

REMOVAL OF POLYCHLOROBIPHENYLS IN OILS BY DIMETHYL-B-CYCLODEXTRIN POLYMERS

Kawano S.¹, Nakano T.^{1,2}, Miyawaki K.³, Kato E.^{1,2}, Kida T.^{1,2}, Akashi M.*^{1,2}

¹Graduate School of Engineering, Osaka University, 2-1, Suita, Osaka 565-0871, Japan, ²NEOS Joint Research Chair, Osaka University, 2-1, Suita, Osaka 565-0871, Japan, ³NEOS Co. Ltd., Konan, Shiga 520-3213, Japan

Introduction

Polychlorobiphenyls (PCBs) are one of persistent organic pollutants which were widely used as insulating fluids in capacitors and transformers. Although their manufacture and commercial use have been prohibited in many countries since the 1970s because of their strong toxicity, environmental persistence, and bioaccumulation, large amounts of insulating oils contaminated with PCBs are still being used or are kept without being appropriately treated in many countries, including Japan.

For the treatment of these PCBs, various chemical destruction methods, such as dechlorination of PCBs with alkalines¹ and supercritical water oxidation of PCBs², have been developed. However, these methods have a serious drawback in that they require high reaction temperature and/or prolonged reaction times to destroy the PCBs. Thus, these methods are not appropriate for efficient treatment of large amounts of insulating oils contaminated by small amounts of PCBs (1-100 ppm). If a new adsorbent is developed, which allows the selective removal of PCBs from insulating oils, and permits the easy recovery of adsorbed PCBs by washing with small amounts of organic solvents, one can significantly reduce the amount of PCB-contaminated insulating oils. The development of such an innovative adsorbent is strongly desired from the viewpoints of energy conservation and environmental protection.

Cyclodextrin (CDs) are a class of cyclic oligosaccharides consisting of several α -(1,4)-linked D-glucopyranose units. They have a cavity into which a guest molecule of an appropriate size and shape is incorporated in aqueous solution mainly through the hydrophobic interactions (Fig. 1). The ability of CDs to form inclusion complexes with organic molecules has been applied to many areas³. Since the size and shape of PCBs are suitable to be incorporated into the CD cavity, it can be expected that the appropriate chemical modification of CDs would lead to the inclusion of PCBs in oils. Recently, we formed that 6-*O*-tert-butyltrimethylsilylated β -cyclodextrin (TBDMS- β -CD) can form inclusion complexes with polychlorinated⁵ and polycyclic aromatic compounds⁶ in nonpolar media such as benzene and cyclohexane. Beside, a channel-type γ -CD assembly effectively adsorbed PCBs such as mono-, di-, and tri-chlorobiphenyls in nonpolar solvents and insulating oil⁷. On the other hand, these CD adsorbents showed little adsorption capability for bulky PCBs. Since large fractions of global PCB stockpiles to be treated are higher chlorinated biphenyls, the development of CD derivatives which enable the removal of any kinds of PCBs including higher chlorinated biphenyls is essential for practical use as an adsorbent for PCBs in oils. In this work, we prepared cyclodextrin polymers (CDPs) by the crosslinking of various CD derivatives with diisocyanates, and examined their ability to adsorb PCBs in oils.

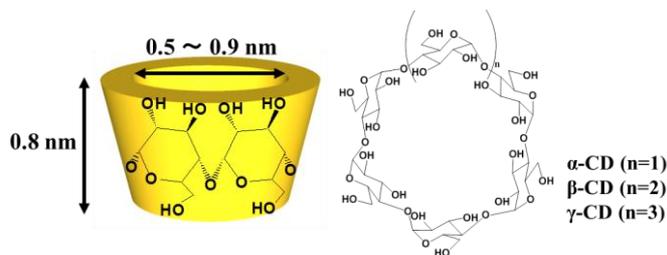


Fig. 1. Chemical structures of cyclodextrins (CDs).

Materials and Methods

CDPs consisting of β -CD, 2,6-di-*O*-methylated β -CD (DM- β -CD), and γ -CD were prepared by the polycondensation reaction with difunctional crosslinking reagents (3 mol equiv.) such as 4,4'-methylenebis(phenyleneisocyanate) (Scheme 1). After the reaction, the reaction mixture was poured into water and the resulting precipitates were collected by the filtration. The obtained solids were washed with the deionized water, followed by lyophilization to give the products as a powder. The CDPs thus obtained were characterized with fourier transform-infrared spectra (FT-IR), and scanning electromicroscopy (SEM). The adsorption capability of the CDPs towards PCBs in oils were examined by passing the PCBs solution through a column packed with

