Notes

Spontaneous 1:1 Alternating Cooligomerizations of 4,5-Cyclohexano-2-oxazoline with Acrylic Acid and with β-Hydroxyethyl Acrylate

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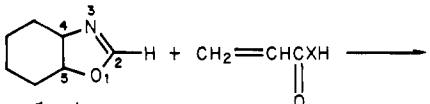
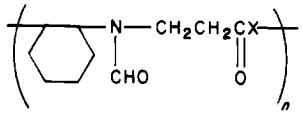
The present study reports an extension of "No Catalyst Alternating Copolymerization via Zwitterion Intermediates", in which a nucleophilic monomer (M_N) and an electrophilic monomer (M_E) are combined to produce a zwitterion of the key intermediate.[1] In the above copolymerizations, cyclic imino ethers, such as 2-oxazolines and 5,6-dihydro-4*H*-1,3-oxazines, have been adopted as M_N and combined with the electrophilic monomers β-propiolactone, acrylic acid (AA), and β-hydroxyethyl acrylate (HEA).[2] In the present study, monomers of a bicyclic 2-oxazoline system, 4,5-*trans*- and 4,5-*cis*-cyclohexano-2-oxazolines (**1a** and **1b**, respectively), were employed as new M_N's, which were combined with AA and with HEA to produce 1:1 cooligomers **2** and **3**.



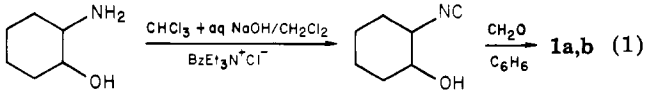
1a, trans
b, cis

AA, X = O
HEA, X = OCH_2CH_2O



2a, cis; X = O
b, trans; X = O
3, cis; X = OCH_2CH_2O

Synthesis of Monomer. The two isomers **1a** and **1b** have been prepared for the first time according to reaction 1. First, 2-aminocyclohexanols **4** (trans and cis) were



4a, trans
b, cis

5a, trans
b, cis

(1)

prepared,[3,4] and these were converted to 2-hydroxycyclohexyl isocyanides **5** (trans and cis) by the Hofmann carbylamine reaction.[5] Then, **5** was transformed into the bicyclooxazoline **1** by copper-catalyzed cyclization[6] to give **1a** (trans isomer) and **1b** (cis isomer) in 41% and 31% yields based on **4**, respectively.

In the ^1H NMR spectra (Figure 1) the methine protons H-4 and H-5 of the trans isomer **1a** appear at δ 2.7–3.8 whereas those of the cis isomer **1b** appear at much lower field, at δ 3.7–4.2 (H-4) and δ 4.3–4.7 (H-5). According to a ^1H NMR study of 2-aminocyclohexanol[7] the signals of methine protons of NCH and OCH equilibrating in the axial and equatorial positions are shifted downfield compared with those of the axial-fixed methine protons. The chemical shift difference of the above signals of **1a** and **1b**

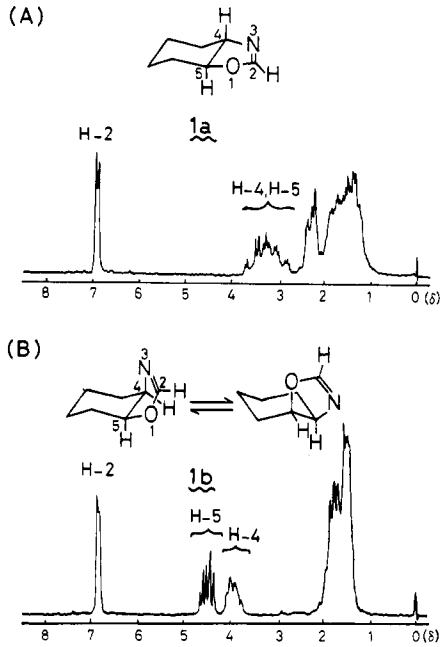


Figure 1. ^1H NMR spectra ($CDCl_3$, 60 MHz) of the trans-monomer **1a** (A) and the cis-monomer **1b** (B).

