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Polymeric chiral crown ethers

9. Synthesis and chiral recognition ability of copolymers with (*S*)-binaphtho-21-crown-6 and D-manno-21-crown-6 units by cyclocopolymerizations of α,ω-divinylethers with monovinylether*

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Summery

Copolymerizations of (S)-3,3'-dimethyl-2,2'-bis[2-(2-vinyloxyethoxy)ethoxy]-1,1'-binaphthyl (S-MVN) or 1,3:4,6-di-*O*-benzylidene-2,5-bis-*O*-[2-(2-vinyloxyethoxy)ethyl]-D-mannitol (D-BVM) with isobutyl vinyl ether (IBVE) were carried out with $BF_3{\bullet}OEt_2$ in CH_2Cl_2 at 0 °C. The copolymers obtained were soluble in $CHCl_3$ and THF, and consited of (S)-binaphtho-21-crown-6 or D-manno-21-crown-6 units and IBVE, i.e., poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE). These host copolymers dominantly formed complexes with L-phenylglycine methyl ester, whose properties were similar to those for homopolymers of S-MVN and D-BVM.

Introduction

Cationic cyclopolymerization of α,ω-divinyl ethers is a facile method for producing polymers with various types of crown ether units (1). Recently, we reported that the copolymerization of α,ω-divinylethers and monovinylether with conventional cationic initiators proceeds without crosslinking to give copolymers with crown ether units (2). The high cyclization tendency of α,ω-divinylether in homo- and copolymerization is attributed to the intramolecular solvation of the uncyclized growing-carbocation originating from α,ω-divinylether. In the host-guest complexation, poly[(benzo-19-crown-6)-*co*-IBVE]s, which were prepared by the copolymerization of 1,2-bis[2-(2-vinyloxyethoxy)ethoxy]benzene and isobutyl vinyl ether (IBVE), showed the cation-binding property toward alkali-metal picrates, regardless of the mole fraction of crown ether units. Of interest, therefore, is the synthesis of copolymers with optically active crown ether units by copolymerization of α,ω-divinylether with monovinylether and the effect of monovinylether units on their chiral recognition property.

In this paper, we report on the syntheses of copolymers with different mole fractions of chiral crown ether units by the cationic copolymerizations of (S)-3,3'-dimethyl-2,2'-bis[2-(2-vinyloxyethoxy)-ethoxy]-1,1'-binaphthyl (S-MVN) and 1,3:4,6-di-*O*-benzylidene-2,5-bis-*O*-[2-(2-vinyloxyethoxy)ethyl]-D-mannitol (D-BVM) with IBVE, and on the

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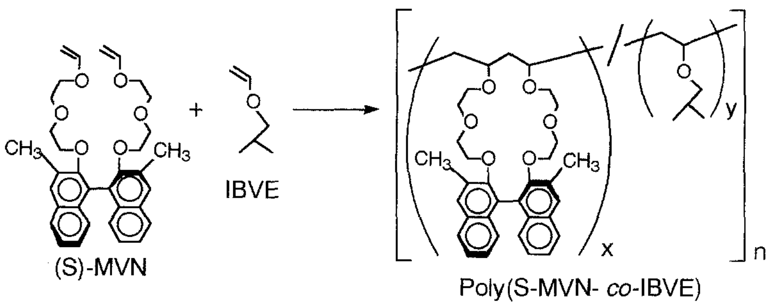
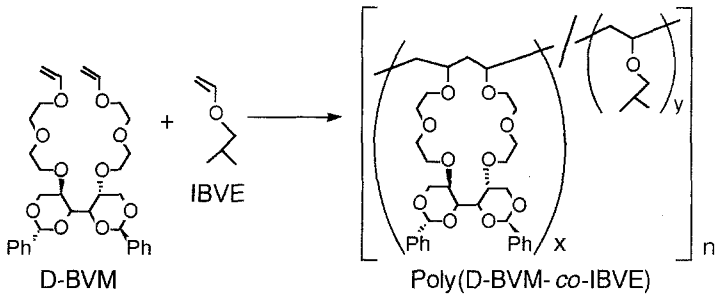




chiral recognition property of poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE) toward racemic phenylglycine methyl ester.

Experimental

Materials: The syntheses of (S)-3,3'-dimethyl-2,2'-bis[2-(2-vinyloxyethoxy)ethoxy]-1,1'-binaphthyl (S-MVN) and 1,3:4,6-di-*O*-benzylidene-2,5-bis-*O*-[2-(2-vinyloxyethoxy)ethyl]-D-mannitol (D-BVM) were reported in previous papers (3,4). Isobutyl vinyl ether (IBVE) and boron trifluoride etherate ($BF_3{\bullet}OEt_2$) were purified by distillation of commercial products under reduced pressure. Dichloromethane was purified by the usual method and distilled over calcium hydride.

