

Asymmetric Anionic Polymerization of 7-Cyano-7-alkoxycarbonyl-1,4-benzoquinone Methides

¹Takahiro Uno, ¹Noboru Nakagaki, ¹Shoko Iizuka, ¹Takeshi Nagai, ²Masataka Kubo and ¹Takahito Itoh

¹Graduate School of Engineerig, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, Japan.

²Graduate School of Regional Innovation Study, Mie University, 1577 Kurimamashiya-cho, Tsu 514-8507, Japan.

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ABSTRACT

7-Cyano-7-alkoxycarbonyl-1,4-benzoquinone methides (**1**) with various alkoxy groups were polymerized by using chiral anionic initiators. The effect of the alkoxy groups on the specific rotation and stereoselectivity of the obtained polymers and oligomers were investigated in detail. The specific rotations of polymers decreased with an increase in the bulkiness of substituent, and the polymer with the highest specific rotation was obtained from the monomer (**1b**) bearing ethoxy group.

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INTRODUCTION

Naturally occurring polymers such as proteins, polysaccharides, and nucleic acids have many chiral centers whose configurations are perfectly controlled, and some of them show the characteristic functionalities such as molecular recognition ability and catalytic activity because of their highly controlled structure. To construct the functional polymers that will be as effective as naturally occurring polymers, for example, synthesis of optically active polymers, in one of the most interest and important topics in the field of polymer chemistry. Asymmetric polymerization is one of promising methods to synthesize optically active polymers, and there are many reports about the asymmetric polymerizations based on vinyl monomers, diene monomers, cyclic olefin monomers, aldehyde monomers, isocyanate monomers and so on.

Previously, we have investigated the polymerization behaviors of 1,4-benzoquinone methide derivatives (QMs) with various substituent on exomethylene carbon, and found that the radical and anionic polymerizations of many QMs take place (Iwatsuki S.,1993; Itoh, T.,1996; Itoh, T.,2000) Here, when the polymerization of prochiral QMs with two different substituents on the exomethylene carbon take place, many chiral centers could be generated in the main chain through the polymerization process. In other word, a novel optically active polymer should be formed (Fig 1).

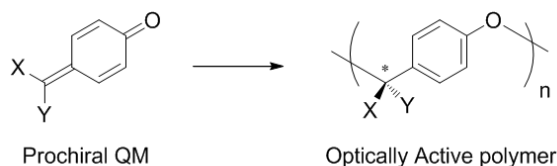


Fig. 1: Preparation of optically active polymer by polymerization of prochiral QM monomers.

1,4-benzoquinone methides with various alkoxy groups (1a-1d), were prepared according to a procedure reported in literature [4]. Asymmetric anionic polymerizations were carried out in glass ampoule equipped with a three-way stopcock. A given amount of 1a-1d was placed in the ampoule, dried under reduced pressure, and then filled with nitrogen. Into it was added dry dichloromethane by a syringe, and the resulting solution was cooled to -78°C . The polymerizations were initiated by the addition of initiator solution, which was prepared by mixing lithium 4-isopropylphenoxide (^tPrPhOLi) (1.0 equiv.) and (S)-(-)-2,2'-isopropylidenebis (4-phenyl-2-oxazoline) ((-)-PhBox) (1.1 equiv.) in dry toluene at room temperature just before use, and the reaction mixture was stirred for a given times. The polymerization was terminated by adding an excess amount of acetic anhydride to introduce an acetyl group at the terminal end. The resulting solution was poured into a large excess amount of hexane, and the deposited polymer was collected by centrifugation, and dried in vacuo.

Corresponding Author: Takahiro Uno, Graduate School of Engineerig, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, Japan.

