

Poly(isocyanide) as a Chiral Adsorbent in Liquid Column Chromatography

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Liquid chromatography on a column packed with optically active poly(*tert*-butylisocyanide) leads to the partial resolution of $\text{Co}(\text{acac})_3$ and four optically active organic compounds.

Poly(isocyanide) has a helical backbone of a carbon chain owing to the steric interference of side groups.¹ The polymer is chiral even though it has no asymmetric carbons. Optically

pure poly(isocyanides) are synthesized by polymerization in the presence of chiral amine catalysts.¹ In the present study, optically active poly(isocyanide) has been used as a chiral adsorbent for chromatographic resolution. Previously, the application of a polymer of helical backbone to a chiral adsorbent has been reported in the case of poly-(triphenylmethane methacrylate) in chromatographic resolution.²

Poly(*tert*-butylisocyanide) was synthesized from *tert*-butylisocyanide in the presence of $\text{Ni}(\text{ClO}_4)_2$ and (*R*)-phenylethylamine¹ and was characterized by NMR. The degree of polymerization was estimated to be 18 from the ratio of monomer to end group. The polymer (0.1 g) was dissolved in dichloromethane (50 ml) and silica gel (1.5 g) (0.040–0.063 mm) (Fractosil 200, Merck) was added. The yellowish polymer was completely adsorbed by silica. The polymer-coated silica prepared was packed into a stainless tube of 24 cm \times 4 mm.

Racemic $\text{Co}(\text{acac})_3$ (Hacac = pentane-2,4-dione) was placed on the column and eluted with 4:1 (v/v) H_2O –MeOH at 25°C. Fig. 1 is a chromatogram in which one peak is observed at $V = 30.6$ ml with a shoulder at $V = 38.0$ ml. The circular dichroism spectra of the collected fractions indicated that the peak at $V = 30.6$ ml and the shoulder at 38.0 ml corresponded to the Δ and Λ isomers of $\text{Co}(\text{acac})_3$, respectively. The resolution of this compound was confirmed by separate experiments in which each enantiomer was eluted separately on the column.

Table 1 contains the chromatographic results of ten other optically active compounds. As a result, five compounds, including $\text{Co}(\text{acac})_3$, are found to be partially resolved. Chromatography was also performed at 5°C with the purpose

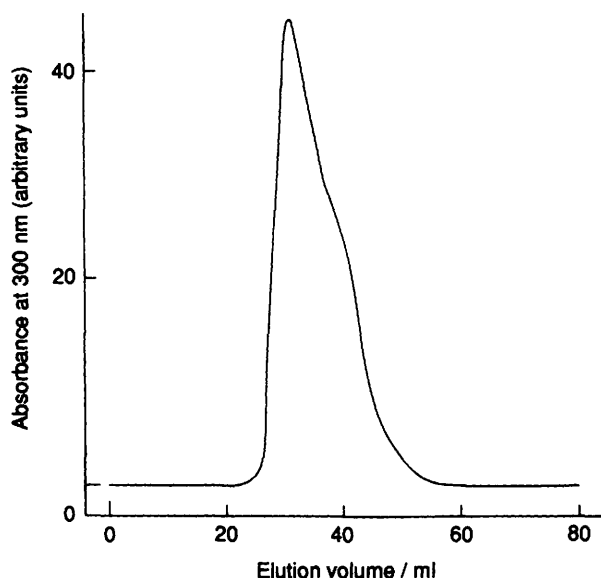


Fig. 1 Chromatogram of elution of $\text{Co}(\text{acac})_3$ (1.0×10^{-7} mol) with 4:1 (v/v) H_2O –MeOH on a poly(*tert*-butylisocyanide) column (24 cm \times 4 mm) at 25°C. The concentration of $\text{Co}(\text{acac})_3$ is monitored by the absorbance at 300 nm.

Table 1 Chromatographic results on a poly(*tert*-butylisocyanide) column at 25°C

| Compound | Optical isomer | Retention volume/ml | Separation factor | Solvent |
|--------------------------------------------------|-----------------------|---------------------|-------------------|----------------------------------|
| Menthol | (–)-isomer | 5.1 | 1.14 | MeOH |
| | (+)-isomer | 5.8 | | |
| Carvone | (–)-isomer | 5.5 | 1.00 | MeOH |
| | (+)-isomer | 5.5 | | |
| Citronellal | (–)-isomer | 5.5 | 1.00 | MeOH |
| | (+)-isomer | 5.5 | | |
| $\text{Cr}(\text{acac})_3$ | Δ -isomer | 43.3 | 1.09 | H_2O –MeOH (4/1) |
| | Λ -isomer | 47.2 | | |
| $\text{Co}(\text{acac})_3$ | Δ -isomer | 30.6 | 1.24 | H_2O –MeOH (4/1) |
| | Λ -isomer | 38.0 | | |
| $\text{Ru}(\text{acac})_3$ | Δ -isomer | 41.3 | 1.00 | H_2O –MeOH (4/1) |
| | Λ -isomer | 41.3 | | |
| 1,1-Phenyl-ethylamine | (<i>R</i>)-isomer | 8.1 | 1.05 | MeOH |
| | (<i>S</i>)-isomer | 8.5 | | |
| <i>O,O'</i> -Dibenzoyl tartaric acid (anhydrous) | (+)-isomer | 7.1 | 1.12 | MeOH |
| | (–)-isomer | 6.4 | | |
| Alanyl alanine | (<i>R,R</i>)-isomer | 5.5 | 1.00 | MeOH |
| | (<i>S,S</i>)-isomer | 5.5 | | |
| Binaphthol | (<i>R</i>)-isomer | 37.3 | 1.02 | MeOH |
| | (<i>S</i>)-isomer | 36.5 | | |

of improving separation efficiency in the case of $\text{Co}(\text{acac})_3$. No increase of separation was observed although the retention volume increased to 34.2 ml and 42.4 ml for the Δ and Λ isomers, respectively.

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