Articles

In Situ Polycondensation of *p-tert*-Butylphenol in the Presence of Poly(ethylene glycol)s for Preparation of Polyrotaxanes

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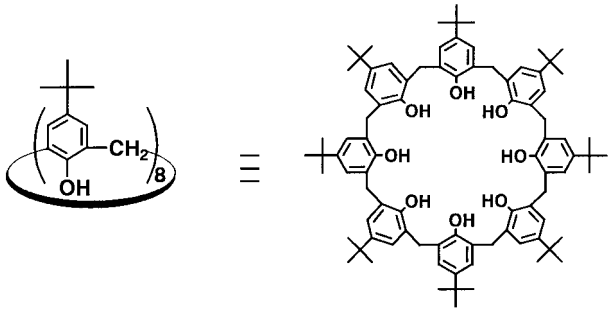
ABSTRACT: A new polyrotaxane was formed by the polycondensation of *p-tert*-butylphenol (BP) with paraformaldehyde in the presence of poly(ethylene glycol)s, (PEG)s, of various molecular weights. The polyrotaxane of BP oligomers with PEG was obtained when the PEG of average molecular weights between 1000 and 10 000 were used in the polycondensation. The polyrotaxane yield and the composition were dependent on the molecular weight of PEG. The molecular structure was determined by FT-IR and ^{1}H NMR spectroscopies and the thermal properties by DSC measurements. ^{1}H NMR spectra of the complexes showed a pair of doublets in the methylene region, which correspond to the methylene protons between phenolic rings in *p-tert*-butylcalixarenes. The FT-IR spectra and DSC curves were different from those of the blend of linear *p-tert*-butylphenolic resins with PEG and pure *p-tert*-butylcalix[8]arene, respectively. Calixarenes slipped off the backbone PEG by heating the polyrotaxane in ethylene glycol at 180 °C. The structure of the dethreaded calixarenes was determined by ^{1}H NMR, and they were found to be *p-tert*-butylcalix[8]arenes and a few *p-tert*-butylcalix[4]arenes. From the characteristic results it was found that the polyrotaxane obtained by the in situ polycondensation of BP was composed of *p-tert*-butylcalix[8]-arenes penetrated by PEG; that is, this was a calix[8]arene-based polyrotaxane.

Introduction

Phenolic resin is readily prepared by addition−condensation reaction of phenols with formaldehyde under acidic or basic conditions. The resin is characterized as three-dimensional networks with hydrogen bonding among phenolic hydroxyl groups. These structural features contribute to preparation of blends, molecular composites, and interpenetrating polymer networks (IPN). Actually, the blends[1−7] and the IPN complexes[8] of phenolic resins with other polymers containing carbonyl or nitrile groups and ether or sulfone linkages have been reported, and the polymer−polymer interaction and the miscibility, arising from intermolecular hydrogen bonds, were determined by Fourier transform infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC).

On the other hand, it is well-known that the polycondensation of para-substituted phenols with formaldehyde in nonpolar solvent leads to the formation of cyclic oligomers, which are named "calixarenes".[9] Calixarenes have a unique cavity surrounded by benzene rings and cyclic arranged OH groups. For example, the structure of *p-tert*-butylcalix[8]arene is shown in Scheme 1. They can form inclusion complexes with neutral molecules as well as with metal cations. Recently, the inclusion complexes of macrocycles with linear polymeric backbones are prepared, which are represented as "polyrotaxanes".[10−16] Two main classes of polyrotaxanes have been reported: one is cyclodextrin-based polyrotaxanes,[11−14,16a] and the other is crown ether-based ones.[15,16b−e] Since polyrotaxanes are composed of cyclic molecules penetrated by a linear backbone without covalent bonds between these molecules, new properties and applications are expected. The structure of calixarenes is like that of cyclodextrins so that calixarenes will be also expected to form inclusion complexes with linear polymers.

Scheme 1. Structure of *p-tert*-Butylcalix[8]arene



In this paper, a new polyrotaxane of phenolics with linear polymer is prepared by the polycondensation of *p-tert*-butylphenol with paraformaldehyde in the presence of poly(ethylene glycol)s, (PEG)s. The structure and the thermal properties are determined by ^{1}H NMR and FT-IR spectroscopies and DSC measurements. From these results the formation of a calixarene-based polyrotaxane is discussed.

