

An Optically Active Stereoregular Polyphenylacetylene Derivative as a Novel Chiral Stationary Phase for HPLC

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Stereoregular polyphenylacetylene bearing (*R*)-1-phenylethylcarbamoyl groups showed high chiral recognition as a chiral stationary phase for HPLC and resolved racemates such as *trans*-stilbene oxide, Tröger's base and alcohols.

Chromatographic enantioseparation, particularly by HPLC, is a practical and useful method not only for analyses but also for obtaining enantiomers.¹ The development of chiral stationary phases (CSPs) is the key to this separation technique, and many CSPs for HPLC have been prepared. Among them, CSPs consisting of chiral polymers such as phenylcarbamate derivatives of polysaccharides² and one-handed helical poly-(triphenylmethyl methacrylate)³ are interesting and attractive because the highly ordered structure of the polymers, in these cases the helical conformation of the main chain, plays an important role for effective chiral recognition. Optically active polyacetylenes prepared by polymerization of acetylenes having chiral substituents have been considered to have a helical structure.⁴ Therefore, chiral polyacetylenes with a helical conformation may be useful as novel CSPs for HPLC. In the present study, we prepared two types of polyphenylacetylene derivatives bearing (*R*)-1-phenylethylcarbamoyl groups at the *para* position on the phenyl groups, and evaluated their chiral recognition ability as a CSP for HPLC.

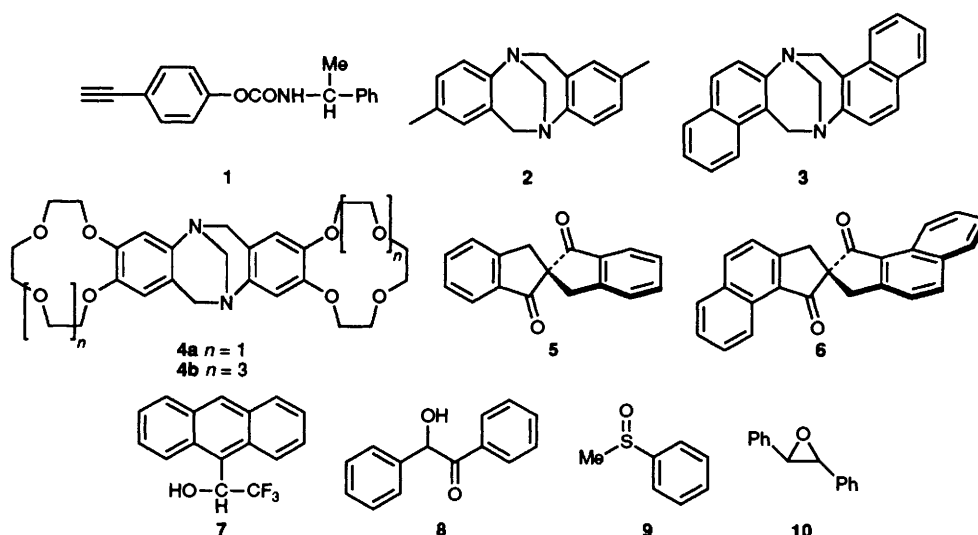
The optically active monomer (*R*)-(+)-4-(1-phenylethylcarbamoyl)phenylacetylene **1**, was prepared from 4-(*tert*-butyldimethylsiloxy)phenylacetylene, followed by desilylation and reaction with (*R*)-(+)-1-phenylethyl isocyanate.† The monomer **1** was polymerized with [$\text{RhCl}(\text{nbd})_2$] (nbd = norbornadiene)⁵ at 30 °C to afford a high molecular mass polymer ($M_n = 32.0 \times 10^4$, estimated by gel permeation chromatography using polystyrene standards). The UV-VIS and ¹H NMR spectra of the polymer obtained (poly-**1a**) indicated that it had a conjugated polyene structure and an almost complete *cis*-transoidal conformation,⁶ respectively.‡ The polymer showed intense CD bands in the UV-VIS region which may be induced by the predominant one-handed helical conformation of the main chain as previously reported for other optically active polyacetylene derivatives.⁴ The monomer **1** did not polymerize with $\text{WCl}_6/\text{Ph}_4\text{Sn}$. In order to investigate the effect of stereoregularity and conformation of the main chain on the chiroptical property, the polyacetylene was prepared by a different route. First, 4-(*tert*-butyldimethyl-

siloxy)phenylacetylene was polymerized in toluene using a $\text{WCl}_6/\text{Ph}_4\text{Sn}$ catalyst,⁷ followed by desilylation with tetrabutylammonium fluoride. The resultant poly(4-hydroxyphenylacetylene) was allowed to react with (*R*)-(+)-1-phenylethyl isocyanate in pyridine to give poly{(*R*)-4-(1-phenylethylcarbamoyl)phenylacetylene} (poly-**1b**; $M_n = 2.5 \times 10^4$). The elemental analysis of poly-**1b** indicated that the 1-phenylethylcarbamoyl group was almost quantitatively introduced onto each hydroxy group. This polymer has the same chiral side groups as poly-**1a**, but the ¹H NMR spectrum showed very broad peaks at δ 5.5–8.0, indicating that poly-**1b** may not be stereoregular in the main chain configuration and conforma-

