ADSORPTION OF POLYCHLORINATED BIPHENYL (PCBs) ATROPISOMER BY CYCLODEXTRIN POLYMER

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Introduction

Atropisomers are stereoisomers resulting from hindered rotation about single bonds where the steric strain barrier to rotation is high enough to allow for the isolation of the conformers. To elucidate assignment enantiomer-specifically for PCB atropisomers, and to develop new analytical method, various CD-polymers were synthesized.

Materials and methods

Standard solution:

19 atropisomers of PCBs (Table 1) were obtained from AccuStandard Inc. and each solution was diluted in 2,2,4-trimethylpentane.

GC/MS analysis

For the analysis 450-GC/320-MS (Bruker) was used with a 10 m Rapid-MS column (ID: 0.25 mm; df: 0.25um) for MS spectra analysis and for rapid screening, and the GC/MS was used with a 30m BGB172 capillary column (0.25mm id, BGB Analytik AG) for enantioselective analysis. Identification and quantification of atropisomers were performed using GC/MS-SIM, GC-MS/MS. Helium was used for carrier gas, Argon was used for CID gas.

CD polymer

The CD polymers were prepared by the reaction of β-CD and γ-CD with various kinds of crosslinkers.

Results and discussion:

Enantioselective analysis

No data are available for PCB-183 enantioselective assignment. To elucidate assignment of (+) and (-) PCB-183, using chiral recognition ability of CD polymer, the enantiomeric fraction (EF) value was measured. The enantiomeric enrichment of PCB atropisomer was expressed as EF value , defined as $EF = A_1/(A_1 + A_2)$ where A_1 and A_2 are the first and second eluting enantiomer, respectively. A racemic compound in theory will have an EF =0.5; any significant deviation from 0.5 indicates a shift in enantiomeric composition. Any significant enrichment was not detected in these CD polymer (Table 4). EF values of PCB-183 in TBDMS-β-CD and Terephthaloyl-γ-CD were slightly reduced to 0.470, 0.468 respectively.

Adsorption of PCB by CD polymer

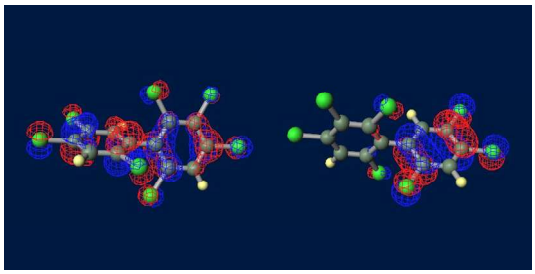
The removal of PCBs from insulating oil by γ-CD polymers as a new adsorbent was reported previously[1]. Among the γ-CD polymers thus obtained, the polymer crosslinked with terephathaloyl units showed the highest adsorption capability towards PCBs. Using this type of polymer (more than 45 wt% of insulating oil) as an adsorbent, any kinds of PCBs including 3,3',5,5'-TeCB, whose initial concentrations were 50 ppm, were completely removed from the insulating oil. It was also found that the adsorbed PCBs were easily recovered from the γ-CD polymer by simply washing with acetone, and PCBs were completely removed from the insulating oil even by the regenerated adsorbent, indicating that the γ-CD polymer can be easily regenerated and recycled.

Table 1 PCB atropisomers and chemical stuructures

Congener	Structure	Structure	CAS No.	Type
45	2,2',3,6	236 - 2	70362 - 45 - 7	ATROP-I
84	2,2',3,3',6	236 - 23	52663 - 60 - 2	ATROP-I
88	2,2',3,4,6	2 - 2346	55215 - 17 - 3	ATROP-II
91	2,2',3,4',6	236 - 24	68194 - 05 - 8	ATROP-I
95	2,2',3,5',6	236 - 25	38379 - 99 - 6	ATROP-I
131	2,2',3,3',4,6	2346 - 23	61798 - 70 - 7	ATROP-II
132	2,2',3,3',4,6'	234 - 236	38380 - 05 - 1	ATROP-I
135	2,2',3,3',5,6'	235 - 236	52744 - 13 - 5	ATROP-I
136	2,2',3,3',6,6'	236 - 236	38411 - 22 - 2	ATROP-I
139	2,2',3,4,4',6	2346 - 24	56030 - 56 - 9	ATROP-II
144	2,2',3,4,5',6	2346 - 25	68194 - 14 - 9	ATROP-II
149	2,2',3,4',5',6	236 - 245	38380 - 04 - 0	ATROP-I
171	2,2'3,3',4,4',6	2346 - 234	52663 - 71 - 5	ATROP-II
174	2,2',3,3',4,5,6'	2345 - 236	38411 - 25 - 5	ATROP-I
175	2,2',3,3',4,5',6	2346 - 235	40186 - 70 - 7	ATROP-II
176	2,2',3,3',4,6,6'	2346 - 236	52663 - 65 - 7	ATROP-I,II
183	2,2',3,4,4',5',6	2346 - 245	52663 - 69 - 1	ATROP-II
196	2,2',3,3',4,4',5,6'	2345 - 2346	42740 - 50 - 1	ATROP-II
197	2,2',3,3',4,4',6,6'	2346 - 2346	33091 - 17 - 7	ATROP-II

