We thank Mr. Kurt Bunney for the purification and characterization of **3**.

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Synthesis of Poly[3-(4-vinylphenoxy)phthalide-*co*-acrylonitrile] and the Selective Transport Properties of Its Membranes

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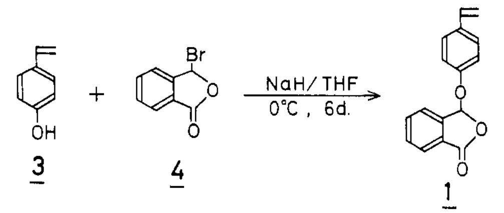
ABSTRACT: A new vinyl monomer containing the lactone moiety 3-(4-vinylphenoxy)phthalide (**1**) was synthesized and copolymerized with acrylonitrile (**2**). The sequence distributions of the copolymers were investigated by ^{13}C NMR spectroscopy. A penultimate model was used to interpret the propagation process in the copolymerization. The reactivity ratios in the solution polymerization at 45 °C were evaluated: $r_1 = 0.23$, $r_1' = 0.41$, $r_2 = 0.08$, and $r_2' = 0.11$. Radical reactivity indices and frontier electron densities for **1** and **2** were calculated. The membrane prepared from this copolymer showed selective transport properties for alkali metal ions. The selectivity in the transport of alkali metal ions by electrodialysis depended on the fraction of the opened phthalide moiety, i.e., lactone moiety. The present membrane, of which the fraction of opened lactone is small, showed an appreciable ability to separate Li^+ from Na^+ and K^+.

The ability to carry out active and selective transport of ions is of great interest in connection with the technological application of a biomembrane. Many carriers of metal ions, such as cyclic polyethers, chelating reagents, and ionophores, have been considered, but most of them have been investigated in the form of a liquid membrane or a blended membrane. On the other hand, synthetic membranes do not show appreciable selective transport properties for metal ions, except a polyamine sulfone derivative,[1] poly(tetrahydropyran-2,6-diyliminocarbonyl),[2] poly(sodium 3-*O*-vinylbenzylgluconate-*co*-acrylonitrile),[3] poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) (**6**),[4] and poly[3-[3-(4-hydroxyphenyl)phthalidyl]-4-hydroxystyrene-*co*-4-hydroxystyrene].[5] The selective transport abilities of the former two were revealed by hydrophobic and hydrophilic properties of the membrane, and those of the latter three were caused by the interaction between fixed carriers and metal ions, and the hydrophilic–hydrophobic balance. The last two membranes showed an active transport of alkali metal ions in addition to selective transport. With the lactone-containing polymer membrane, it was proved that the selectivity for alkali metal ion transport depends on both the affinity of the metal ions for the carboxylate formed by the ring opening of a lactone[4] and the hydrophobicity or hydrophilicity of the membrane.[4,5] The hydrophobic membrane, in which the fraction of ring-opened lactone is small, exhibits the following selectivity in alkali metal ion transport: $K^+ > Na^+ > Li^+$.[4] In order to obtain a membrane which has an appreciable selectivity for Li^+, a polymer having phenoxyphthalide as a hydrophobic moiety in the side chain, poly[3-(4-vinylphenoxy)phthalide-*co*-acrylonitrile] (**5**), was synthesized by a radical copolymerization.

The propagation process in the copolymerization of 3-(4-vinylphenoxy)phthalide (**1**) and acrylonitrile (**2**) was found to follow a penultimate model by ^{13}C 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 showed an improved selective transport ability for Na^+ and K^+ from Li^+.

Scheme I



3 4 1

Experimental Section

Materials. 3-(4-Vinylphenoxy)phthalide (1) was synthesized from 4-vinylphenol (3) and 3-bromophthalide (4) as shown in Scheme I. Compounds 3 (mp 70.0–71.0 °C) and 4 (mp 78.0–80.0 °C) were synthesized by the hydrolysis of 4-acetoxystyrene[6] and by the bromination of phthalide,[7] respectively. Twenty-four grams (0.20 mol) of 3 was added to a suspension of 5.8 g (0.24 mol) of sodium hydride in 100 cm^3 of dry tetrahydrofuran (THF). To the suspension was added dropwise 100 cm^3 of a THF solution containing 51 g (0.24 mol) of 4. The mixture was stirred for an additional 6 days at 0 °C and then washed with water and poured into a benzene–tetrachloromethane mixture. 3-(4-Vinylphenoxy)phthalide (1) was obtained as a white precipitate. Recrystallization from methanol gave 33 g (65%) of colorless needles, mp 118.0–119.0 °C.

