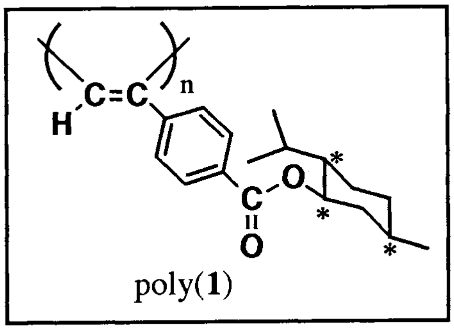
CHEMISTRY LETTERS, pp. 2009-2012, 1993.

Chiral Helical Conformation of the Polyphenylacetylene Having Optically-Active Bulky Substituent

Toshiki AOKI,* Masayuki KOKAI, Ken-ichi SHINOHARA , and Eizo OIKAWA
Department of Material and Chemical Engineering, Faculty of Engineering,
Niigata University, Ikarashi 2-8050, Niigata 950-21

Poly[p-{L-(-)-menthoxycarbonyl}phenylacetylene]s prepared by [Rh(norbornadiene)Cl]$_2$ as a polymerization catalyst exhibited a much higher $[\alpha]_D^{20}$ (= - 605) than that(= - 68.8) of the monomer and a very high molar ellipticity(more than 10^4) at the $\pi-\pi^*$ region in the CD spectrum: A chiral helical conformation of the main chain in solution is suggested. The solid membrane of this polymer showed enantioselective permeability (54%ee) for DL-tryptophan.

Optical resolution through a solid membrane is expected to realize a large scale treatment of racemic modifications. However, there are only few reports on solid membranes for optical resolution including our results.[1,2] Chiral helical polymers are very promising as optical resolution membrane materials[2] but there are very few examples for such polymers, especially for those having good solid-membrane-forming property. In order to obtain a new kind of such polymers, we designed and synthesized a polyphenylacetylene having an optically-active bulky substituent. Since a polyphenylacetylene has a rigid main-chain and benzene rings, it is expected to show good solid-membrane-forming property and have a high stereoregularity.



poly(**1**)

Polymerization of p-(L-(-)-menthoxycarbonyl)phenylacetylene {**1**,[3] $[\alpha]_D^{20}$ = - 68.8 (c 0.580, $CHCl_3$) } by using [Rh(norbornadiene)Cl]$_2$(**Rh**) [4,5] or WCl_6(**W**) [6] as a polymerization catalyst led to (-)-poly[p-(L-(-)-menthoxycarbonyl)phenylacetylene]s,which exhibited a much higher optical rotation { poly(**1**)-**Rh**; $[\alpha]_D^{20}$ = - 605 (c 1.0, $CHCl_3$), poly(**1**)-**W**; - 501 (c 0.190, $CHCl_3$)} [7] (Table 1). The source of these high optical activities was traced to UV-VIS absorption bands associated with the poly(phenylacetylene) backbone structure by measuring its circular dichroism(CD) spectrum and UV-VIS spectrum.[8] The CD spectrum(Fig.1) showed a Cotton effect with a high molar ellipticity of -71000(at 272 nm) and +37000 (at 310 nm) deg•cm^2•dmol^{-1}, which were one order of magnitude higher than that of known chiral polyacetylenes. [9-11] Since the Cotton effect was attributed to $\pi-\pi^*$ transition of the poly(phenylacetylene) chromophore, the main chain of poly(**1**) was found to have an induced chiral conformation. In other words, the high $[\alpha]_D^{20}$ was able to be interpreted as arising from a twisted conformation with an excess of one sense of these polymers. [12,13] Since Tabata et al.[14] showed that polyphenylacetylene could adopt a stable helical conformation by calculation, this twisted conformation of poly(**1**) may be a helical one. This interpretation was supported by the strong dependence of these $[\alpha]_D$ values on temperature and solvent (Fig. 2).

