NOTE

Effects of Preparation Temperature on the Hydroperoxide Retention Properties of Cyclodextrin Polymer Gels

Kouichi ASAKURA, Hirokazu KAWAGUCHI, Takayuki KANAUCHI,
Nobutoshi TANAKA, Sadao YOSHIKAWA, and Koji SUZUKI

Faculty of Science and Technology, Keio University,
(3-14-1, Hiyoshi, Kohoku-ku, Yokohama-shi, 〒 223)

Two types of α -, β - and γ -cyclodextrin polymer gels were prepared by cross-linking of cyclodextrins with epichlorohydrin in alkali at 25 and 50°C. The degree of cross-linking of the polymer gels prepared at 25°C was slightly higher than that of the corresponding polymer gels prepared at 50°C. The resulting gels were used as the stationary phase for liquid chromatography. The separation of a mixture of tetralin (1) and tetralin monohydroperoxide (2) was attempted using hexane as the mobile phase. The retention time of (1) was basically the same in all cases. In contrast α -, β - and γ -cyclodextrin polymers prepared at 25°C retained (2) longer than the corresponding polymers prepared at 50°C.

1 Introduction

Cyclodextrin has an ability to form inclusion complexes with various compounds^{1), 2)}. We previously reported that cyclodextrins formed inclusion complexes with hydroperoxides of tetralin, methyl oleate, methyl linoleate, and methyl linolenate in preference to the parent molecules^{3), 4)}.

There are some reports which mention the feasibility using cyclodextrin polymer gels for the stationary phase in liquid chromatography^{5), 6)} and as catalysts^{7)~9)}. They are also effective for the separation of nucleic acid⁹⁾, the optical resolution of racemic compounds⁸⁾, and as catalysts for regio-specific reactions^{7)~9)}.

Cyclodextrins were usually immobilized by cross-linking with epichlorohydrin in alkali. It is reported that there are two major preparation procedures, one is the method in which the cyclodextrin is reacted with epichlorohydrin at room temperature¹⁰⁾, and the other involves the reaction at 50°C^{5)~9)}. In spite of the extensive research on the utilization of cyclodextrin polymer gels by

many investigators, the properties of these two kinds of polymer gels have not been compared yet.

In this study, two types of α -, β - and γ -cyclodextrin polymer gels were prepared at 25 and 50°C. To clarify the difference in hydroperoxide retention properties of these two types of gels, they were utilized as the stationary phase for liquid chromatography, and the retention time of tetralin (1) and tetralin monohydroperoxide (2) was measured.

2 Experimental

2.1 Materials

α -, β -, γ -cyclodextrin and epichlorohydrin (guaranteed reagents) were purchased from Tokyo Kasei Kogyo Co., Ltd. Hexane (HPLC solvent) and (1) (extra pure) were purchased from Wako Pure Chemical Industries, Ltd. (1) was purified by distillation under reduced pressure (bp 75~76°C/10 mmHg). The monohydroperoxide (2) was prepared by autoxidation of (1), and purified and determined according to our previous method³⁾.

Corresponding author : Kouich ASAKURA

2.2 Preparation of cyclodextrin polymer gels

Cyclodextrin polymers, α -CD-P-1, β -CD-P-1 and γ -CD-P-1, were prepared by cross-linking the cyclodextrins with epichlorohydrin in alkali at 25°C according to the Solms's method¹⁰ and pulverized with a mortar, and 200~320 mesh gels were collected by sieving.

The other type of cyclodextrin polymers, α -CD-P-2, β -CD-P-2 and γ -CD-P-2, were synthesized at 50°C according to the Hoffman's method⁹, and 200~320 mesh gels were obtained.

The degree of crosslinking was calculated according to the previously reported method¹¹.

