C, respectively.

The separation analysis was carried out on a Shimadzu GC-8A gas chromatograph equipped with a 1-m long column packed with Porapak Q.

The separation factor, α , is defined as

$$\alpha = \frac{Y_{\text{Water}}/Y_{\text{Ethanol}}}{X_{\text{Water}}/X_{\text{Ethanol}}}$$

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 1-(2-Methylpropenoyloxy)phthalimide (**1**)

Figure 1 shows the ^{13}C NMR spectrum of **1**. The signals of d (132.2 ppm) and e (130.3 ppm) were assigned to the vinyl carbons. ^1H NMR spectrum showed δ 7.74 (m) for phthalide protons; 5.82 (s) and 6.38 (s) for β protons of the vinyl group; 1.99 (s) for methyl protons. The IR spectrum (KBr) of **1** showed bands at 1840 and 1800 cm^{-1} (C=O, phthalimide), 1745 cm^{-1} (C=O, ester), and 1625 cm^{-1} (C=C). *Anal.* Calcd for $\text{C}_{12}\text{H}_9\text{NO}_4$: C, 62.33%; H, 3.93%; N, 6.06%. Found: C, 63.0%; H, 3.8%; N, 6.2%.

Poly{1-(2-methylpropenoyloxy)phthalimide}

Compound **1** was polymerized to give a white powder ($\eta_{\text{sp}}/c = 0.108 \text{ dm}^3 \text{ g}^{-1}$).

Figure 1. 50.1 MHz ^{13}C NMR spectrum of a CDCl_3 solution of **1** at 30°C .

Table I. Result for the copolymerization of 1-(2-methylpropenyloxy)phthalimide (**1**) and acrylonitrile (**2**)^a

Exptl. No.	Monomer		DMF cm ³	Time m	Yield mg	mol fraction of 1 in		η_{sp}/c dm ³ g ⁻¹
	1 /g	2 /g				Monomer	Polymer	
1	0.358	0.955	6.0	480	183	0.100	0.208	0.080
2	0.717	0.849	6.0	270	207	0.200	0.368	0.084
3 ^b	1.075	0.743	6.0	120	144	0.300	0.481	0.086
4 ^b	1.075	0.478	4.5	65	81.5	0.400	0.588	0.097
5 ^b	1.075	0.318	3.6	52	96.3	0.500	0.653	0.103
6	1.075	0.212	3.0	48	133	0.600	0.781	0.116
7	1.004	0.127	2.4	40	91.5	0.700	0.809	0.116
8	1.004	0.074	2.1	38	91.8	0.800	0.871	0.107
9	1.075	0.036	2.0	39	98.8	0.900	0.954	0.103
10 ^c	1.157	5.047	3.0	4 ^d	5.04 ^e	0.050	0.040	0.362

^a Polymerization temperature, 45°C ; $(\text{AIBN})/(\text{monomer}) = 1/200$ (mol/mol). Reduced viscosity was measured at $c = 1.0 \text{ g dm}^{-3}$ (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 Time/day.

^e Yield/g.

Characterization of the Copolymer Poly{1-(2-methylpropenyloxy)phthalimide-co-acrylonitrile} (Poly(**1-co-2**))

Copolymerizations were achieved in a high yield when the reaction time was prolonged. Table I shows the results of the co-

polymerization.

The IR spectrum (KBr) of poly(**1-co-2**) (experiment 10) showed bands at 1810 and 1785 cm^{-1} ($\text{C}=\text{O}$, phthalimide), 1750 cm^{-1} ($\text{C}=\text{O}$, ester), and 2250 cm^{-1} ($\text{C}\equiv\text{N}$), indicating that the copolymers had expected

Figure 2. 50.1 MHz ^{13}C NMR spectrum of a $\text{DMSO}-d_6$ solution of poly(1-co-2) (containing 0.481 mol fraction of 1) at 100°C .

structures.

Figure 2 shows one of ^{13}C NMR spectra of the copolymer. The signals of the nitrile carbon (f, 121 ppm) and the methyl carbon (h, 21 ppm), which were sensitive to the microstructure of the polymer chains, split in the range of about 5 ppm, reflecting the triads. Figure 3 shows ^{13}C NMR spectra of the copolymer whose monomer ratio (1 and 2) were 3:7 (experiment 3), 4:6 (Experiment 4), and 5:5 (experiment 5). Six kinds of signals split in these spectra were assigned as follows: for the nitrile carbon (f) of 2 unit, 222, 221 and 122, 121; for the methyl carbon (h) of 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 for stereochemical configurations even for $^{13}\text{C}\{^1\text{H}\}$ resonance, the fraction of triads was calculated from the areas obtained by in-

tegration of the signals, as shown in Table II.

The monomer reactivity ratios $r_1 = 1.90$ and $r_2 = 0.39$ were obtained¹² on the base of the chemical composition and the triad fraction of the copolymers. As shown in Table II and Figure 4, 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 a.u.

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.

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,

Figure 3. 50.1 MHz ^{13}C NMR spectra of a DMSO- d_6 solution of poly(1-co-2) at 100°C.