Table 1. Polymerization[a] of **1** and characteristics of poly(**1**)

No.	Monomer[b]	Catalyst[c]	Yield %	$\bar{M}w$[d] $\times 10^5$	$\bar{M}w/\bar{M}n$[d]	Cis%[e] mol%	$[\alpha]_D^{20}$ (Conc. g/dl)[f]
1	**1**	Rh	72.3	26.3	2.09	100	- 605 (1.00)
2	**1**[g]	Rh	92.5	8.8	2.69	96	- 586 (0.72)
3[h]	**1**	W	13.1	0.92	1.77	- [i]	- 501 (0.19)
4	**2**	Rh	86.0	5.17	3.21	100	+ 19.2 (0.38)
5	**1+PhA**[j]	Rh	66.6	13.1	2.44	- [i]	- 500 (0.13)
6	**PhA**	Rh[k]	21.0	1.78	2.59	96	-

a)Polymerized in triethylamine at r.t. for 10 min for No.1, 2 h for No.2, 4 h for No.3. [monomer]= 0.20 mol/l, [catalyst] = 0.67 mmol/l. The polymers were purified by reprecipitation from chloroform to methanol. b) See text for the code. c)Rh = $[Rh(nbd)Cl]_2$, W=WCl_6. d) Determined by GPC. e) Determined by the ratio of the intensity of the peak at δ 5.82, 6.6 and 7.7 ppm.16) f) In chloroform. g)[catalyst] = 0.08 mmol/l. h)Polymerized in toluene at r.t. for 20 h . [monomer]= 0.67 mol/l, [catalyst]=8.17 mmol/l. i) It could not be determined because these peaks were broad and overlapped. j)Copolymerization of **1** with phenylacetylene(**PhA**). **1/PhA** in the feed = 10/90(mol%), **1/PhA** in the copolymer = 25/73(by mol%), 52/48(by wt%) determined by ^{1}H-NMR. k)$[Rh(cyclooctadiene)PPh_3]PF_3$.

The absolute values of $[\alpha]_D$ of poly(**1**)-Rh increased with a decrease in temperature. This may be because the reversal of the helix was suppressed at low temperatures. Same behavior about helical polyisocyanates has been reported.15)

Polyacetylenes involve 4 types of backbone configurations: cis-transoidal(c-t), cis-cisoidal(c-c), trans-transoidal(t-t), and trans-cisoidal(t-c).17) It has been shown that the polyphenylacetylenes prepared with $[Rh(norbornadiene)Cl]_2$ possess about 100% c-t structure4) and those with WCl_6 did trans-rich structure.18) The monomer(**1**) also afforded a polymer with a different structure by $[Rh(norbornadiene)Cl]_2$ or WCl_6 catalyst : Poly(**1**)-**Rh** had a high cis content but poly(**1**)-**W** did not (Table 1). However, both poly(**1**)-Rh and poly(**1**)-**W** showed a high optical rotation. This may be because both poly(**1**)s have a helical conformation. This is supported by the calculation results in the papers by Tabata et al.14) and Berlin et al.19) They reported that polyphenylacetylenes, in spite of their different configurations, could adopt helical conformations.

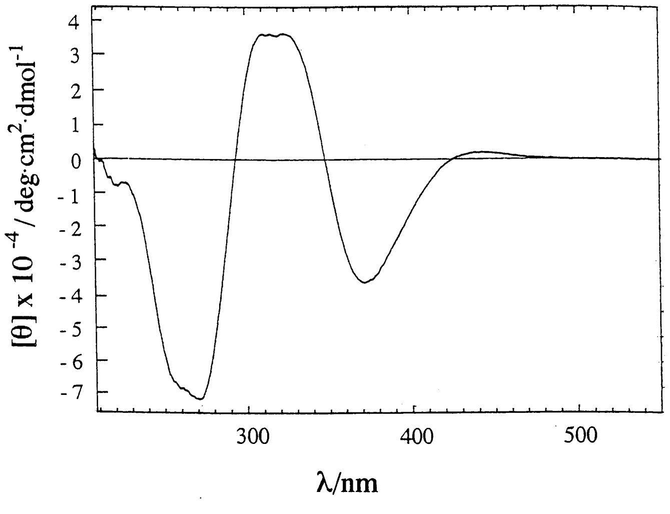


Fig. 1. Circular dichroism spectrum of poly(**1**)-Rh (No. 2 in Table 1) in tetrahydrofuran(0.192 mg/ml) at ca. 22 °C.