Experimental Section

Materials. Commercially available *p-tert*-butylphenol, paraformaldehyde, 37% formalin, NaOH, concentrated HCl,

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acetone, CH_2Cl_2, *N*,*N*-dimethylformamide (DMF), and ethylene glycol (all from Nacalai Tesque Inc.) were used without further purification. Tetrahydrofuran (THF) (Nacalai Tesque Inc.) was distilled and then used for measurements of gel permeation chromatography (GPC). Poly(ethylene glycol)s of average molecular weights, MW, = 600, 1000, 2000, 3100, and 10 000 and poly(propylene glycol) of MW = 2000 were purchased from Nacalai Tesque Inc. The average molecular weights of these polymers were determined by GPC, and the values were in agreement with those given by the company.

Preparation. *Standard Linear Oligomers of p-tert-Butylphenol.* Standard linear oligomers of *p-tert*-butylphenol, *n*BP (*n* is the degree of polymerization), with degrees of polymerization (DP's) = 2, 3, 4, 5, 6, 7, and 10 were prepared according to the literature.[17,18]

p-tert-Butylphenolic Resin. p-tert-Butylphenol (150 g), 37% formalin (80 g), and concentrated HCl (17 mL), as a catalyst, were charged in a three-necked flask equipped with a reflux condenser and a stirrer. The mixture was refluxed for 4 h. After cooling to room temperature, the aqueous phase was removed by decantation, and the crude resin was dissolved in acetone. The resin was precipitated by pouring the acetone solution into a large amount of water. The resin was dried in a vacuum at 30 °C for 2 days (yield: 167 g, number-average molecular weight (M_n) = 800 and ratio of weight- to number-average molecular weight (M_w/M_n) = 1.3 determined by GPC).

Complex for Weight Ratio of PEG to p-tert-Butylphenol = 1.2/1 in Xylene. p-tert-Butylphenol (7.5 g), paraformaldehyde (3.2 g), PEG (9.0 g), and NaOH (0.4 g) were added in 50 mL of xylene and heated at 100 °C for 8 h, removing condensed water. The reaction mixture was refluxed for 4 h. After cooling to room temperature, the solution was evaporated under reduced pressure to obtain a crude product. Uncomplexed PEG was removed by washing the product with water. Complexes were isolated from the residue by silica gel column chromatography eluting with CH_2Cl_2−hexane (vol 1:1), with acetone, and then with DMF.

Complex for Weight Ratio of PEG to p-tert-Butylphenol = 1.2/1 in Bulk. p-tert-Butylphenol (7.5 g), paraformaldehyde (3.2 g), and PEG (9.0 g) were melted at 60 °C, and then NaOH (0.4 g) was added and mixed. The mixture was heated at 100 °C for 2 h, removing condensed water, and then was more heated at 120 °C for 8 h. After cooling to room temperature, uncomplexed PEG was removed by washing the crude product with water. Complexes were isolated from the residue by silica gel column chromatography eluting with CH_2Cl_2−hexane (vol 1:1), with acetone, and then with DMF.

Blend. p-tert-Butylphenol resin (1 g) or standard linear *p-tert*-butylphenol oligomer (1 g) and PEG (1.2 g) were melted and mixed at 120 °C for 4 h. After cooling to room temperature, the crude product was washed with water to remove uncomplexed PEG. The blend was dried in a vacuum at 30 °C for 2 days.

End-Blocked PEG. PEG (5 mmol of OH groups) and triphenylmethyl chloride (13.9 g, 50 mmol) were dissolved in 100 mL of dry $CHCl_3$, and then triethylamine (20 mL) was added portionwise at room temperature. After the mixture was stirred for 24 h at room temperature, the solvent was removed by evaporation. The residue was dissolved in 50 mL of acetone and precipitated into 500 mL of water. The precipitate was washed with hexane (5 times) to remove triphenylmethyl chloride. The product was further purified by silica gel column chromatography eluting with CH_2Cl_2. ^{1}H NMR (acetone-d_6): 3.54−3.69 (m, −OCH_2CH_2−), 7.22−7.36 (m, 9H), 7.45−7.52 (m, 6H).

Dethreading. Polyrotaxane (1 g) was heated in 40 mL of ethylene glycol at 180 °C for 32 h. Dethreaded compounds was filtered off, washed with water and methanol, and dried in a vacuum. Dethreaded calixarenes were isolated from the residue by silica gel column chromatography eluting with $CHCl_3$−hexane (vol 1:1).