Table 1 Resolution of enantiomers 1–10 on poly-**1a**

Racemate	Eluent ^a	k'_1 ^b	α ^c	R_s ^d
1	A	4.61(–)	1.09	0.50
2	A	0.63(+)	1.26	0.79
	B	0.14(+)	1.50	0.48
3	B	0.80(+)	1.19	0.94
4a	B	0.81	1.57	2.00
4b	B	1.15	1.44	1.67
5	B	0.24(+)	1.29	0.42
6	B	1.00(+)	1.37	0.78
7	A	1.38	1.18	0.87
8	A	1.86	1.09	0.65
9	A	3.75(–)	1.04	
10	C	1.20(–)	1.13	0.46

^a Eluent; hexane–propan-2-ol (90:10) (A), methanol (B), hexane (C). Flow rate 0.5 ml min⁻¹. ^b Capacity factor of the first-eluted enantiomer, $k'_1 = (t_1 - t_0)/t_0$, where t_1 is the retention time of the first-eluted enantiomer, t_0 is dead time. Optical rotation of the first-eluted enantiomers is shown in parentheses. ^c Separation factor $\alpha = k'_2/k'_1$, where k'_2 is the capacity factor of the second-eluted enantiomer. ^d Resolution factor $R_s = 2(t_2 - t_1)/(W_1 + W_2)$, where W_1 and W_2 represent the band width of the first- and second-eluted enantiomers, respectively.



tion. The polymer did not show any significant CD bands in the 500–300 nm range. These results suggest that a regular main chain conformation may be essential for a helical conformation and for induced CD to be shown.

The chiral recognition ability of poly-**1a** and poly-**1b** as CSPs for HPLC was evaluated. § Packing materials were prepared in the same way as before using macroporous silica gel (Dai-sogel-1000).² The resolution results for some racemates are shown in Table 1. ¶ The poly-**1a** showed high chiral recognition ability and can resolve some racemates such as Tröger's base (**2**) and its derivatives (**3**, **4**), spiropyran derivatives (**5**, **6**), benzoin (**8**), *trans*-stilbene oxide (**10**), and racemic alcohols. The polymer has polar chiral carbamoyl side groups, which may participate in differentiating enantiomers, especially in a nonpolar eluent system. Interestingly, poly-**1b** showed poor chiral recognition in both methanol and hexane–propan-2-ol systems, and only partially separated **2** and **10** using hexane–propan-2-ol as the eluent. These results clearly indicate that the one-handed helical conformation induced by a stereoregular main chain with chiral side groups is essential for effective chiral recognition.

In conclusion, the present findings indicate that optically active stereoregular polyacetylenes may provide novel polymeric CSPs, and other optically active polyacetylenes prepared previously may also be applicable as CSPs for HPLC.

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Footnotes

† Elemental analysis and ¹H NMR were satisfactory. Mp 123.5–124.5 °C, [α]_D²⁵ +134 (THF, c 0.94).

‡ Selected data for poly-**1a** UV–VIS, CD data [THF, ϵ (λ /nm)]: 6790 (250), 3440 (325), 2990 (391); [θ](λ): 0 (540), 1750 (438), 0 (413), –18900 (366), 0 (340), 23100 (316), 0 (288), –28000 (268), –21000 (254), –28000 (242), 0 (223); ¹H NMR (CDCl₃, 60 °C, SiMe₄) δ 1.41 (3H, d, CH₃), 4.77 (1H, m, –CH–), 5.67 (1H, s, =CH), 5.80 (1H, br, NH), 6.58–6.72 (2H, d, Ph), 7.08–7.40 (7H, m, Ph); satisfactory elemental analysis was obtained.

§ All chromatographic experiments were performed on a JASCO TRIROTAR-II liquid chromatograph equipped with UV (JASCO-875-UV) and polarimetric (JASCO 181-C) detectors.

¶ Racemates, **2**, **7**–**10** are commercially available, **5** and **6** were gifts from Professor N. Harada of Tohoku University, and **3** and **4** are new compounds whose elemental analyses and ¹H NMR spectra were satisfactory.

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