Acrylonitrile (2), *N,N*,-dimethylformamide (DMF), and 2,2′-azobis(isobutyronitrile) (AIBN) were purified in the usual manner.

Copolymerization. Compounds 1 and 2 in varying molar ratios were placed in an ampule with 0.5 mol % of AIBN and sealed under a nitrogen atmosphere. The copolymerization was carried out at 45 °C under stirring by oscillation. The mixture was poured into methanol 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 Measurements. The viscosity of the copolymer was measured with a 0.2 g dm^{-3} DMF solution at 40 °C.

Spectroscopic Measurements. ^{1}H and ^{13}C NMR spectra were obtained with Varian HA-100D (100 MHz) and JEOL FX100 (25.0 MHz) instruments, respectively. Typical conditions for ^{13}C NMR measurement were as follows: spectral width, 5 kHz; acquisition time, 0.8192 s; data points, 8192; pulse width, 8 μs (41.1°); pulse interval 2.0 s; number of transients, 100 for 1 and 16000 for 5.

The spectrum of 1 was measured at ambient temperature, using a 100 g dm^{-3} CDCl$_3$ solution with tetramethylsilane (Me$_4$Si) as an internal standard, and the spectrum of 5 was measured at 100 °C, using a 100 g dm^{-3} dimethyl-d_6 sulfoxide (Me$_2$SO-d_6) solution with hexamethyldisiloxane (HMDS) as an internal standard. The ^{13}C chemical shift of HMDS was 2.00 ppm downfield from Me$_4$Si.

IR spectra were taken on a Hitachi EPI-G2 spectrophotometer.

Calculations. All the calculations have been carried out by the INDO MO method.[8] The radical reactivity index (RRI),[9] 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 rth 2pπ atomic orbitals in the ith and jth 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.

The frontier electron density ($f_r^{(R)}$) is defined by

$$f_r^{(R)} = (C_r^{(HO)})^2 + (C_r^{(LU)})^2$$

where $C_r^{(HO)}$ and $C_r^{(LU)}$ are the coefficients of the 2pπ atomic orbital in the highest occupied and the lowest unoccupied MO's, respectively.

Preparation of Membrane. The membrane was made from a 120 g dm^{-3} DMF solution of 5 (content of 1, 5.6 mol %). The casting solution was poured onto a glass plate, and the solvent was allowed to evaporate at 40 °C for 1 h. The thickness of the membrane was ca. 20 μm.

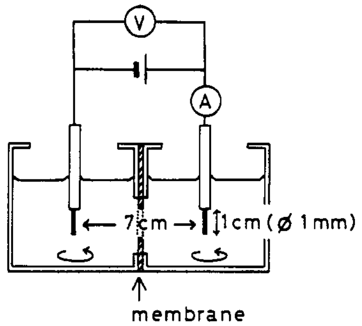


Figure 1. Rough sketch of the electrodialysis cell (volume, 40 cm^3; effective membrane area, 3.0 cm^2).

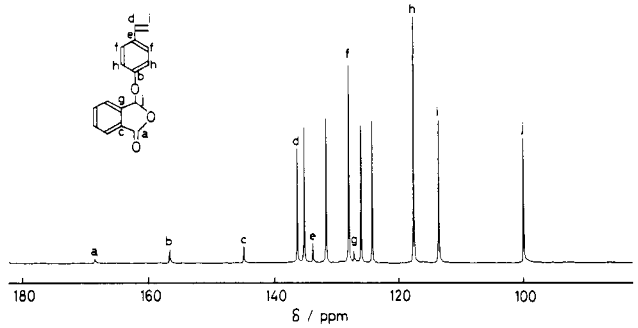


Figure 2. 25.0-MHz ^{13}C NMR spectrum of a CDCl$_3$ solution of 1 at ambient temperature.