Measurements. GPC measurements were carried out by a Shimadzu HPLC LC-6A equipped with two TSKgel G3000HXL columns or two TSKgel GMHXL columns and a TOSOH UV-8011 spectrophotometer (270 nm) and a Mitsumi RI monitor SF-1107 as detectors and THF as an eluent at 1.0 mL/min. The chromatograms were analyzed by a Shimadzu C-R4A data processor. Poly(oxyethylene) (POE) and polystyrene standards were used as the GPC calibration. ^{1}H NMR spectra were recorded on a JEOL FX-100S FT-NMR spectrometer at 100 MHz and also by a JEOL FX-400S FT-NMR spectrometer at 400 MHz. $CDCl_3$ and acetone-d_6 were used as solvents, and tetramethylsilane (TMS) was used as a reference. FT-IR spectra were obtained by a Jasco FT/IR-3 spectrophotometer with a KBr disk. DSC measurements were run by a Shimadzu DSC-50 at a heating rate of 10 °C/min under a N_2 atmosphere.

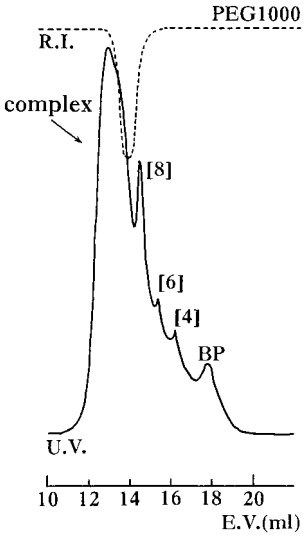


Figure 1. GPC chromatogram of the product obtained by the polycondensation of *p-tert*-butylphenol with paraformaldehyde in the presence of PEG1000 at PEG/BP weight ratio in feed = 1.2/1. The peaks corresponding to *p-tert*-butylcalix[8]arene, *p-tert*-butylcalix[6]arene, *p-tert*-butylcalix[4]arene, and *p-tert*-butylphenol monomer are marked with [8], [6], [4], and BP, respectively.

Results and Discussion

Preparation of Complexes. We have tried to prepare inclusion complexes of *p-tert*-butylcalix[8]arenes with poly(ethylene glycol)s, (PEG's), of average molecular weights (MW) = 1000 and 3000 by statistical threading in chloroform. Because *p-tert*-butylcalix[8]-arene has a cavity (its diameter = about 4.8 Å) to allow inclusion of a PEG chain (the diameter = about 3.1 Å), it was expected to form complexes of polyrotaxane type. However, the complex could not be obtained. So, we try to form a polyrotaxane of phenolics with PEG by in situ polycondensation of *p-tert*-butylphenol (BP) with paraformaldehyde in the presence of PEG using NaOH as a catalyst. To find out a suitable condition for the preparation of polyrotaxanes, the effect of the weight ratio of PEG to BP in feed (PEG/BP weight ratio) was examined. The typical GPC chromatogram of the crude product obtained by the polycondensation of BP in PEG of MW = 1000 (PEG1000) in bulk at PEG/BP weight ratio = 1.2/1 is shown in Figure 1. The figure also shows the chromatogram of PEG1000, which was detected by a refractive index (RI) monitor. The peaks corresponding to *p-tert*-butylcalix[8,6,4]arenes could be found in the figure. A peak at slightly higher molecular weight than that of PEG1000 could be also observed; however, it has never been observed under similar conditions except for no use of PEG1000. This peak was also found in the chromatogram of the crude product obtained by the polycondensation using end-blocked PEG1000 with tri-

Table 1. Polycondensation of *p-tert*-Butylphenol in the Presence of Poly(ethylene glycol) of MW = 1000 in Xylene or in Bulk at 110−120 °C for 10 h[a]

			weight fraction (%)[c]				
run no.	PEG/BP[b]	solvent	calix[8]arene	calix[6]arene	calix[4]arene	BP	complex
1	0/100	xylene	67	11	22	0	0
2	1/170	xylene	67	10	20	0	3
3	1/35	xylene	67	9	19	0	0
4	1/13	xylene	71	0	22	0	7
5	1/3.5	xylene	33	8	21	22	16
6	1.2/1	xylene	3	3	7	69	18
7	2.9/1	xylene	5	3	6	61	25
8	1.2/1		10	6	7	19	58
9	2.9/1		10	13	3	25	49
10	14/1		0	0	0	77	23

[a] Molar ratio: BP/HCHO/NaOH = 1/2/0.2. [b] Weight ratio of poly(ethylene glycol (PEG) of MW = 1000 to *p-tert*-butylphenol (BP). [c] Determined by GPC.