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}
3	3/7	Obsd	0.26	0.51	0.23	0.26	0.52	0.22
		Calcd ^a	0.30	0.50	0.20	0.27	0.50	0.23
4	4/6	Obsd	0.18	0.52	0.30	0.40	0.44	0.16
		Calcd ^a	0.20	0.49	0.31	0.40	0.46	0.14
5	5/5	Obsd	0.14	0.43	0.43	0.51	0.39	0.10
		Calcd ^a	0.12	0.45	0.43	0.52	0.40	0.08

^a Calculation by terminal model with $r_1 = 1.90$ and $r_2 = 0.39$.

the polymerization proceeded *via* a head-to-tail mechanism.

From *RR*I 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 Water–Ethanol Mixture through the Present Membrane

Figure 5 shows the results of the pervaporation experiment, where weight fractions of

Figure 4. Polymer vs. monomer composition in the copolymerization of 1-(2-methylpropenyloxy)phthalimide (**1**) and acrylonitrile (**2**) (polymerization temp, 45°C).

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

Position	<i>RRI</i> ^a	$f_r^{(R)}$
a	2.71	—
b	5.77	—
c	3.45	0.624
d	3.59	0.870

^a *RRI* was calculated, taking the value $\lambda = -0.15$ a.u.

water in permeate, total flux, and separation factor (α) are plotted as a function of weight fractions of water in feed. These experiments were carried out at 15°C through the poly(1-co-2) membrane, whose mol fraction of **1** was 0.040. Figure 5(a) clearly shows that the present membrane preferentially permeated water. No swelling was observed during all pervaporation experiments.

Figure 5(b) shows the effect of feed composition on flux and separation factor (α) at 15°C. As shown in Figure 5(b), the α values were over 620 during all runs. Especially, the value of α was as high as 1200 when the weight fraction of water in feed was 0.682. 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 reports, spectroscopic approach was carried out to detect the selective hydrogen-bonding interaction between water and imide units in a poly(maleimide-co-acrylonitrile) membrane² or carboxylic acids in a poly(acrylic acid-co-acrylonitrile) membrane.⁵ In the present paper, low solubility of **1** into water made a spectroscopic approach

Figure 5. Effect of feed composition on the separation of water-ethanol, flux, and separation factor (α) in water-ethanol pervaporation through poly(1-co-2) membrane (**1** fraction, 0.040) at 15°C.

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 6.

The relationship between ethanol flux and ethanol concentration in feed is shown in Figure 6(a) and that between water flux and its concentration in feed in Figure 6(b). Ethanol flux shows an exponential profiles, while water flux is a Michaelis-Menten profile. From these profiles, the permeation path for ethanol is considered to be different from that for water.

The water flux approached an asymptotic limit as water concentration in feed increased, that is, a typical Michaelis-Menten profile was observed. This suggests that water was permeated through the present membrane by a carrier-mediated mechanism. In the present paper, however, a carrier (imide and ester groups in **1** unit) was immobilized in the membrane. The water flux may be represented by the following equation^{5,6}:

Figure 6. Effect of water and ethanol concentrations on their fluxes in water-ethanol pervaporation through poly(1-co-2) membrane (1 fraction, 0.040) at 15°C.

$$J = \frac{D}{l} \frac{K[C]_0[\text{H}_2\text{O}]_{\text{feed}}}{1 + K[\text{H}_2\text{O}]_{\text{feed}}} \quad (1)$$

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 carrier (fixed carrier) and water; $[C]_0$ denotes the carrier concentration in the membrane; $[\text{H}_2\text{O}]_{\text{feed}}$ is the water concentration in the feed. A Lineweaver-Burk plot (Figure 7) was obtained by using the data shown in Figure 6(b). The slope and the intercept in Figure 7 gave values of K and D . Obtained values were as follows: $D = 1.14 \pm 0.12 \times 10^{-8} \text{ m}^2 \text{ h}^{-1}$; $K = 4.96 \pm 0.51 \times 10^{-5} \text{ mol}^{-1} \text{ m}^3$. Such a relationship between water flux and water concentration in feed was considered to be attributed principally to the hydrogen-bonding interaction between water and 1 unit in the

Figure 7. Relationship between reciprocal of flux of water and reciprocal of water concentration through poly(1-co-2) membrane (1 fraction, 0.040).

membrane.

We previously reported^{2,5,6} that the selectivity and the flux is dependent on operating temperatures. Accordingly, the effect of operating temperatures on the permeation through the present membrane was investigated under the conditions that the weight fraction of water in feed was fixed around 0.6 and the separation experiments were carried out at -13° , 0° , 15° , or 30°C . Figure 8 shows the dependence of the membrane permeabilities on the operating temperature. When the hydrogen-bonding interaction is a dominant factor to govern the selectivity, it is, in general, expected that the selectivity toward water might increase with lowering the operating temperature, as was observed in poly(maleimide-co-acrylonitrile).² On the other hand, both selectivities and the total fluxes tended to decrease with lowering the operating temperature as shown in Figure 8. Separation factors of the present membrane and poly(maleimide-co-acrylonitrile) membrane² indicated that the hydrogen-bonding interaction between 1 unit (carrier) in the present membrane and water might be stronger than that between maleimide unit in a poly(maleimide-co-acrylonitrile) membrane and water. Such a strong interaction of the present membrane hindered the mi-

Figure 8. Effect of operating temperature on water-ethanol pervaporation through poly(1-co-2) membrane (1 fraction, 0.040; weight fraction of water in feed, ~0.6).

gration of water among carriers from the up-stream to the down-stream or (and) the desorption (or evaporation) of water from the membrane toward the down-stream. Therefore, both selectivities and fluxes decreased with lowering the operating temperature as shown in Figure 8.

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