Table 2 EF value of PCB-183 standard (n=7)

	EF	
monitoring ion	mean	standard deviation
324	0.483	0.005
326	0.486	0.005
361	0.488	0.003
396	0.485	0.003



PCB-183 PCB-183-II

Table 3 Cyclodextrin Polymer using experiment

	Adsorbent
II	TBDMS-β-CD
III	TIPS-β-CD
IV	Terephthaloyl-γ-CD-1
V	Terephthaloyl-γ-CD-2
VI	Terephthaloyl-γ-CD-3
VII	Bz-β-CD
VIII	Bz-γ-CD
IX	α-CD
X	β-CD
XI	γ-CD

TBDMS: *tert*-Butyldimethylsilyl;
TIPS: TriIsopropylsylyl ;
Bz : Benzyl ;
Terephthaloyl : Terephthalic acid

Table 4 EF value of PCB-183 standard with cyclodextrin polymer

		EF	
	Polymer	mean	standard deviation
I	Control	0.480	0.005
II	TBDMS-β-CD	0.470	0.016
III	TIPS-β-CD	0.482	0.005
IV	Terephthaloyl-γ-CD-1	0.486	0.002
V	Terephthaloyl-γ-CD-2	0.468	0.010

Table 5 Adsorption ratio for atropisomers by cyclodextrin polymer

	CB-45 236-2	CB-95 236-25	CB-88 2346-2	CB-91 236-24	CB-84 236-23	CB-136 236-236
TBDMS-β-CD	0.45	0.50	0.50	0.57	0.46	0.53
TIPS-β-CD	0.20	0.20	0.20	0.04	0.14	0.27
Terephthaloyl-γ-CD-1(K-12-13)	0.42	0.37	0.37	0.25	0.35	0.34
Terephthaloyl-γ-CD-2(K-12-11)	0.83	0.80	0.80	0.77	0.85	0.76
Terephthaloyl-γ-CD-2(K-12-11)	0.83	0.80	0.80	0.80	0.84	0.77
Terephthaloyl-γ-CD-3(K-9-65)	0.71	0.62	0.62	0.57	0.64	0.48
Bz-β-CD	0.43	0.46	0.46	0.40	0.42	0.42
Bz-γ-CD	0.46	0.49	0.49	0.48	0.44	0.51
α-CD	0.21	0.25	0.25	0.36	0.22	0.29
β-CD	0.36	0.40	0.40	0.39	0.33	0.40
γ-CD	0.35	0.38	0.38	0.37	0.33	0.38

	CB-135 235-236	CB-144 2346-25	CB-149 236-245	CB-139 2346-24	CB-131 2346-23	CB-132 234-236
TBDMS-β-CD	0.34	0.44	0.56	0.86	0.69	0.70
TIPS-β-CD	0.12	0.00	0.19	0.44	0.28	0.21
Terephthaloyl-γ-CD-1(K-12-13)	0.29	0.18	0.35	0.48	0.39	0.38
Terephthaloyl-γ-CD-2(K-12-11)	0.79	0.76	0.81	0.81	0.84	0.84
Terephthaloyl-γ-CD-2(K-12-11)	0.79	0.79	0.82	0.82	0.84	0.86
Terephthaloyl-γ-CD-3(K-9-65)	0.52	0.47	0.58	0.65	0.65	0.61
Bz-β-CD	0.25	0.27	0.43	0.72	0.57	0.58
Bz-γ-CD	0.29	0.36	0.51	0.80	0.66	0.63
α-CD	0.12	0.25	0.28	0.63	0.41	0.40
β-CD	0.25	0.27	0.42	0.64	0.53	0.51
γ-CD	0.26	0.27	0.41	0.66	0.53	0.47

	CB-176 2346-236	CB-175 2346-235	CB-183 2346-245	CB-174 2345-236	CB-171 2346-234	CB-197 2346-2346	CB-196 2346-2345
TBDMS-β-CD	0.72	0.32	0.89	0.30	0.90	0.91	0.31
TIPS-β-CD	0.38	0.20	0.65	0.13	0.49	0.72	0.15
Terephthaloyl-γ-CD-1(K-12-13)	0.35	0.29	0.71	0.30	0.56	0.54	0.25
Terephthaloyl-γ-CD-2(K-12-11)	0.71	0.81	0.89	0.81	0.86	0.72	0.80
Terephthaloyl-γ-CD-2(K-12-11)	0.73	0.80	0.91	0.78	0.85	0.71	0.81
Terephthaloyl-γ-CD-3(K-9-65)	0.46	0.46	0.80	0.43	0.74	0.58	0.45
Bz-β-CD	0.58	0.35	0.82	0.25	0.79	0.81	0.26
Bz-γ-CD	0.66	0.38	0.86	0.34	0.82	0.85	0.28
α-CD	0.51	0.12	0.75	0.07	0.66	0.72	0.16
β-CD	0.55	0.31	0.78	0.29	0.77	0.78	0.30
γ-CD	0.51	0.31	0.80	0.23	0.77	0.77	0.24

References:

1. Kida T, Nakano T, Fujino Y, Matsumura C, Miyawaki K, Kato E, Akashi M.(2008); *Anal. Chem.*, 80(1): 317-20.