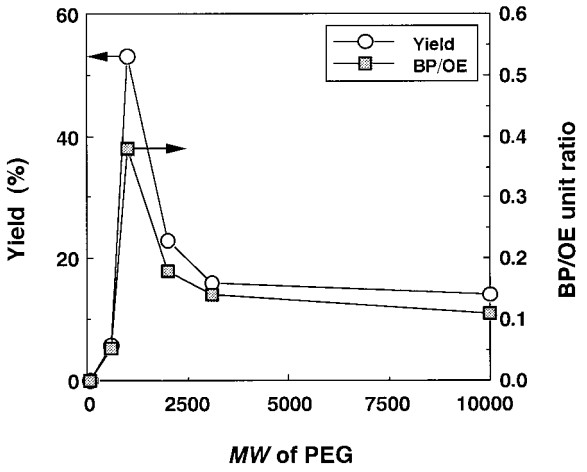


Figure 2. Dependence of complex yield and BP/OE unit ratio on the molecular weight of PEG.

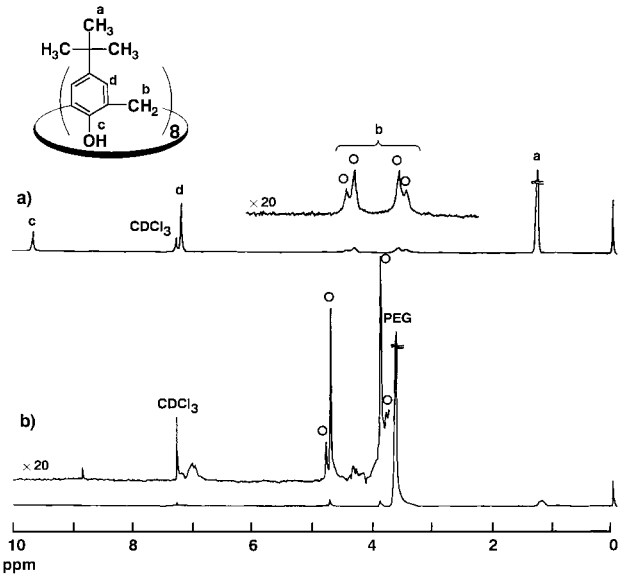


Figure 3. ^{1}H NMR spectra of (a) *p-tert*-butylcalix[8]arene and (b) the complex using PEG1000. The peaks corresponding to "methylene *protons* between phenolic units in calixarene" are marked with circle "O".

tyl groups. This indicates that the peak is not related to products formed by a condensation of phenolics with OH groups at the ends of PEG1000. Thus, the peak will be due to the complexes of phenolic oligomers with PEG1000. The polycondensation results in the presence of PEG1000 are summarized in Table 1. The table indicates that (1) in xylene the complex fraction increases with increasing PEG/BP weight ratio in feed, despite low conversion, and (2) the increase of the complex fraction is conducted with decrease of the *p-tert*-butylcalix[8]arene fraction. This suggests that the complex may be composed of *p-tert*-butylcalix[8]arene and PEG1000. Finally, (3) the complex is much more efficiently obtained by the polycondensation in bulk than that in xylene. On the basis of these results, subsequent experiments were carried out in bulk at PEG/BP weight ratio = 1.2/1, which is the run no. 8 condition in Table 1.

