Supporting Information

Synthesis and Structure of Cyclic Oligo(*p*-phenylene oxide)s, $\lceil(C_6H_4\text{-}O)_n\rceil$ (n = 6 – 10)

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Crystal Structure Determination. Crystals were mounted in glass capillary. The data were collected at a temperature of -160 ± 1 °C to a maximum 2θ value of 55.0° on Rigaku Saturn CCD area detector. Calculations were carried out by using the program package Crystal Structure for Windows. The structure was solved by direct methods and expanded using Fourier techniques. A full matrix least squares refinement was used for non-hydrogen atoms with aniosotropic thermal parameters. Atomic scattering factors were obtained from the literature.[9] Crystallographic data and details of refinement of the cyclic oligo(*p*-phenylene oxide)s are summarized in Table S-1.

TABLE S-1. Crystallographic Parameters of Cyclic Oligo(*p*-phenylene oxide)s

	(**C-6**)$_2$(CH_2Cl_2)$_3$	**C-7**·($CHCl_3$)$_2$	**C-8**·($CHCl_3$)$_2$	**C-9**·($CHCl_3$)(C_6H_{14})
Empirical Formula	$C_{75}H_{54}Cl_6O_{12}$	$C_{44}H_{30}Cl_6O_7$	$C_{50}H_{34}Cl_6O_8$	$C_{61}H_{51}Cl_3O_9$
Formula Weight	1359.96	883.43	975.53	1034.43
Crystal System	Triclinic	monoclinic	Triclinic	Triclinic
Space Group	P-1 (# 2)	$P2_1/n$ (# 14)	P-1 (# 2)	P-1 (# 2)
a, Å	10.127(8)	14.61(2)	9.596(7)	10.566(9)
b, Å	12.462(9)	10.187(15)	14.145(10)	14.099(11)
c, Å	25.76(2)	26.99(4)	17.077(13)	19.13(1)
α, *deg*	84.40(4)		83.87(4)	77.94(4)
β, *deg*	84.69(3)	101.36(3)	81.88(3)	74.87(3)
γ, *deg*	78.62(3)		87.12(3)	76.71(3)
V, Å^3	3163(4)	3938(11)	2280(3)	2642.8(35)
Z	2	4	2	2
D_{calcd}, g cm^{-1}	1.428	1.490	1.421	1.300
No. of date	17660	28432	16649	15257
No. of obsd. date	4234	2616	5569	3439
No. of Variables	892	544	611	655
$R(F_0)$	0.069	0.056	0.081	0.110
$R_w(F_0)$	0.104	0.050	0.133	0.159
GOF	0.997	0.907	0.954	0.784

Thermogravimetric Analysis and Differential Scanning Carolimetry

Results of thermogravimetric analysis and differential scanning carolimetry of the obtained cyclic oligo(*p*-phenylene oxide)s are summarized in Table S-2. Temperature of 5% weight loss, T_d^5, is raised with increment of the ring size . DSC of **C-6** showed no melting point of **C-6**, presumably due to its higher melting point than decomposition temperature. Melting points of **C-8** and **C-10** are 350 and 148 °C, respectively. First scan of **C-9** shows a single endothermic peak at 280 °C, whereas second scan of **C-9** shows two endothermic peaks at 210 and 273 °C. These results indicate some phase transition takes place at the temperature. The melting points of **C-6**, **C-8**, **C-9**, and **C-10** decrease in this order. On the other hand, melting point of **C-7** is 190 °C, which is exceptionally lower than other cyclic oligo(*p*-phenylene oxide)s. This is probably due to the more flexible structure of **C-7** as revealed by X-ray crystal structure analysis. The melting points of poly(*p*-phenylene oxide) and linear hexamer are 171 °C, which is lower than the cyclic oligo(*p*-phenylene oxide)s.

TABLE S-2. Thermogravimetric Analysis and Differential Scanning Carolimetry of Cyclic Oligo(*p*-phenylene oxide)s

	T_d^5/°C	T_m/°C
C-6	340	-
C-7	380	190
C-8	408	350
C-9	450	210 and 280
C-10		148