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Synthesis and properties of novel vinyl polymers bearing azacrown ether side chain

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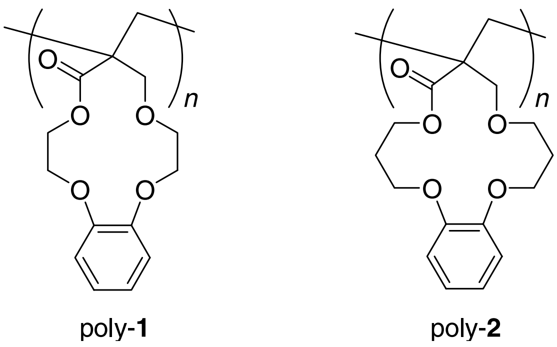
Summary

Novel vinyl polymers bearing monoazacrown ether-type side chains with a number average molecular weigh of over 5000 were radically synthesized from the 16-membered α-methylenemacrolide monomers. The obtained polymers possessed a Na^+ or K^+ selective extraction ability, whereas K^+ was preferentially extracted by the monomers. The polymer having the *N*-(2-naphthoyl)azacrown ether pendant groups showed a selective UV-responsive complexation with Li^+ in 1,2-dichloroethane-CH_3CN.

Introduction

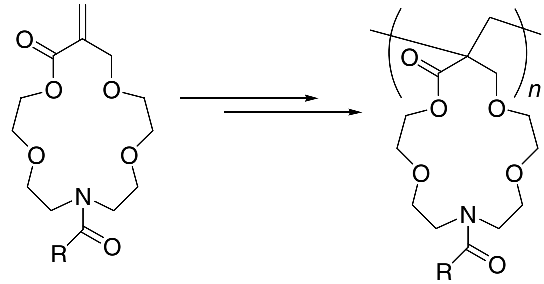
Many polymers bearing crown ether pendant groups have been synthesized due to their attractive functions, such as metal and molecular recognition abilities [1-11]. They often have crown ether moieties hanging from the main-chain, which are introduced by the polymerization of a monomer having a crown ether group as the substituent. Recently, we reported a novel type of polymer with crown ether side chains perpendicularly fixed on the main-chain, such as poly-**1** and poly-**2** (Scheme 1), constructed by the polymerization of macrocyclic α-(alkoxymethyl)acrylates, that is, α-methylenemacrolides with a crown ether-type framework [12-14].



Scheme 1.

These monomers possess two polymerizable groups, a methacrylic *exo*-methylene for the vinyl polymerization and a lactone for the ring-opening process. The chemospecific polymerizations were attained by radical and anionic methods for the former and using an enzymatic system for the latter [15,16]. The synthesized poly-**1** and poly-**2** showed new functionalities of selective alkali-ion extractabilities and cobalt ion transport abilities as a synthetic ion channel, based on the characteristic polymer structure.

In this study, novel macrocyclic α-(alkoxymethyl)acrylates bearing a 16-membered monoazacrown ether structure, **3** and **4**, were radically polymerized (Scheme 2) and the selective binding ability for the alkali metals of the obtained polymers was investigated.



R = 1-naphthyl: **3**
2-naphthyl: **4**

Scheme 2.

Experimental

Instruments

The ^{1}H NMR spectra were measured using a Mercury 200 (200 MHz) or Varian Unity-Inova (500 MHz) spectrometer in $CDCl_3$. The infrared (IR) and ultraviolet (UV) spectra were recorded using a Horiba FT-720 spectrometer and JASCO Ubest-55 spectrophotometer, respectively. The mass (MS) spectra were taken using a Shimadzu QP-5000 mass spectrometer. The size exclusion chromatographic (SEC) analyses were performed using a Hitachi L-7400 equipped with a Hitachi L-7400 UV detector and TSK G3000H and G7000H columns connected in series [eluent: tetrahydrofuran (THF), flow rate = 1.0 ml/min]. Calibration was carried out using standard polystyrenes.

Materials

The macrocyclic monomers, **3** and **4**, were synthesized from ethyl α-(bromomethyl)acrylate [17] with the corresponding diols in a total yield of 73% for **3** and 54% for **4** as previously reported [12-16].

3: ^{1}H NMR: δ 3.38-4.44 (m, 18H, $-OCH_2-$ and $-NCH_2-$), 5.74 (m, 1H, vinyl), 6.34 (m, 1H, vinyl), 7.39-7.86 (m, 7H, aromatic). IR (neat, cm^{-1}): 2946, 2867, 1720, 1633, 1508, 1471, 1309, 1267, 1130, 804. Mass (EI): *m/z* 413 $[M]^+$.

4: ^{1}H NMR: δ 3.54-4.32 (m, 18H, $-OCH_2-$ and $-NCH_2-$), 5.74 (m, 1H, vinyl), 6.33 (m, 1H, vinyl), 7.44-7.78 (m, 7H, aromatic). IR (neat, cm^{-1}): 2947, 2868, 1718, 1635, 1475, 1309, 1269, 1130, 820. Mass (EI): *m/z* 413 $[M]^+$.