Electrodialysis. A poly(methyl methacrylate) cell consisting of two chambers was used in the electrodialysis, as shown in Figure 1. The membrane was laid out in the middle of the two chambers of the cell. The effective membrane area was 3.0 cm^2. A 40-cm^3 portion of solution containing two kinds of alkali metal hydroxides (5.0×10^{-1} mol dm^{-3}) was placed in each chamber. An appropriate amount of concentrated hydrochloric acid was added in both chambers in order to control the fraction of opened lactone. The degree of opened lactone in the membrane was estimated from its IR spectrum. The electrodialysis was carried out at 40 °C with magnetic stirring. The applied voltage was 7.0 V between two platinum electrodes (thickness = 1.0 mm, length = 1.0 cm). The selectivity in alkali metal ions transferred was analyzed after passage of electricity equivalent to 10% of the metal ions.

Quantitative Analysis of Alkali Metal Ions. The concentrations of alkali metal ions were measured with atomic absorption spectrophotometers (Jarrell-Ash AA780 and AA8200).

Results and Discussion

Characterization of 3-(4-Vinylphenoxy)phthalide (1). Figure 2 shows the ^{13}C NMR spectrum of 1. The signals of d (136 ppm) and i (113 ppm) were assigned to the vinyl carbons. In the ^{1}H NMR spectrum, the signals of the α and β protons of the vinyl group appeared at 6.5–6.8 and 5.1–5.7 ppm (from Me$_4$Si), respectively ($J_{\mathrm{trans}} \simeq 18$, $J_{\mathrm{cis}} \simeq 11$, and $J_{\mathrm{gem}} \simeq 1$ Hz). The IR spectrum of 1 showed the specific absorption of the lactone moiety at about 1780 cm^{-1}. Anal. Calcd for C$_{16}$H$_{12}$O$_3$: C, 76.17; H, 4.80; O, 19.03. Found: C, 76.07; H, 4.85; O, 19.22.

Poly[3-(4-vinylphenoxy)phthalide]. Compound 1 was polymerized to give a white powder ($\eta_{\mathrm{sp}}/c = 0.036$ dm^3 g^{-1}, softening point 200–220 °C).

Characterization of the Copolymer Poly[3-(4-vinylphenoxy)phthalide-*co*-acrylonitrile] (5). Copolymerizations were achieved in high yield when the reaction time was prolonged. Table I shows the results of the copolymerization.

Figure 3 shows one of the ^{13}C NMR spectra of 5. The signals of the nitrile carbon (g, $\simeq$120 ppm) and the C$_1$ carbon of the benzene ring (d, $\simeq$140 ppm), which were sensitive to the microconformation of the polymer chains, split in the range of about 5 ppm, reflecting the triads. Figure 4 shows the ^{13}C NMR spectra of 5 whose monomer

Table I
Results for the Copolymerization of 3-(4-Vinylphenoxy)phthalide (1) and Acrylonitrile (2)[a]

	monomer					mol fraction of 1 in		
exp no.	1/g	2/g	DMF/cm³	time/min	yield/mg	monomer	polymer	$(\eta_{sp}/c)/(\mathrm{dm}^3\ \mathrm{g}^{-1})$
1	0.422	0.800	3.8	25	32.8	0.100	0.364	0.175
2	0.713	0.600	3.8	32	32.9	0.200	0.452	0.187
3	0.815	0.400	3.8	50	16.6	0.300	0.526	0.133
4	0.760	0.240	3.8	75	10.0	0.400	0.525	0.115
5	0.950	0.200	3.8	75	18.6	0.499	0.558	0.133
6	1.140	0.160	3.8	90	54.4	0.600	0.609	0.127
7	0.887	0.080	3.0	100	36.0	0.699	0.609	0.072
8	0.760	0.040	2.5	105	20.4	0.800	0.703	0.048
9	0.854	0.020	2.7	130	19.0	0.900	0.905	0.030
10[b]	0.422	0.800	3.8	80	140	0.100	0.358	
11[b]	0.950	0.200	3.7	250	140	0.499	0.560	
12[b]	0.854	0.020	3.0	420	108	0.900	0.744	

[a] Polymerization temperature, 45 °C; (AIBN)/(monomer) = 1/200 (mol/mol). Reduced viscosity was measured at c = 0.20 g dm^{-3} (DMF, 40 °C). [b] These polymers were prepared for the calculation of the triad fractions.