Table I
Cooligomerizations of 4,5-Cyclohexano-2-oxazolines (M_N) with AA and with HEA (M_E)[a]

no.	M_N	M_E	time, h	temp, °C	% yield	cooligomer structure	MW
1[b]	**1a**	AA	125	88	48	**2a**	1300[c]
2	**1a**	AA	130	100	55	**2a**	1200[c]
3	**1a**	AA	150	180	68	**2a**	1500[d]
4	**1b**	AA	130	100	53	**2b**	1400[d]
5	**1a**	HEA	105	100	44	**3**	1300[c]
6	**1b**	HEA	105	100	homooligomer of HEA		

[a] [1] = [M_E] = 3.0 mmol each in 1.0 mL of PhCN under nitrogen in the presence of *p*-methoxyphenol (0.01 mmol) as a radical inhibitor unless otherwise noted. [b] [1] = [M_E] = 2.4 mmol each in 0.2 mL of CD_3CN. [c] Determined by vapor pressure osmometry (Corona 117 molecular weight apparatus) in DMF at 55 °C. [d] Determined by vapor pressure osmometry (Corona 117 molecular weight apparatus) in $CHCl_3$ at 35 °C.

can probably be understood in an analogous manner. Therefore, it is reasonable to consider that under the NMR measurement conditions (35 °C) **1a** is present in the form shown in Figure 1A whereas **1b** is rapidly equilibrating between the conformers shown in Figure 1B in terms of the NMR time scale. Similar phenomena have also been observed with 2-methyl-4,5-cyclohexano-2-oxazoline.[8]

Cooligomerization. Reactions of **1** with equimolar amounts of AA and HEA gave 1:1 alternating cooligomers **2** and **3** (Table I). Cooligomerizations with **1** as M_N required higher temperatures and longer reaction times to obtain cooligomers than the copolymerizations with unsubstituted 2-oxazoline.[2] The structure of the cooligomers was determined by ^1H NMR, IR, and elemental analyses.

In the reactions of **1a** and **1b** with AA, alternating cooligomers **2a** and **2b** were produced ($\overline{DP}$ = 6.3–7.9). In the IR spectra of both cooligomers two characteristic carbonyl bands were observed at 1730 (ester) and 1660

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Table II
Elemental Analyses of Cooligomers

sample no.		% C	% H	% N
2	calcd[a]	60.90	7.67	7.10
	found	61.18	7.71	6.82
4	calcd[a]	60.90	7.67	7.10
	found	61.02	7.72	7.13
5	calcd[b]	59.73	7.94	5.81
	found	59.56	7.73	5.57

[a] Calculated for the 1:1 composition $(C_{10}H_{15}NO_3)_n$. [b] Calculated for the 1:1 composition $(C_{12}H_{19}NO_4)_n$.

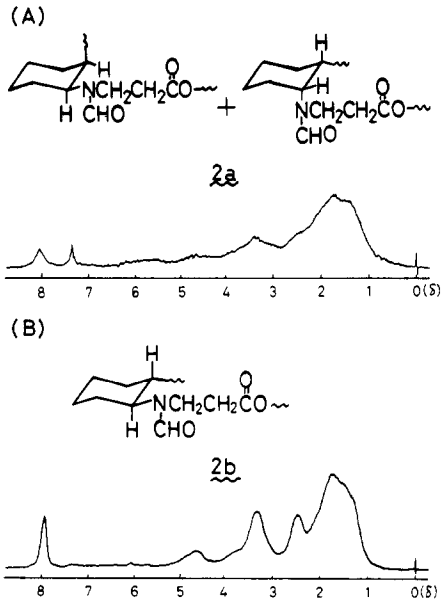
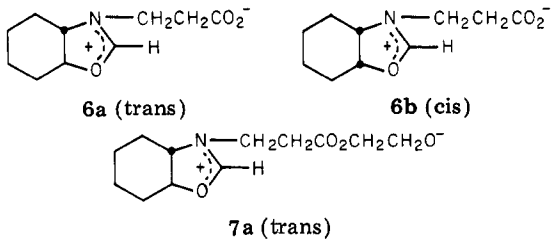


Figure 2. ^1H NMR spectra ($CDCl_3$, 60 MHz) of cooligomers **2a** (A) and **2b** (B).

cm^{-1} (amide). The **1a**–HEA system gave alternating cooligomer **3**, showing IR bands at 1734 (ester) and 1655 cm^{-1} (amide). However, reaction of **1b** and HEA gave a homooligomer of HEA in low yield (11%). Results of elemental analyses of the cooligomers support the 1:1 composition of **1** and AA or HEA (Table II).