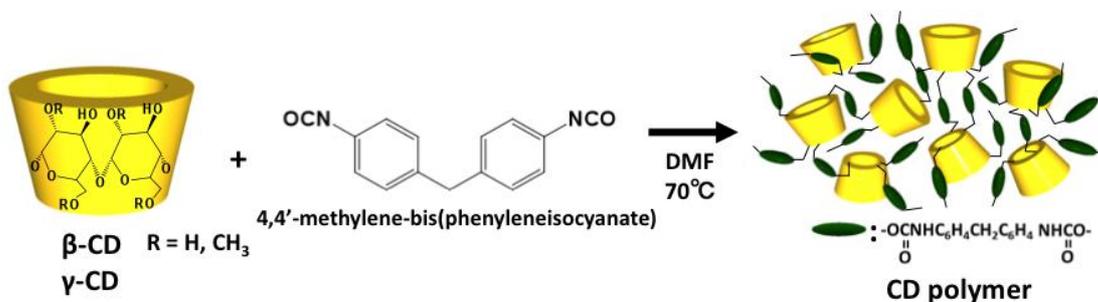
CDPs, and measuring the concentration of PCBs in the solution emerging from the end column with a gas chromatograph-tandem mass spectrometry (GC/MS/MS). Initial concentrations of PCBs were 0.01 and 1 ppm in isooctane and insulating oil, respectively. Amounts of CDPs used for the column packing were 180 and 200 mg. The experiments were carried out at 25 and 80 °C.

4-Monochlorobiphenyl (4-MCB), 3,4-dichlorobiphenyl (3,4-DiCB), 4,4'- dichlorobiphenyl (4,4'-DiCB), 3,3',4-trichlorobiphenyl (3,3',4-TriCB), 3,4,4'-trichlorobiphenyl (3,4,4'-TriCB), 2,2',6,6'-tetrachlorobiphenyl (2,2',6,6'-TeCB), 3,4,4',5- tetrachlorobiphenyl (3,4,4',5-TeCB), 3,3',5,5'- tetrachlorobiphenyl (3,3',5,5'-TeCB), 2,2',4,5,5'-pentachlorobiphenyl (2,2',4,5,5'-PeCB), 3,3',4,4',5,5'-hexachlorobiphenyl (3,3',4,4',5,5'-HeCB) and 2,2',3,3',5,5'-hexachlorobiphenyl (2,2',3,3',5,5'-HeCB) were chosen as PCBs (Fig. 2).

Results and Discussion

While the β -CD polymer (poly(β -CD)) and γ -CD polymer (poly(γ -CD)) formed organogels after the reaction, the polymer consisting of 2,6-di-*O*-methylated β -CD (poly(DM- β -CD)) gave a particle dispersion solution. The latter polymer was obtained as a light powder after lyophilization.

SEM image shows microscopic structures of the CDPs (Fig. 3). Poly(DM- β -CD) gave porous structures formed by the assembly of particles with a size of 100 to 200 nm (Fig. 3a). On the other hand, poly(β -CD) showed xerogel structures composed of three-dimensional networks (Fig. 3b).



Scheme 1. Preparation of CDPs by polycondensation of CDs with crosslinker

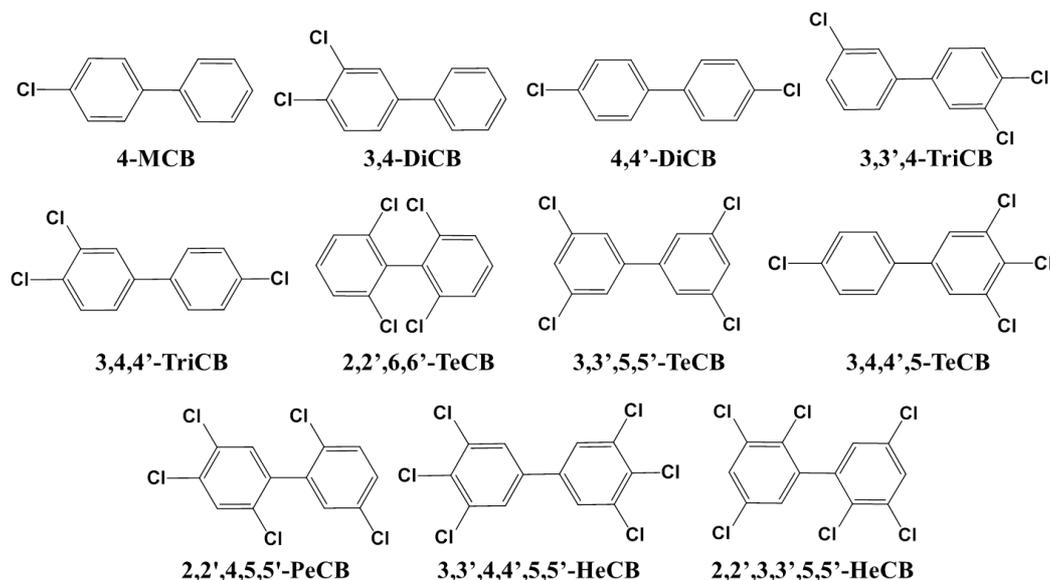


Fig. 2. Chemical structures of various PCBs.

