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Optical Resolution of Alcohols and Amines on Poly[(S)-(-)-p-(p-tolylsulfinyl)styrene] by Means of HPLC

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Poly[(S)-(-)-p-(p-tolylsulfinyl)styrene], which exert high donor ability, can be counted among the efficient stationary phase of the optical resolution of chiral aromatic alcohols and amines by means of HPLC.

In recent years, numerous attempts have been made to make use of a chiral polymer in the optical resolution of a number of chiral organic compounds by means of high-performance liquid chromatography(HPLC).[1)] During the course of our research concerned with the preparation of optically active polymers containing an asymmetric sulfur atom,[2)] we have now found that poly[(S)-(-)-p-(p-tolylsulfinyl) styrene] can serve as a good chiral stationary phase to resolve chiral alcohols and amines which have an aryl group. Sulfoxides have a donor property and have been reported to form a hydrogen-bonded complex with iodine[3)] and phenol.[4)] This unique nature of sulfoxides have prompted us to use the present polymer as the stationary phase of the optical resolution of alcohols and amines. (S)-(+)-p-(p-Tolylsulfinyl)styrene(**1**), $[\alpha]_D^{20}$ +2.70°($CHCl_3$), was prepared by the reaction of (R)-(-)-menthyl-(S)-(-)-p-toluenesulfinate with p-vinylphenylmagnesium chloride in dry THF.[2c)] The polymerization of (S)-**1** was carried out by the usual sealed tube method in benzene using 2,2'-azobisisobutyronitrile. Poly-(S)-**1** used here exhibited the following properties. $[\alpha]_D^{20}$ -10.7°($CHCl_3$), MW(measured by vapor pressure osmometer in $CHCl_3$): 8700, IR(KBr): 1048 cm^{-1}(S→O). In order to see the donor ability of poly-(S)-**1**, its association with phenol was observed in chlorobenzene by IR. The association constant, K, and the $\Delta\nu_{OH}$-value were 7.0 dm^{-3}mol and 330 cm^{-1}, respectively.[5)]

To cite a typical experiment, poly-(S)-**1** was ground to a powder(mean particle size: 7 μm) and packed in a stainless steel column(30 x 0.4(id)cm). The optical resolution was carried out with a Toyo Soda HLC-803 apparatus equipped with a Toyo soda UV-8011 detector at 20 °C. The eluent and the flow rate were hexane and 0.25 ml min^{-1}, respectively.

The typical results for the resolution of a variety of alcohols and amines which have an aryl group are summarized in Table 1. Most of the results for the resolution on this column are fairly well, except for that of the substituted alcohols(Compounds **2** and **3**). The best result has been obtained from the resolution of a phenol(Compound **5**), affording Rs = 2.78. Similar investigations for the simple aliphatic alcohols and amines were also carried out to elucidate the

Table 1. Optical Resolution of Racemic Alcohols and Amines on Poly-(S)-**1** Column

Compounds	k_1' a)	α a)	Rs a)
α-Methylbenzyl alcohol(**2**)	1.77(R)	1.13	0.59
α-Isopropylbenzyl alcohol(**3**)	1.83(+)	1.19	0.51
α-Cyanobenzyl alcohol(**4**)	1.71(R)	1.23	1.31
o-(1-Methylbenzyl)phenol(**5**)	1.72(R)	1.84	2.78
α-(Ethoxycarbonyl)-m-hydroxy-benzylamine(**6**)	2.14(+)	1.60	2.57
1,1'-Bi-2-naphthol(**7**)	2.71(R)	1.21	1.60
α-Methylbenzylamine(**8**)	1.86(R)	1.61	1.90
α-Isopropylbenzylamine(**9**)	1.88(+)	1.67	2.25

a) The capacity factor(k_1'), the separation factor(α), and the resolution factor(Rs) were calculated according to the reported method(Ref. 1).

resolution ability of this column for these compounds. However, these attempts were unsuccessful. This fact seems to suggest that the interaction of hydrogen bond of the aliphatic alcohols and amines is scarcely affected by the donor ability of poly-(S)-**1** in this resolution.

In summary, inspection of the result suggests that poly-(S)-**1**, which has high donor ability, should be counted among the efficient stationary phase and is satisfactorily applicable to the optical resolution of alcohols and amines which have an aryl group. In this resolution, the ability of the chiral sulfinyl group of poly-(S)-**1** to form the hydrogen-bonded complex seems to play an important role. Additional investigations are in progress.

References

1) For example: Y. Okamoto, Z-K. Cao, R. Aburatani, and K. Hatada, Bull. Chem. Soc. Jpn., 60, 3999(1987), and the references cited therein; "Special Issue on Optical Resolution by Liquid Chromatography," ed by S. Hara and J. Cazes, J. Liq. Chromatogr., 9, 283(1986). 2) a) N. Kunieda, M. Kinoshita, and M. Imoto, Polym. Lett., 1971, 241; b) N. Kunieda, H. Wada, J. Shibatani, and M. Kinoshita, Makromol. Chem., 172, 237(1973); c) N. Kunieda, J. Shibatani, Y. Fujiwara, and M. Kinoshita, ibid., 175, 2509(1974). 3) P.S. Drago, B. Wayland, and R.L. Carlson, J. Am. Chem. Soc., 85, 3125(1963); P. Klaeboe, Acta Chem. Scand., 18, 999(1964). 4) T. Gramstad, Spectrochim. Acta, 19, 829(1963); R.H. Figueroa, E. Roig, and H.H. Szmant, ibid., 22, 1107(1966). 5) IR measurements: [Poly-(S)-**1**] = 0.01-0.05 mol dm^{-3}, [Phenol] = 0.05 mol dm^{-3} at 20 °C. The association constant(K) and the $\Delta\nu_{OH}$-value determined by following the change of the band of OH stretching frequency of phenol located at 3538 cm^{-1}.

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