The ^1H NMR spectra of **2a** and **2b** are shown in Figure 2. Signals of **2a** are much broader than those of **2b**. The signal assignment of **2b** is as follows: a singlet at δ 8.0 (NCHO, 1H), a broad signal at δ 4.5–5.1 ($CO_2CH<$, 1 H), broad signals at δ 3.0–4.0 ($NCH<$ + NCH_2, 3 H), and broad signals at δ 1.0–2.8 ($C(O)CH_2$ and CH_2 of the cyclohexane ring, 10 H). In the spectrum of **2a** the proton of NCHO appears as two singlets (δ 8.0 and 7.4) and the methine proton of $CO_2CH<$ appears at δ 4.5–6.3 as two very broad signals. Other signals of **2a** are seen in the corresponding regions of **2b**. The signal broadening of **2a** in comparison with **2b** may be explained as follows. With ring opening of **1b** by electrophilic attack at C-5 the configuration at the carbon is inverted and hence the stereochemistry of the cyclohexane ring in **2b** takes a stable diequatorial conformation. On the other hand, **2a** is in axial–equatorial equilibrium therefore **2a** is present under the NMR measurement conditions in both N-axial–O-equatorial and N-equatorial–O-axial forms. Two kinds of NCHO and $CO_2CH<$ signals can be attributed to the existence of the two stereoisomers of polymer **2a**.

Reaction Mechanism. The cooligomerizations probably proceeded via zwitterion intermediates such as **6a**, **6b**, and **7a**. Subsequent reactions between the respective intermediates led to the production of cooligomers **2a**, **2b**,

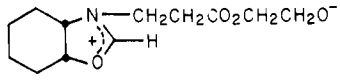


6a (trans) 6b (cis)

7a (trans)

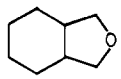
and **3**.[1] In these bicyclic systems the ring-opening propagation involves nucleophilic attack at C-5 with inversion of configuration at the carbon according to an S_N2 reaction. The reactivity of this mode of reaction is much reduced in comparison with that of the polymerization reactions of monocyclic 2-oxazolines.[2] Therefore, the present reactions required higher reaction temperatures and produced cooligomers.

The reaction of **1b** and HEA did not yield cooligomer but produced a homooligomer of HEA in low yield. Probably zwitterion **7b** was first formed and then **7b** in-



7b (cis)

duced the anionic homopropagation of HEA. The difference in behavior of **1a** and **1b** toward HEA may be caused by the different ring-opening polymerizability of **7a** and **7b** derived from **1a** and **1b**, respectively. In support of this observation we mention the cationic ring-opening polymerization of *trans*- and *cis*-8-oxabicyclo[4.3.0]nonanes (**8a** and **8b**).[9] Trans-isomer **8a** polymerized readily but



8a, trans
b, cis

cis-isomer **8b** failed to polymerize, mainly due to the smaller ring strain of **8b**. Although the reaction mode and site for **8** are different from those for **1**, the ring-strain argument may be applied to the case of **1**, too, since both have the structure of the bicyclo[4.3.0] system. Therefore, trans-isomer **1a** is probably more strained than cis-isomer **1b** and hence **7a** has a higher ring-opening reactivity than **7b**. Consequently, **7a** gave cooligomer **3**, but in the case of **7b** the reaction of **7b** with HEA was preferable compared with that between **7b**, leading to the production of homopolymer of HEA.

In the reactions of **1** and AA, on the other hand, the homopolymerizability of AA is very low and hence the ring-opening reaction of **6a** and **6b** became preferable to give 1:1 alternating cooligomers, **2a** and **2b**, respectively.

Experimental Section

Materials. Benzonitrile was purified by distillation under nitrogen and acetonitrile-d_3 was dried over molecular sieves. Acrylic acid (AA) and β-hydroxyethyl acrylate (HEA) were commercial reagents and were purified by distillation under nitrogen. *trans*-2-Aminocyclohexanol (**4a**) was prepared according to the reported procedure, using cyclohexene oxide instead of 2-chlorocyclohexanol.[3] *cis*-2-Aminocyclohexanol (**4b**) was obtained by using a phenyloxazoline intermediate.[4]

***trans*-2-Hydroxycyclohexyl Isocyanide (5a).** To a solution of *trans*-2-aminocyclohexanol (**4a**) (30.0 g, 260 mmol), triethylbenzylammonium chloride (2.0 g), and $CHCl_3$ (36 mL) in 300 mL of CH_2Cl_2, 50% aqueous NaOH solution (150 mL) was added gradually with stirring, so that the solvent was refluxed gently. After the addition was complete, the mixture was refluxed for an additional 4 h. After the mixture cooled to room temperature,

300 mL of water was added and the product was extracted with CH_2Cl_2 and dried over anhydrous K_2CO_3. Crude **5a** was obtained by vacuum evaporation of solvent at room temperature; IR $\nu_{N\equiv C}$ 2120 cm^{-1}).