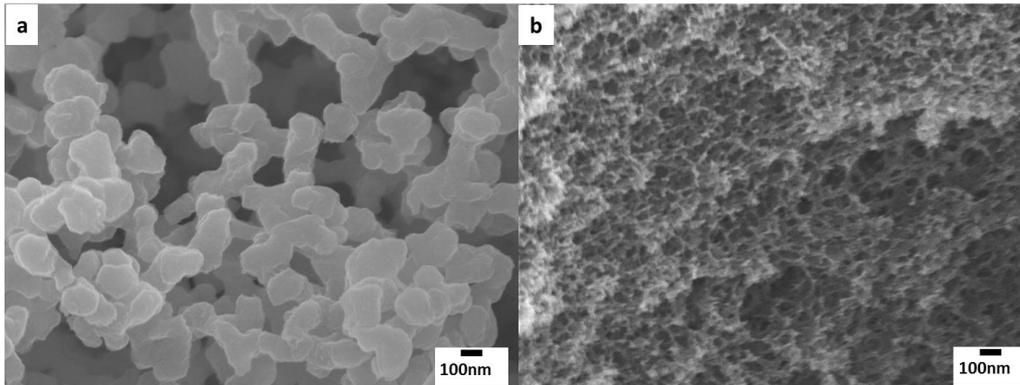


Fig. 3. SEM images of xerogels obtained after lyophilization of (a) Poly(DM- β -CD) and (b) Poly(β -CD) dispersed in water.