Table II
Experimental and Theoretical Triad Fractions

			triad fraction					
sample	M_1/M_2		F_{111}	$F_{112} + F_{211}$	F_{212}	F_{222}	$F_{211} + F_{122}$	F_{121}
10	1/9	obsd	0.00	0.08	0.92	0.19	0.54	0.27
		calcd[a]	0.00	0.08	0.92	0.19	0.54	0.27
11	1/1	obsd	0.05	0.43	0.52	0.03	0.20	0.77
		calcd[a]	0.05	0.43	0.52	0.01	0.18	0.81
12	9/1	obsd	0.47	0.43	0.10	0.00	0.00	1.00
		calcd[a]	0.48	0.46	0.06	0.00	0.02	0.98

[a] Calculation by penultimate model with r_1 = 0.23, r_1' = 0.41, r_2 = 0.08, and r_2' = 0.11.

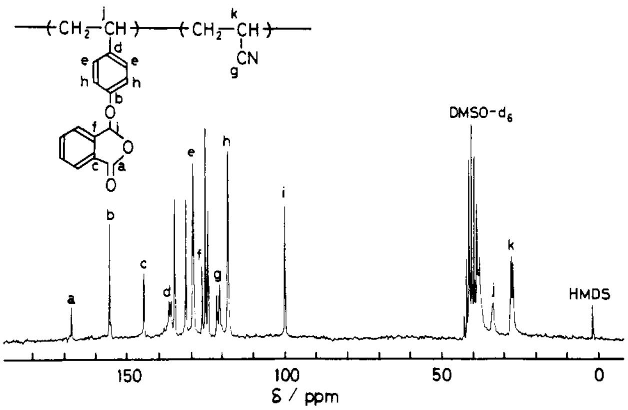


Figure 3. 25.0-MHz ^{13}C NMR spectrum of a Me$_2$SO-d_6 solution of 5 (containing 40.2 mol % 1) at 100 °C.

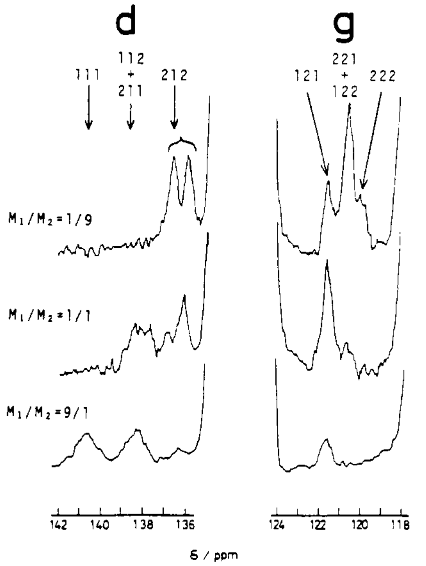


Figure 4. 25.0-MHz ^{13}C NMR spectra of a Me$_2$SO-d_6 solution of 5 at 100 °C.

ratios (1 and 2) were 1:9 (experiment 10), 1:1 (experiment 11), and 9:1 (experiment 12). Six kinds of signals split in these spectra were assigned as follows: for the nitrile carbon (g), 222, 221 and 122, 121; for the C$_1$ carbon of the benzene ring, 212, 112 and 211, 111 (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.

As the nuclear Overhauser effect caused by the total proton decoupling does not affect the relative intensities among the peaks assigned to the chemically equivalent carbons except for the stereochemical configurations even for ^{13}C{^{1}H} resonance, the fraction of triads was calculated from the areas obtained by integration of the signals, as shown in Table II.

Since monomer 1 is very bulky, the propagation process of this copolymerization is considered to be influenced by not only the terminal monomer unit but also the penultimate unit of the growing chain and is interpreted with a penultimate model.

The monomer reactivity ratios $r_1 = k_{111}/k_{112} = 0.23$, $r_1' = k_{211}/k_{212} = 0.41$, $r_2 = k_{222}/k_{221} = 0.08$, and $r_2' = k_{122}/k_{121} = 0.11$ were obtained on the basis of the chemical composition and the triad fractions of the copolymers.[10] As shown in Table II and Figure 5, the triad fraction and the chemical composition diagram calculated from these monomer reactivity ratios coincide with those of experiments. A considerable difference between r_1 and r_1' implies a steric influence of penultimate monomer unit 1 on the reactivity of the growing chains.