Polymerization

The polymerization was carried out with α,α'-azobisisobutyronitrile (AIBN) as the initiator in THF ([monomer]/[initiator] = 50, [monomer] = 1.0 M) at 60 °C for 48 h. The product was isolated as the MeOH-benzene (10/1 (v/v))-insoluble fraction by centrifugation and drying under reduced pressure at 60 °C.

Alkali metal extraction experiments were conducted using picrate salts according to previously reported procedures [5,6,12].

Results and discussion

The monomers, **3** and **4**, were radically polymerized with AIBN in toluene at 60 °C (Table 1). The hexane-benzene (10/1 (v/v))-insoluble polymers were obtained in moderate yields with a number average molecular weight (M_n) of over 5000. Figure 1 shows the ^{1}H NMR spectra of the obtained poly-**3** and the peaks are assigned as shown in the figure. No vinyl proton was detected, indicating that the polymer has a normal vinyl polymer structure produced through the chemospecific reaction. It was also confirmed that the chemospecific vinyl polymerization proceeded during the polymerization of the monomer **4**.

Table 1. Polymertization of **3** and **4** in toluene at 60 °C for 48 h (initiator: AIBN; [monomer]/[initiator] = 50)

Run	Monomer	Yield^a (%)	M_n x 10^{-3b}	M_w/M_n^{b}
1	**3**	64	5.8	1.4
2	**4**	53	5.2	1.4

[a]hexane-benzene (10/1 (v/v))-insoluble part; [b]determined by SEC (polystyrene standard)

The alkali metal ion complexing abilities of the obtained poly-**3** and poly-**4** were examined. The extraction tests were performed with a polymer solution in 1,2-dichloroethane and aqueous alkali metal picrate solution under dark conditions (Figures 2 and 3) [5,6,12]. The UV value observed for the aqueous layer after extraction using 1,2-dichloroethane without including azacrown ether compounds

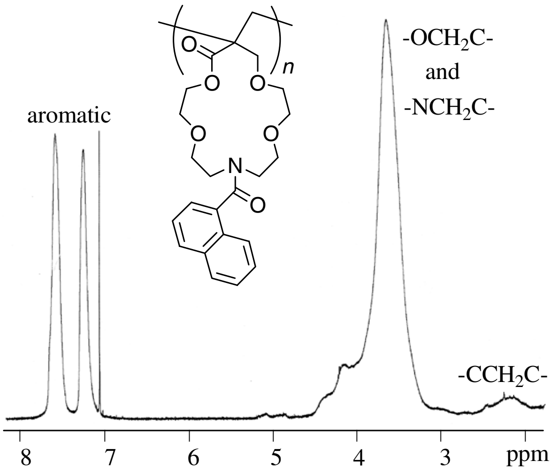


Figure 1. ^{1}H NMR spectrum of poly-**3** (Table 1, run 1) ($CDCl_3$, 60 °C)

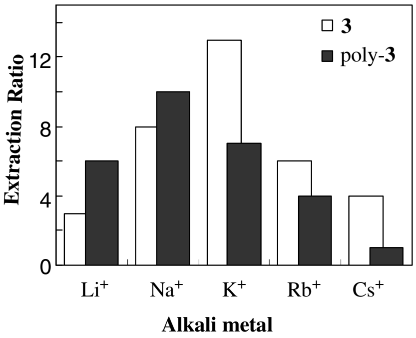


Figure 2. Extraction ratio of alkali metal picrates by **3** or poly-**3** into the 1,2-dichloroethane phase ([picric acid] = 3.9 x 10^{-2} M, [alkali metal hydroxide] = 1.0 x 10^{-2} M, [polymer] = 3.5 x 10^{-3} M/unit, determined by UV absorption intensity at 350 nm)

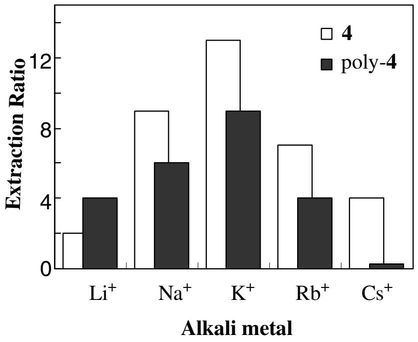


Figure 3. Extraction ratio of alkali metal picrates by **4** or poly-**4** into the 1,2-dichloroethane phase ([picric acid] = 3.9 x 10^{-2} M, [alkali metal hydroxide] = 1.0 x 10^{-2} M, [polymer] = 3.5 x 10^{-3} M/unit, determined by UV absorption intensity at 350 nm)

was used as a reference, and the ratios of change of the UV absorption intensity at 315 nm for the aqueous layer extracted by a polymer or monomer solution are exhibited. The monomers **3** and **4** showed a similar tendency for the extractability and preferentially extracted potassium ion. Although a stronger binding ability for K^+ than the other alkali metals was again observed for poly-**4**, poly-**3** showed the selective extraction for Na^+. Accordingly, a slight difference in the structure of the amide groups substituted on the azacrown ether side chains significantly affected the extraction ability.