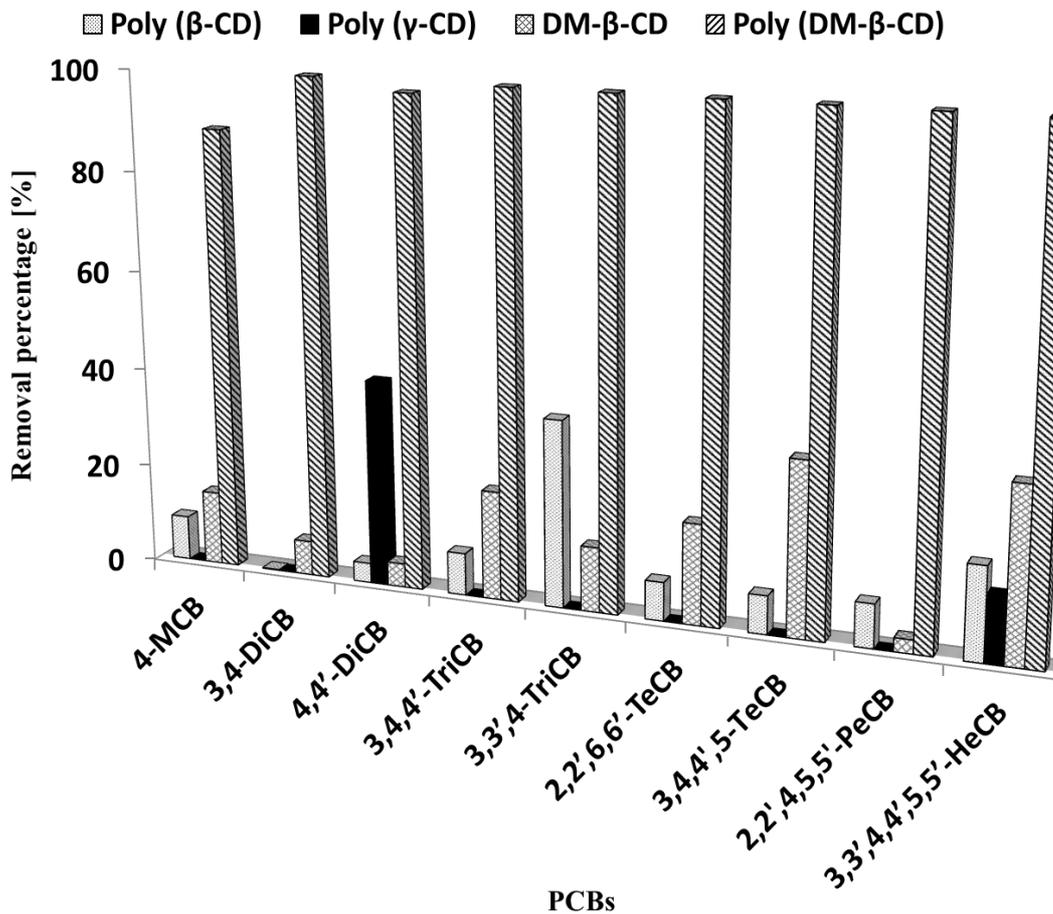


Fig. 4. Removal percentage of PCBs from isooctane by various CD polymers and a CD derivative.

Fig. 4 shows removal percentage of PCBs from isooctane by various CDPs (Poly(DM- β -CD), poly(β -CD), poly(γ -CD), and a DM- β -CD monomer. Poly(DM- β -CD) showed almost complete removal of the PCBs including bulky PCBs. On the other hand, poly(β -CD) and poly(γ -CD) had much lower adsorption ability. DM- β -CD monomer also had low adsorption capability. The result suggests that PCBs are surrounded with plural CD molecules connecting to each other through crosslinkers as well as inclusion complexes between CDs and PCBs. Poly(DM- β -CD) also constructs monolithic structures consisting of submicron-sized particles and high surface area, which can cause high affinity in oil, resulting in high adsorption property against PCBs.

Adsorption experiment from insulating oil was performed by Poly(DM- β -CD). While removal percentage of 3,3',5,5'-TeCB and 2,2',3,3',5,5'-HeCB was low at 25 °C, almost complete removal of the PCBs was achieved by increasing temperature to 80 °C. In higher temperature, viscosity of insulating oil decreases and the CDP can have high affinity with insulating oil, resulting in high removal percentage of PCBs. The adsorbed PCBs could be recovered from the CDP by washing with appropriate organic solvents. It indicates that the CDP can be easily regenerated and possibly recycled in the future process.

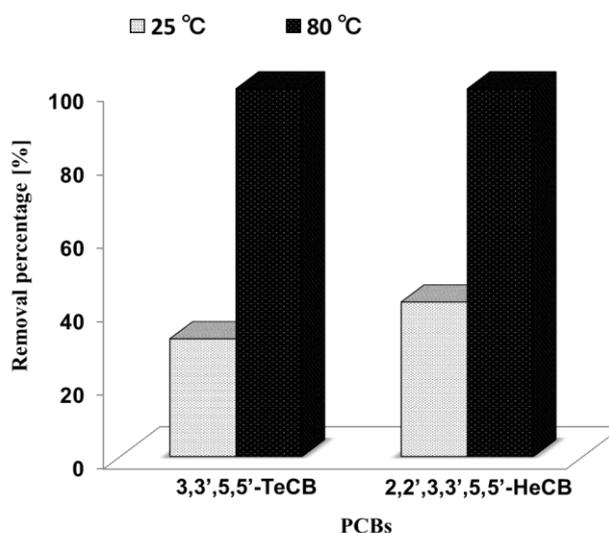


Fig. 5. Removal percentage of PCBs from insulating oil by poly(DM- β -CD) as a function of temperature.

References

1. Ohno M.; Kaneda H.; Hirata K. *Organohalogen Compounds* **1997**, *31*, 415.
2. Hatakeda K.; Ikushima Y.; Sato O.; Aizawa T.; Saito N. *Chem. Eng. Sci.* **1999**, *54*, 3079.
3. Szejtli J.; Osa T. *Comprehensive Supramolecular Chemistry*, Atwood J. L.; Davies J. E. D.; MacNicol D. D.; Vogtle F.; Lehn J.-M. (ed.), Pergamon, Oxford, **1996**, 3.
4. Van Etten R. L.; Sebastian J. F.; Clowes G. A.; Bender M. L. *J. Am. Chem. Soc.* **1967**, *89*, 3242.
5. Kida T.; Fujino Y.; Miyawaki K.; Kato E.; Akashi M. *Org. Lett.* **2009**, *11*, 5282.
6. Kida T.; Iwamoto T.; Fujino Y.; Tohnai N.; Miyata M.; Akashi M. *Org. Lett.* **2011**, *13*, 4570.
7. Kida T.; Nakano T.; Fujino Y.; Matsumura C.; Miyawaki K.; Kato E.; Akashi M. *Anal. Chem.* **2008**, *80*, 317.