***trans*-4,5-Cyclohexano-2-oxazoline (1a).** A solution of crude **5a** and cuprous oxide (600 mg) in 430 mL of anhydrous benzene was heated to reflux until the infrared N≡C band of **5a** disappeared. After filtration, the solvent was evaporated, and distillation of the residue gave analytically pure **1a**: 13.4 g, 41% yield from **4a**; bp 68–69 °C (14 mmHg); IR 1592 ($\nu_{N=C}$), 1072 cm^{-1} (ν_{C-O-C}); mass spectrum, *m/e* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.90; H, 8.95; N, 11.16.

***cis*-4,5-Cyclohexano-2-oxazoline (1b)** was similarly obtained from **4b** prepared by the procedure previously reported,[4] to give **1b** in 31% yield [Kugelrohr, bp 75 °C (18 mmHg)]: IR 1628, 1612 ($\nu_{N=C}$), 1090 cm^{-1} (ν_{C-O-C}); mass spectrum, *m/e* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.01; H, 9.01; N, 11.25.

Cooligomerization. A typical procedure was as follows. In a sealed tube **1a** (3 mmol), AA (3 mmol), and *p*-methoxyphenol (0.01 mmol) were placed in 1.0 mL of benzonitrile under nitrogen. The mixture was allowed to react at 130 °C. After 100 h, the reaction mixture was poured into a large amount of diethyl ether to precipitate the oligomeric materials. The product was isolated by decantation and purified further by reprecipitation from chloroform into diethyl ether. The pale yellow solid cooligomer obtained was dried in vacuo and weighed.

References and Notes

(1) Reviews: (a) Saegusa, T. *CHEMTECH* **1975**, *5*, 295. (b) Saegusa, T.; Kobayashi, S.; Kimura, Y.; Ikeda, H. *J. Macromol. Sci., Chem.* **1975**, *A9*, 641. (c) Saegusa, T. *Angew. Chem.* **1977**, *89*, 867. (d) Saegusa, T.; Kobayashi, S. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 62*, 79. (e) Saegusa, T.; Kobayashi, S. *Pure Appl. Chem.* **1978**, *50*, 281. (f) Saegusa, T.; Kobayashi, S. *J. Macromol. Sci., Chem.* **1979**, *A13*, 295.

(2) (a) Saegusa, T.; Kobayashi, S.; Kimura, Y. *Macromolecules* **1974**, *7*, 139. (b) Saegusa, T.; Kimura, Y.; Kobayashi, S. *Ibid.* **1977**, *10*, 236. (c) Saegusa, T.; Kimura, Y.; Kobayashi, S. *Ibid.* **1977**, *10*, 239.

(3) Wilson, N. B. A.; Read, J. *J. Chem. Soc.* **1935**, 1269.

(4) Johnson, W. S.; Schubert, E. N. *J. Am. Chem. Soc.* **1950**, *72*, 2189.

(5) Weber, W. P.; Gokel, G. W. *Tetrahedron Lett.* **1972**, 1637.

(6) Ito, Y.; Kobayashi, K.; Saegusa, T. *Tetrahedron Lett.* **1978**, 2087. Hydroxy isocyanides are known to give 2*H*-oxazolines: Gerhard, F.; Schöllkopf, U. *Ibid.* **1968**, 6231. Meyers, A. I.; Adickes, H. W. *Ibid.* **1969**, 5151.

(7) Pavia, A.; Winternitz, F.; Wylde, R. *Bull. Soc. Chim. Fr.* **1966**, 2506.

(8) Bannard, R. A. B.; Gibson, N. C. C.; Parkkari, J. H. *Can. J. Chem.* **1971**, *49*, 2064.

(9) Kops, J.; Spanggard, H. *Makromol. Chem.* **1974**, *175*, 3089.