Another very interesting result of this

work is the steep change(from - 497 to - 772) of the specific rotation of poly(**1**)-**W** at 40 to 45 °C (Fig. 2). This might be due to the conformational change. The steep change occurred in case of poly(**1**)-**W** but not of poly(**1**)-**Rh**. The reason for this finding may be less stability of the helix of poly(**1**) -**W** (t-t and t-c) compared to that of poly(**1**)-**Rh**(c-t).

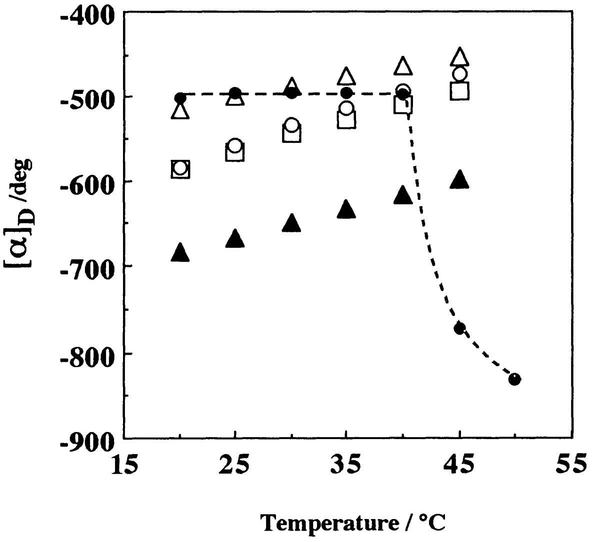


Fig. 2. Temperature and solvent dependence of optical rotations of poly(**1**).
poly(1)-Rh(No. 2 in Table 1) in 1,2-dichloroethane (△) , tetrahydrofuran (○), chloroform (□), toluene (▲), poly(1)-W(No. 3 in Table 1) in chloroform (●)

The helical conformation with an excess of one sense was thought to be induced by the bulky optically-active side group, L-menthoxycarbonyl group. This was supported by the lack of all the following observations in case of a phenylacetylene having a small optically-active side group, (+)-poly[p-{(+)-2-methylbutoxy}phenylacetylene] { poly(**2**) }[20] : high optical rotation, strong temperature dependence of $[\alpha]_D$, and a Cotton effect, which were clearly distinct from those of poly(**1**). Moreover, since the copolymer of **1** with phenylacetylene(PhA) { **1** unit in the copolymer = 27 mol%[21] (52 wt%)} showed a high $[\alpha]_D^{20}$(= -500)(Table 1, No.5), **1** was found to induce a helical conformation with an excess of one sense to phenylacetylene comonomer unit in the copolymer main-chain. If the chiral main chain had been present only in a **1** unit in the copolymer, the $[\alpha]_D^{20}$ would have been -135, which was calculated from $[\alpha]_D^{20}$ of the homopolymer and the composition of **1** unit in the copolymer.

The important features of poly(**1**)-Rh having a high stereoregularity described above were its very high molecular weight(Mw >10^6) and good solubility. Polyacetylenes having a high molecular weight and high stereoregularity generally tend to be insoluble. However, poly(**1**)s were easily soluble in benzene, toluene, xylene, carbon tetrachloride, 1,2-dichloroethane, chloroform, and tetrahydrofuran(and insoluble in methanol, diethyl ether, and hexane). Therefore this polymer was easily fabricated to a tough membrane by a solvent-casting method. The CD spectrum of the polymer in the membrane[22] was similar to that in solution, indicating that the polymer had also a helical conformation with an excess of one sense in a solid membrane. When 0.5 wt% DL-tryptophan aq. solution was fed , %ee of the permeate through the membrane was 54-55 %ee for 600-3000 h showing a D-(+)-enantiomer selective permeability(P= 1.8 X 10^{-12} m^2/h), and when 0.05 wt% DL-tryptophan methanol solution was used , %ee was 8-15 %ee for 240-600 h(P= 5.4 X 10^{-9} m^2/h). Since this polymeric membrane is very tough and flexible, the low permeability will be improved by applying a pressure and using a membrane with a larger area and a thinner thickness.

Partial financial support by a Grant-in-Aid for Encouragement of Young Scientists(No. 04750732) from the Ministry of Education, Science, and Culture, Asahi Glass Foundation, and Yamaguchi Foundation are gratefully acknowledged.