It is known that the aza-15-crown-5 derivatives have a hole cavity matched to the sodium cation [18-20]. Therefore, the carbonyl group of the amides in the monomers may assist in the preferential binding to the potassium ion, whereas this amide assisted binding on the azacrown ether pendant group of the polymers may be prevented due to the crowded structure of the azacrown ether, which is continuously fixed on the main-chain without flexibility, especially, in poly-**3** having 1-naphthoyl groups.

Since the polymers showed the characteristic alkali ion extractability, further investigation of the UV spectral changes of the polymers by adding various alkali metals, that functions as an UV-responsive chemosensor material for alkali metal ions, was carried out. Figure 4 and 5 depict the UV spectra of the polymers in the absence or presence of alkali metal hexafluorophosphate in 1,2-dichloroethane-CH_3CN (1/1(v/v)) ([polymer] = 7.0 x 10^{-5} M, [MPF_6] = 7.0 x 10^{-3} M). The spectral change was hardly observed between the poly-**3** in the absence and presence of the alkali metals, such as Li^+, Na^+, and K^+. However, the absorption intensity was significantly reduced when $LiPF_6$ was added to a solution of poly-**4**, although Na^+ and K^+ did not affect the UV absorption of poly-**4**.

The UV spectra of poly-**4** in the presence of $LiPF_6$ with various [Li^+]/[monomer unit] ratios are shown in Figure 6. The absorption intensity around 275 nm clearly decreased with an increase in the Li^+ concentration, and the polymer solution became turbid with the addition of 200 equivalents of $LiPF_6$. These results indicate that lithium cation was selectively recognized by poly-**4** in 1,2-dichloroethane-CH_3CN, and the structure of the naphthoyl groups substituted on the azacrown ether side chains again have a significant influence on the complexing ability of the alkali metals.

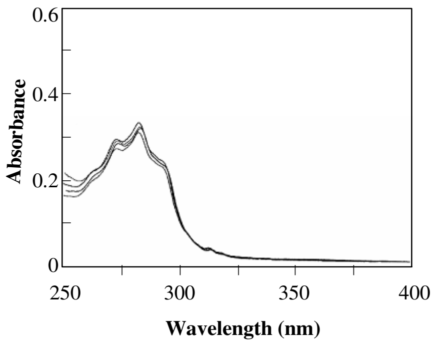


Figure 4. UV spetra of poly-**3** in the absence and presence of $LiPF_6$, $NaPF_6$, and KPF_6 ($[MPF_6] = 7 \times 10^{-3}$ M, $[MPF_6]/[poly\text{-}\mathbf{3}] = 100$, solvent = 1,2-dichloroethane-CH_3CN (1/1 (v/v)))

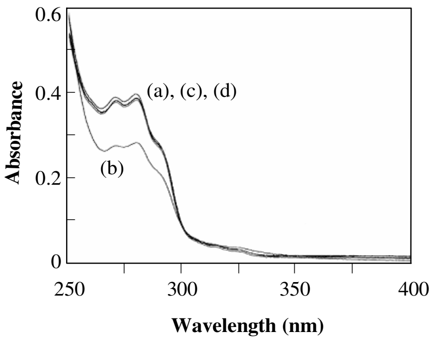


Figure 5. UV spetra of poly-**4** in the absence (a) and presence of $LiPF_6$ (b), $NaPF_6$ (c), and KPF_6 (d) ($[MPF_6] = 7 \times 10^{-3}$ M, $[MPF_6]/[poly\text{-}\mathbf{4}] = 100$, solvent = 1,2-dichloroethane-CH_3CN (1/1 (v/v)))

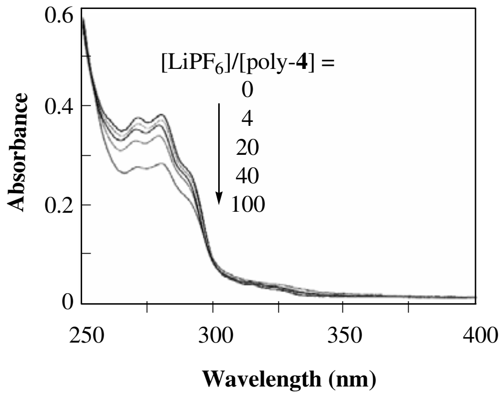


Figure 6. UV spetra of poly-**4** in the absence and presence of $LiPF_6$ ($[poly\text{-}\mathbf{4}] = 7 \times 10^{-5}$ M, solvent = 1,2-dichloroethane-CH_3CN (1/1 (v/v)))

Conclusions

Novel vinyl polymers bearing the perpendicularly fixed 16-membered monoazacrown ether-type side chains showed characteristic alkali metal ion complexing abilities, which were different from those of the monomers, and are significantly affected by the structure of the amide groups substituted on the azacrown ether.

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