A Cardo Polyquinoline from an AB Monomer

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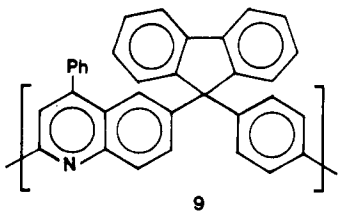
Aromatic polymers containing pendent rings in which a carbon of the ring is also a member of the polymer main chain—and therefore a quaternary carbon—have been shown to possess enhanced solubility in organic solvents and higher glass transition temperatures than the analogous polymers without this ring or cardo structure.[1] Cardo polyquinolines prepared from symmetrical AA bis(*o*-amino ketone) and BB bis(ketomethylene) monomers containing the appropriate ring structures are amorphous.[2] These AA–BB cardo polyquinolines, in which the quaternary carbon in the ring has replaced oxygen links connecting quinoline and biphenylene units in the chain, have better solubility in organic solvents and glass transition temperatures that are as much as 140 °C higher than the oxygen-linked analogues. In this paper, the synthesis of an AB cardo monomer and the polymer obtained therefrom are reported.

Results and Discussion

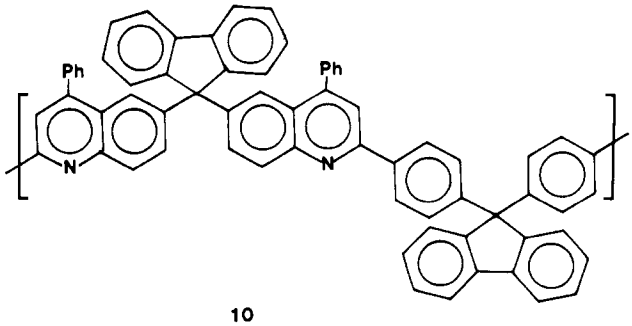
In order to construct the aromatic *o*-amino ketone and ketomethylene groups attached to the cardo unit, it was advantageous to generate the unsymmetric cardo carbon early in the synthesis by introducing functionalities that later could be converted into the appropriate polyquinoline-forming groups. The synthesis was accomplished in eight relatively simple steps (Scheme I). Reaction of (4-ethylphenyl)magnesium bromide[3] and 9-fluorenone produced the carbinol 9-hydroxy-9-(4-ethylphenyl)fluorene (**1**) in isolated yields of 90%. The crude alcohol underwent condensation with aniline[4] to introduce the arylamine portion, thus forming the unsymmetric arylalkyl amine 9-(4-aminophenyl)-9-(4′-ethylphenyl)fluorene (**2**) in 50% yields. Oxidation of the amino group with *m*-chloroperbenzoic acid (*m*-CPBA)[5] gave 9-(4-nitrophenyl)-9-(4′-ethylphenyl)fluorene (**3**). Oxidation of the benzylic carbon with catalytic amounts of silver persulfate[6] in an acetonitrile–water two-phase system generated the acetyl unit. The 40% yields of 9-(4-nitrophenyl)-9-(4′-acetylphenyl)-fluorene (**4**) were low compared to the yields reported[6] for substrates that were liquid under the reaction conditions. Protection of the carbonyl group and subsequent base-assisted condensation of **5** with phenylacetonitrile[7] gave the benzisoxazole **6**. Finally, hydrogenation of the benzisoxazole ring over palladium-on-charcoal generated the *o*-amino ketone function on one side of the monomer while deketalization of **7** with a dilute hydrochloric acid–tetrahydrofuran mixture released the ketomethylene group on the other side of the monomer to give 9-(4-amino-3-benzoylphenyl)-9-(4′-acetylphenyl)fluorene (**8**).

The polymerization of **8** was carried out in a mixture of *m*-cresol and di-*m*-cresyl phosphate at 135–140 °C for 4–6 h to give polyquinoline **9**.



9

Surprisingly, the AB cardo polyquinoline was not soluble in chloroform or *sym*-tetrachloroethane whereas those cardo polyquinolines obtained from the polymerization of AA with BB monomers are soluble in these solvents.[2] Polymer **9** was soluble in strong acids and in *m*-cresol (>20% w/v; $[\eta]_{m\text{-cresol}}$ = 0.24 dL/g). The glass transition temperature of **9** (powdered samples) is 365 °C, 25 °C lower than that of the analogous AA–BB polymer **10** containing fluorene in each monomer unit. Both **9** and **10** are amorphous.



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