Measuements: ^1H NMR spectra were recorded with a Hitachi R 90H instrument. Optical rotations were determined with a Jasco DIP-140 digital polarimeter. The molecular weight of the resulting copolymers was measured by gel permeation chromatography (GPC) in tetrahydrofuran on a WATERS M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex A-802, A-803, and A-805).

Copolymerization procedures: All the copolymerizations were carried out with $BF_3{\bullet}OEt_2$ in dichloromethane using side-armed ampoules. At the end of the polymerization, the reaction mixture was poured into a large amount of methanol. The resulting copolymers were purified by reprecipitation from chloroform-methanol.

Chiral recognition toward racemic phenylglycine methyl ester: The chiral recognition of chiral polymers was evaluated as described in a previous paper (5).

Results and discussion

Syntheses of Copolymers with Chiral Crown Ether Units

For the syntheses of homo- and copolymers with crown ether units, the polymerization with BF_3•OEt_2 in dichloromethane is suitable (1,2). The higher comonomer concentration is needed for a copolymerization with a lower mole fraction of α,ω-divinylether in monomer feed, because the copolymerization rate extreamely decreased with decreasing mole fraction of α,ω-divinylether. Table 1 lists the results of the copolymerizations of S-MVN and D-BVM with IBVE. All the copolymerizations proceeded homogeneously and the copolymers obtained were soluble in benzene, chloroform, and THF. The number-average molecular weight ($\overline{M}n$) was from 7,900 to 11,000 and from 8,600 to 9,900 for poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE), respectively.

Figure 1 shows the ^{1}H NMR spectra of poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE) obtained with the mole fraction of α,ω-divinylether

Table 1

Copolymerizations of (S)-3,3'-dimethyl-2,2'-bis[2-(2-vinyloxyethoxy)ethoxy]-1,1'-bi-2-naphthyl (S-MVN) and 1,3:4,6-di-*O*-benzylidene-2,5-bis-*O*-[2-(2-vinyloxyethoxy)-ethyl]-D-mannitol (D-BVM) with isobutyl vinyl ether (IBVE) by use of BF_3•OEt_2 in CH_2Cl_2 at 0 °C [a)]

Divinyl ether (DVE)	Mole fraction of DVE in monomer	[DVE+ IBVE] mol•L^{-1}	Time h	Yield %	Mole fraction of DVE units in copolymer [b)]	$\overline{M}n$ [c)] x 10^{-3}	$[\alpha]_D$ [d)]
S-MVN	0.25	0.35	3	64	0.27	7.9	14.4
	0.50	0.20	3	83	0.57	11.0	23.2
	0.75	0.15	1	72	0.79	9.3	30.1
D-BVM	0.25	0.40	2	60	0.26	8.6	-26.3
	0.50	0.20	3	70	0.52	9.1	-30.6
	0.75	0.15	2	89	0.77	9.9	-35.4

a) [BF_3•OEt_2]=1.0 mmol•L^{-1}.
b) Determined by ^{1}H NMR spectra.
c) Determined by GPC (polystyrene calibration)
d) c=1.0 in $CHCl_3$ at 25 °C.

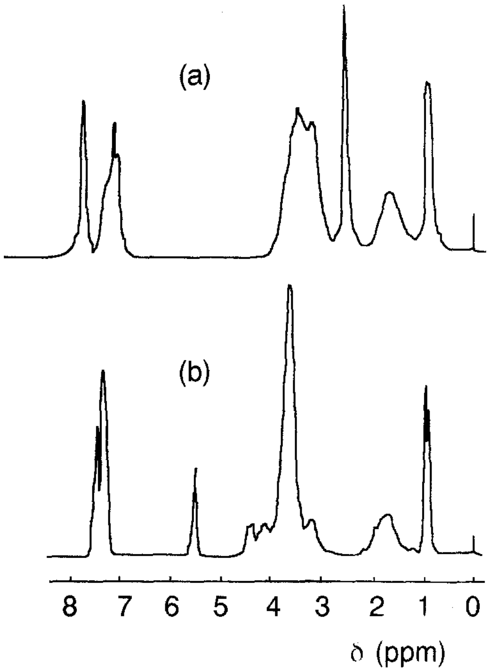
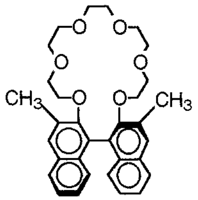


Figure 1. ^{1}H-NMR spectra of (a) poly(S-DVN-*co*-IBVE) and (b) poly(D-BVM-*co*-IBVE) in $CDCl_3$