2.3 Chromatographic separation of tetralin (1) and tetralin monohydroperoxide (2) by cyclodextrin polymer gels

The cyclodextrin polymer gels were packed into a stainless column (4.6 ϕ $\times$ 150 mm). The amounts of the gels used were 1.67, 1.58, 1.74, 1.75, 1.70 and 1.59 g for α -CD-P-1, β -CD-P-1, γ -CD-P-1, α -CD-P-2, β -CD-P-2 and γ -CD-P-2, respectively. Two μ L of a 1 % hexane solution of the equivalent mixture of (1) and (2) was charged on the column, and the compounds were eluted with hexane using an HPLC pump (JASCO 880-PU). The flow rate and temperature were 0.3 mL $\cdot$ min⁻¹ and 25°C, respectively. The column eluates were monitored with a UV detector (254 nm ; JASCO 875-UV).

3 Results and Discussion

3.1 Preparation of cyclodextrin polymer gel

The yields, elemental analysis, and the degree of cross-linking of the polymer gels are shown in Table-1, which shows that each cyclodextrin polymer gel prepared at 25°C (α -CD-P-1, β -CD-P-1, and γ -CD-P-1) has a slightly larger degree of cross-linking than that of the corresponding gel prepared at 50°C (α -CD-P-2, β -CD-P-2 and γ -CD-P-2).

3.2 Hydroperoxide separating ability of cyclodextrin polymer gel column chromatography

Fig.-1, 2 and 3 represent the chromatographic elution patterns using α -, β - and γ -cyclodextrin polymer gels as the stationary phase, demonstrating that (2) was retained longer than (1) by every cyclodextrin polymer gel. This fact indicates that (2) was enclosed in the cyclodextrin cavity more preferentially than (1) as expected.

The retention time of (1) was basically the same in each case. By contrast (2) was much longer retained with α -CD-P-1, β -CD-P-1 and γ -CD-P-1 than that with α -CD-P-2, β -CD-P-2 and γ -CD-P-2, respectively. This fact indicates that the rapid cross-linking reaction at 50°C may presumably make the cyclodextrin cavity close or cleave. On the other hand, the cyclodextrin cavity remained sufficiently after the moderate reaction at 25°C. This result suggests that a lower temperature for the cross-linking reaction is more feasible for the preparation

Table-1 Yields, elemental analysis, and the degree of cross-linking of cyclodextrin polymer gels.

Cyclodextrin polymer gel	Yield (%)	Elemental analysis		Degree of cross-linking
		C (%)	H (%)	
α -CD-P-1	86.9	48.14	6.35	4.2
β -CD-P-1	99.8	48.40	6.53	5.3
γ -CD-P-1	94.2	49.05	6.59	7.4
α -CD-P-2	92.7	47.41	6.64	3.2
β -CD-P-2	93.1	47.16	6.40	3.4
γ -CD-P-2	94.6	47.39	6.48	4.2

Fig.-1 Chromatographic separation of (1) and (2) by α -cyclodextrin polymer gels.

Fig.-3 Chromatographic separation of (1) and (2) by γ -cyclodextrin polymer gels.

Fig.-2 Chromatographic separation of (1) and (2) by β -cyclodextrin polymer gels.

of the cyclodextrin polymer gel.

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シクロデキストリンポリマーゲルの過酸化物 保持能に対する合成温度の影響

朝倉浩一・川口宏和・叶内敬之・
田中信敏・吉川貞雄・鈴木孝治

慶応義塾大学理工学部 (〒223 横浜市港北区日吉 3-14-1)

2種の α -、 β -及び γ -シクロデキストリンポリマーゲルを、シクロデキストリンを25及び50℃にてアルカリ中でエピクロヒドリンによって橋かけすることにより合成した。25℃にて合成したポリマーゲルの橋かけ度は50℃で合成した相当するポリマーゲルよりもやや高かった。得られたゲルは液体カラムクロマトグラフィーの固定相として用いた。テトラリンとテトラリンモノヒドロペルオキシドの混合物の分離を、ヘキサンを移動相として用いて行った結果、テトラリンの溶出時間はいずれの場合もほぼ等しかった。それに対して、25℃で合成した α -、 β -及び γ -シクロデキストリンポリマーは、50℃にて合成した相当するポリマーと比較して、テトラリンモノヒドロペルオキシドを長く保持することが認められた。

連絡者：朝倉浩一