Table III shows the radical reactivity indices (RRI) and the frontier electron densities ($f_r^{(\mathrm{R})}$), where the orbital energy of the radical, λ, which attacks the monomer is assumed to be −0.15 au. Even if the orbital energy of attacking radical is assumed to be −0.05, −0.10, −0.20, or

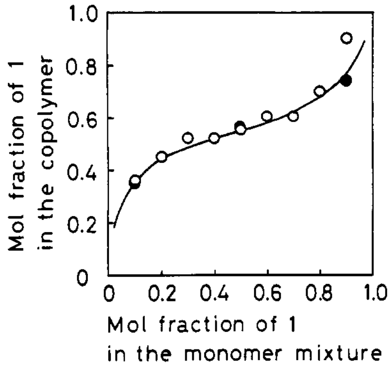
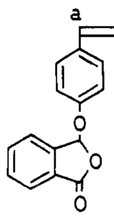
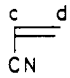


Figure 5. Polymer vs. monomer composition in the copolymerization of 3-(4-vinylphenoxy)phthalide (1) and acrylonitrile (2) (polymerization temperature, 45 °C; initiator, 2,2′-azobis(isobutyronitrile)): (○) conversion 1–4%; (●) conversion ca. 12%.

Table III
Radical Reactivity Indices (RRI) and Frontier Electron Densities ($f_r^{(R)}$) for 1 and 2



1



2

position	RRI^a	$f_r^{(R)}$
a	2.51	0.154
b	2.91	0.356
c	2.50	0.527
d	2.81	0.791

^{a} RRI was calculated by taking the value $\lambda = -0.15$ au.

-0.25 au, these trends are similar to that in Table III. RRI indicates that the reacting position of the monomer toward the growing chain radical is mostly at the b carbon in 1 and at the d carbon in 2. Accordingly, a head-to-tail polymer structure is deduced.

Selective Transport Ability of Alkali Metal Ions through the Present Membrane. Figure 6 shows the results of electrodialysis of the K^+-Li^+ binary system. The apparent selectivity (K^+ transported/Li^+ transported) varied with the fraction of opened lactone (α) in the membrane. The optimum in the apparent selectivity was 2 at $\alpha = 0.5$. In the K^+-Na^+ binary system, the selectivities (K^+/Na^+) were about 1 at any α.

In both systems, the total flux of alkali metal ions increased with α. The increase of the flux was caused by swelling of the membrane. In addition, the membrane for which α is zero still exhibits transport ability for alkali metal ions.

These facts suggest that the membrane prepared by the present method has pores which pass the metal ions and carboxylate carriers of the ring-opened lactone which transport metal ions.

The corrected selectivity for the fixed carboxylate carriers was evaluated by subtraction of the flux of K^+ and Li^+ when $\alpha = 0$ from those for another α. Figure 6 also shows the corrected selectivities. These corrected selectivities show a large increase with increasing fraction of unopened lactone moiety. This tendency implies that the present membrane has the capability of separating Li^+.

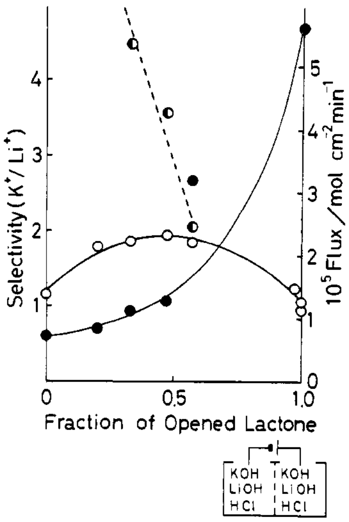


Figure 6. Selectivity and flux vs. the fraction of opened lactone in the electrodialysis system: (●) flux; (○) apparent selectivity; (◐) corrected selectivity.

In the previous paper,[4] it was shown that the selectivity of the alkali metal ions with a membrane made of 6 was affected by both affinity of alkali metal ions to the carboxylate formed by the ring opening of a lactone and hydrophobicity or hydrophilicity of the membrane. The selectivity of the present membrane is caused by the hydrophobicity of the two benzene rings of the lactone moiety as the fixed carrier of metal ions.

Summary

3-(4-Vinylphenoxy)phthalide is synthesized and copolymerized with acrylonitrile. The propagation process of this copolymerization is interpreted by using a penultimate model, and radical reactivity indices support the conclusion that the microstructure of the copolymer is head-to-tail.

The membrane made of this copolymer selectively transported alkali metal ions in the order $K^+ \simeq Na^+ > Li^+$ by electrodialysis. Utility of the 3-phenoxyphthalide moiety as a selective carrier of alkali metal ions is also implied.

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