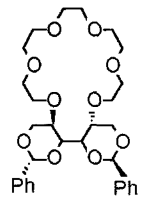
of 0.5 in monomer feed. The characteristic absorption at 6.3-6.6 ppm due to the vinyloxy protons had completely disappeared, and thus, S-MVN and D-BVM polymerized with 100% cyclization. The copolymers obtained under other conditions also contained no residual vinyloxy bond. The incorporation of the comonomer, IBVE, did not inhibit the intramolecular cyclization of S-MVN and D-BVM. Since α,ω-divinylether polymerizes with a cationic initiator through a cylopolymerization mechanism involving the head-to-tail addition (1b,6), the cyclic constitutional units in the copolymer are (S)-binaphtho-21-crown-6 and D-manno-21-crown-6. The mole fractions of S-MVN and D-BVM units in the copolymers, which were determined by ^{1}H NMR spectra, were azeotropic, though slightly larger than those in monomer feeds

Chiral Recognition by Opticaly Active Host Polymers

Table 2 lists the chiral recognition property of the host polymers, poly[((S)-binaphtho-21-crown-6)-*co*-IBVE]s and poly[(D-manno-21-crown-6)-*co*-IBVE]s, toward racemic phenylglycine methyl ester ($PhGlyOCH_3$) as a guest. For estimating the chiral recognition ability, the enantiomer distribution constant (EDC) is defined as EDC= $([G_A]_{org} / [G_A]_{aq})/([G_B]_{org} / [G_B]_{aq})$, where $[G_A]_{org}$ and $[G_B]_{org}$, for example, are the concentrations of the more(A) or less(B) soluble guest enantiomers in the CH_2Cl_2 phase, respectively.



(S)-Binaphtho-20-crown-6



D-Manno-20-crown-6

The excess enantiomer of the guest extracted into the CH_2Cl_2 phase containing a host polymer was the L-isomer for the all host-guest systems. The enantioselectivity for homo- and copolymers was based on those for (S)-binaphtho-20-crown-6 (7) and D-manno-20-crown-6 (4) which correspond to the cyclic constitutional units in both polymers. The copolymer composition affected chiral recognition, and the optical purities of guest changed from 14.2 to 20.4 % and from 9.4 to 15.9 %

Table 2

Chiral recognition of DL-$C_6H_5(CO_2CH_3)NH_3{\bullet}PF_6$ ($PhGlyOCH_3$) by the copolymers with (S)-binaphtho-21-crown-6 and D-manno-21-crown-6 units [poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE)] [a]

Molar ratio of 21-crown-6 and IBVE units in copolymers (x/y)	$PhGlyOCH_3$ in CH_2Cl_2 phase		EDC [b]
	optical purity %	dominant cofign.	
poly(S-DVN_x-*co*-$IBVE_y$)			
0.27/0.73	20.4	L	1.72
0.57/0.43	15.0	L	1.45
0.79/0.21	14.2	L	1.46
1.0/0	18.9	L	1.66 [c]
poly(D-BVM_x-*co*-$IBVE_y$)			
0.26/0.74	10.4	L	1.50
0.57/0.43	15.9	L	1.61
0.77/0.23	9.4	L	1.42
1.0/0	14.2	L	1.52 [d]

a) [Crown ether units]=0.2 $mol{\bullet}L^{-1}$ in CH_2Cl_2; $[C_6H_5CH(CO_2CH_3)NH_3{\bullet}PF_6]$= 1.0 $mol{\bullet}L^{-1}$ in H_2O; $[C_6H_5CH(CO_2CH_3)NH_3{\bullet}PF_6]$/ [Crown ether units]=3; temp, 0 °C.

b) The enantiomer distribution constant is defined as $EDC=([G_A]_{org}/[G_A]_{aq})/([G_B]_{org}/[G_B]_{aq})$, where $[G_A]_{org}$ and $[G_B]_{org}$, $[G_B]_{aq}$ and $[G_A]_{aq}$ are the concentration of the more(A) or less(B) soluble guest enantiomers in the CH_2Cl_2 phase, and the concentration in the water phase, respectively.

c) ref. 3.

d) ref. 4.

for poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE), respectively. The EDC values did not systematically depend on the copolymer composition. The maximum values were, however, 1.72 and 1.62 for poly(S-DVN-*co*-IBVE) and poly(D-BVM-*co*-IBVE), respectively, which were slightly larger than those for homopolymers of S-DVN and D-BVM. These results indicate that a difference in distance between two neighboring crown ethers, namely, the crowdedness of the crown ether would affect the chiral recognition ability of the copolymers. The more investigation is, however, nessesary to discuss these effect, because the difference in EDC values was so small.

Acknowledgements

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