References

1) T. Aoki, K. Shinohara, and E. Oikawa, *Makromol. Chem., Rapid Commun.*, **13**, 565(1992).

2) A.Maruyama, N.Adachi, T. Takatsuki, M.Torii, K.Sanui, and N. Ogata, *Macromolecules*, **23**, 2748(1990).

3) This monomer(**1**) was synthesized from p-bromobenzoic acid via L-menthyl p-bromobenzoate and then L- menthyl p-(3-hydroxy-3-methyl-1-butynyl)benzoate in 28.0% yield(based on p-bromobenzoic acid). ^{1}H-NMR ($CDCl_3$) for **1** : δ 8.00(2H, d, phenylene protons), 7.55(2H, d, phenylene protons), 4.93(1H, ddd, $C\underline{H}$- O), 3.23(1H, s, $\underline{H}C$-C), 2.20-1.00(10H, m, $C\underline{H}_2$ and $C\underline{H}$ of menthoxy group), 0.93 (6H, dd, $(C\underline{H}_3)_2CH$), 0.79(3H, d, $C\underline{H}_3CH$) ppm.

4) W. Yang, M. Tabata, S. Kobayashi, K. Yokota, and A. Shimizu, *Polym. J.*, **23**, 1135(1991).

5) A. Furlani, C. Napoletano, and M. V. Russo, *J. Polym. Sci., Polym. Chem.*, **27**, 75(1989).

6) T. Masuda, K. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728(1974).

7) The homopolymers of **1** polymerized by $[Rh(norbornadiene)Cl]_2$ and WCl_6 were designated poly(**1**)-**Rh** and poly(**1**)-**W**, respectively.

8) UV-VIS λmax for poly(**1**)-**Rh** : 269(ε 10600), 297(sh, ε 8300), 347(sh,ε 5350), 408(sh, ε 3700) nm. sh = shoulder.

9) F.Ciardelli, S. Lanzillo, and O. Pieroni, *Macromolecules*, **7**, 174(1974).

10) J. F. Moore, C. B. Gorman, and R. H. Grubbs, *J. Am. Chem. Soc.*, **113**, 1704(1991).

11) M. Yamaguchi, K. Omata, and M. Hirama, *Chem. Lett.*, **1992**, 2261.

12) M. Goodman and S. Chen, *Macromolecules*, **3**, 398(1970).

13) M.M.Green, C. Andreola, B. Munoz, M.P. Reidy, and K. Zero, *J. Am. Chem. Soc.*, **110**, 4063(1988).

14) Y. Nozaki, M. Tabata, K. Yokota, and T. Hoshina, *Polym. Preprints, Jpn.*, **41**, 2875(1992).

15) M.M.Green, M. P. Reidy, R. J. Johnson, G. Darling, D.J. O'Leary, and G. Willson, *J. Am. Chem. Soc.*, **111**, 6452(1989).

16) D. Lee, D. Lee, and K. Soga, *Makromol. Chem., Rapid Commun.*, **11**, 559(1990).

17) C. I. Simionescu, V. Percec, and S. Dumitrescu, *J. Polym. Sci., Polym. Chem.*, **15**, 2497(1977).

18) V. Percec and P. L. Rinaldi, *Polym. Bull.*, **9**, 548(1983).

19) A.A. Berlin and M.I.Cherkashin, *Vysokomol. Sojed.*, **A13**, 2298(1971).

20) This monomer(**2**) was also synthesized from p-bromobenzoic acid[3] { $[\alpha]_D^{20}$ = + 5.90(c 0.525, $CHCl_3$)}. ^{1}H-NMR($CDCl_3$) for **2**: δ 8.00 (2H, d, phenylene protons), 7.55(2H, d, phenylene protons), 4.16(1H, m, $C\underline{H}_2$-O), 3.23(1H, s, $\underline{H}C$-C), 1.82(1H,m,$C\underline{H}$), 1.50 and 1.29(2H, m, $C\underline{H}_2$), 0.99(6H, m, $2C\underline{H}_3$) ppm.

21) Determined by ^{1}H-NMR.

22) The CD spectrum for poly(**1**)-Rh membrane prepared from 1,2-dichloroethane solution: θ = -25 mdeg(265 nm) , 0(292), +29(310), 0(346), -70(376).

(Received August 12, 1993)