RESULT AND DISCUSSION

Asymmetric Anionic Polymerization:

Asymmetric anionic polymerizations of **1a-d** were examined by using ⁱPrPhOLi/(–)-PhBox as a chiral initiator at [monomer]/[initiator] ratio([M]/[I]) of 20 in dichloromethane at –40 °C, and the results are summarized in Table 1. All polymerization reactions proceeded homogeneously, and afforded the optically active polymers having number-average molecular weights (M_n) in the range 2000 to 2700. The polymer yields tended to decrease with increasing the bulkiness of alkoxy groups in the monomers. It seems that an attack of the propagating phenoxide anion upon the exomethylene carbon of the monomers is suppressed gradually with an increase in bulkiness of the alkoxy groups. And also, the molar optical rotation values based on the molar concentration of monomer repeating unit ($[\phi]_{435}$) of the obtained polymers showed a tendency of decrease with increasing the bulkiness of the alkoxy groups (primary alkoxy > secondary alkoxy > tertiary alkoxy), and **1b** provided an optically active polymer with the maximum positive molar optical rotation value ($[\phi]_{435} = +108.9^\circ$). This indicates that higher stereocontrol in the polymers was achieved at a monomer with relatively small primary alkoxy group. It is speculated that a specific conformation might be formed between chiral ligand and alkoxy group of alkoxycarbonyl substituents in the monomer **1**, and then a certain specified polymerization, where the size of the monomer could determine the stereoselectivity, might take place.

Stereoselectivity in Initiation and Propagation Steps:

To investigate the extent of stereocontrol in the formation of an optically active polymer, asymmetric anionic oligomerization of **1b**, which provided an optically active polymer with the maximum positive molar optical rotation, was carried out at [M]/[I] ratio of 2 in dichloromethane at –78 °C for 12 hr, and 1-mer and 2-mer, which correspond to the products formed at the initial stage of polymerization, were isolated and characterized. The results are summarized in Table 2.

Table 1 : Asymmetric anionic polymerization of quinone methides (**1a-1d**) with ⁱPrPhOLi/(–)-PhBox^{a)}

Monomer	R	Yield / %	M_n ^{b)}	$[\phi]_{435}$ ^{c)}
1a	CH ₃	97	2400	+41.8°
1b	CH ₂ CH ₃	96	2700	+108.9°
1c	CH(CH ₃) ₂	52	2000	+50.2°
1d	C(CH ₃) ₃	45	2100	+2.3°

a) $[M]_0 = 0.23$ mol/, $[M]/[I] = 20$, time: 48 h. b) Determined by GPC (polystyrene standard). c) In CHCl₃.

Table 2: Asymmetric anionic oligomerization of **1b** with ⁱPrPhOLi/ (–)-PhBox^{a)}

[M]/[I]	Time / hr	Yield / %	$[\phi]_{435}$ ^{b)}
2	12	1-mer: 15 2-mer: 16	+6.1° +63.0°

a) $[M]_0 = 0.23$ mol/. b) In CHCl₃.

To obtain further information on stereoselectivity in the 1-mer and 2-mer, optical resolutions of them were conducted with high-pressure liquid chromatography (HPLC) analysis on the chiral column using hexane/ethanol (90/10 in vol %) as an eluent. The chromatograms of the optical resolutions of 1-mer and 2-mer are shown in Fig. 2, where top and bottom chromatograms were monitored by CD and UV detectors, respectively. In Fig. 2(a), the 1-mer with a negative CD sign was first eluted and followed by the 1-mer with a positive CD one, indicating that both components are enantiomers. From the peak area obtained on the UV chromatogram, the ratio of the first-eluted enantiomer/the second-eluted one was determined to be 52/48 in mol %. The absolute configuration of the chiral carbon in the 1-mer has not been determined yet. Here, assuming that the first-eluted enantiomer has *R*-configuration and the second-eluted one has *S*-configuration, (*R*)-1-mer is formed in a slight excess amount than (*S*)-1-mer, and the enantiomeric excess (ee) is calculated to be 4% ee(*R*). This indicates that, stereoselectivity in the addition reaction of initiator to monomer, that is initiation reaction, is quite low.

In Fig. 2(b), the four diastereomers of 2-mer are separated completely. From the peak area obtained on the UV chromatogram, the ratio of the first-eluted diastereomer/the second-eluted one/the third-eluted one/the fourth-eluted one was determined to be 37/20/29/14 in mol%. From the stereoselectivity of the 1-mer and the ratio of the peak areas obtained on the UV chromatogram and the CD chromatogram, the first-, the second-, the third-, and the fourth-eluted diastereomers could be assigned reasonably in turn to the (*R,R*)-, (*R,S*)-, (*S,R*)-, and (*S,S*)-diastereomer, respectively. On the basis of this assignment, the diastereomeric excess (de) is calculated to be 30% de(*RR/RS*) for the (*R*)-1-mer and 35% de(*SR/SS*) for the (*S*)-1-mer, respectively. This indicates that the addition reaction of the 1-mer anion to a monomer, that is propagation reaction, might take place stereoselectively regardless of the configurational chirality in a 1-mer anion to produce a 2-mer with an excessive *R*-configurational chiral carbon (37 mol % + 29 mol % = 66 mol %) in comparison with the *S*-configurational chiral carbon (20 mol % + 14 mol % = 34 mol %). Probably, the propagation reaction to

3-mer, 4-mer, 5-mer, and oligomer, and polymer is considered to proceed in same stereoselectivity (R-configuration/S-configuration = 61/39 in mol %).

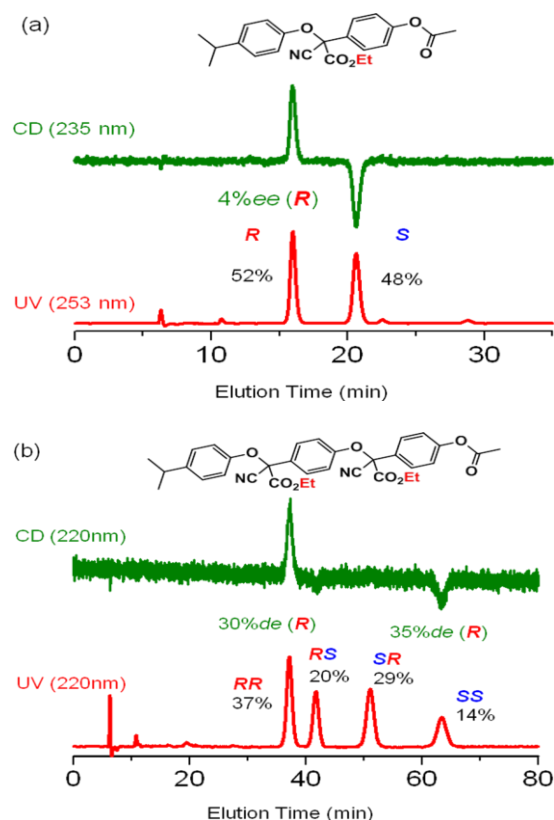


Fig. 2: HPLC chromatograms of optical resolution of 1mer (a) and 2-mer (b) obtained by asymmetric anionic oligomerization of **1b** (column: Daicel Chiralpak AD, eluent: hexane/ethanol = 90/10 (in vol%), flow rate: 0.5 mL/ min). The top and bottom chromatograms were measured by CD and UV detector, respectively.

Conclusions:

Molar optical rotation values of the polymers obtained by the asymmetric anionic polymerizations of **1a-1d** were significantly dependent upon alkoxy groups, and they decreased with an increase in the bulkiness of the alkoxy groups. Polymerization of **1b** bearing ethoxy group afforded the polymer with a maximum value of molar optical rotation, and the ethoxy group was found to be the most suitable substituent for the stereocontrol of the polymer. From optical resolutions of 1-mer and 2-mer in the oligomers obtained by asymmetric anionic oligomerizations of **1b**, it found that the stereoselectivity of the initiation reaction was quite low, but higher stereoselectivity was observed in the propagation reaction.

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