The effect of molecular weight of PEG on the complex formation was examined by using ethylene glycol and PEG's of the molecular weight range from 600 to 10 000. The complex was isolated from the crude product by washing with water and then by silica gel column chromatography. The complex yield was calculated from the weight and composition of the isolated complexes based on the *p-tert*-butylphenolic unit. The dependences of the complex yield and composition on the molecular weight of PEG are shown in Figure 2. The complex could be obtained when the PEG of molecular weight between 1000 and 10 000 was used. The yield was the highest when PEG1000 was used. For the PEG of higher molecular weight it decreased with increasing molecular weight of PEG. The unit ratio of *p-tert*-butylphenolic unit to oxyethylene unit (BP/OE unit ratio) changed with molecular weight of PEG. The BP/OE unit ratio was a maximum at the molecular weight of PEG = 1000, and then the value was lower with increasing the molecular weight. In general, a diffusion rate of reactant is lower, leading to the decrease of the reaction rate, as the viscosity of reaction mixture is increasing. In the in situ complexation, one of the causes of the decreased complex yield may be the increase of viscosity in the reaction mixture with increasing molecular weight of PEG. In addition, when poly(propylene glycol) of MW = 2000 was used as a linear polymer instead of PEG, no complex could be obtained. The complex formation must be influenced by the diameter of the linear polymer used in the polycondensation. These facts indicate that the complexation of phenolics with PEG surely occurs in the in situ polycondensation, and the complex formation will be related to the cyclic conformation of phenolics.

Characteristics of the Complex. The structure of the complexes obtained from the polycondensation in the presence of PEG was determined by spectroscopic methods. The ^{1}H NMR spectrum of the complex using PEG1000 in $CDCl_3$ is shown in Figure 3. The figure also shows the ^{1}H NMR spectrum of *p-tert*-butylcalix[8]-

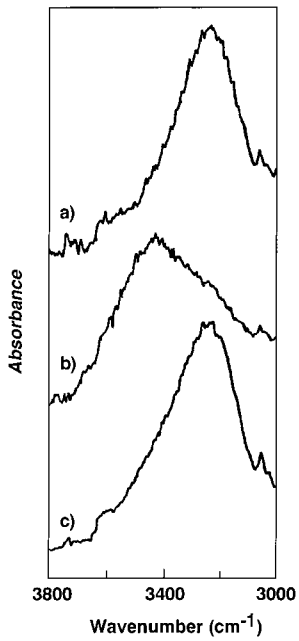


Figure 4. FT-IR spectra of (a) the blend of the *p-tert*-butylphenolic resin with PEG3000, (b) the complex using PEG3000, and (c) *p-tert*-butylcalix[8]arene.

arene, as a typical cyclic oligomer of phenolics, in which a pair of doublets corresponding to methylene protons between phenolic units is displayed. In the spectrum of the complex, we could find a pair of doublets in the methylene region. This indicates that calixarene molecules are involved in the complex. And since the chemical shift of methylene protons in the complex was shifted to lower magnetic field than that of *p-tert*-butylcalix[8]arene, a torsion of the lower rim of the calixarene will occur due to the penetration of PEG.

The strength of hydrogen bonds in the complex was determined by FT-IR. Figure 4 shows the IR spectra of the complex using PEG3000, the blend of the *p-tert*-butylphenolic resin (M_n = 800, M_w/M_n = 1.3) with PEG3000, and also of pure *p-tert*-butylcalix[8]arene. The O−H stretching band (ν_{OH}) in the blend spectrum appeared at 3224 cm^{-1}, which is due to the intermolecular hydrogen bonds between phenolic hydroxyl groups and oxyethylene units. The phenolic hydroxyl groups of calixarenes are form strong intramolecular hydrogen bonds and the ν_{OH} ranges from 3150 to 3300 cm^{-1}.[9] Actually, the ν_{OH} of *p-tert*-butylcalix[8]arene was given to be 3252 cm^{-1} in the figure. On the other hand, the ν_{OH} of the complex was shown at 3424 cm^{-1} and shifted to higher wavenumber by about 200 cm^{-1} than those of the blend and *p-tert*-butylcalix[8]arene. This means that the strength of hydrogen bonds of phenolic hydroxyl groups in the complex decreased by complexing with PEG3000. The reason will be considered that the distance between cyclic arranged hydroxyl groups in the calixarene becomes longer due to the penetration of a PEG chain.

The DSC curve of the complex with PEG1000 is shown in Figure 5 and compared with that of the blend of *p-tert*-butylphenolic resin (M_n = 800, M_w/M_n = 1.3) with PEG1000 (the unit ratio in the blend, BP/OE = about 2/1). The DSC curve of the complex showed three melting endotherms corresponding to the phenolic PEG phase (at 32 °C), the PEG phase (at 48 °C), and the calixarene phase (at 330 °C). The exothermic peak at −3.7 °C may be corresponding to the crystallization of

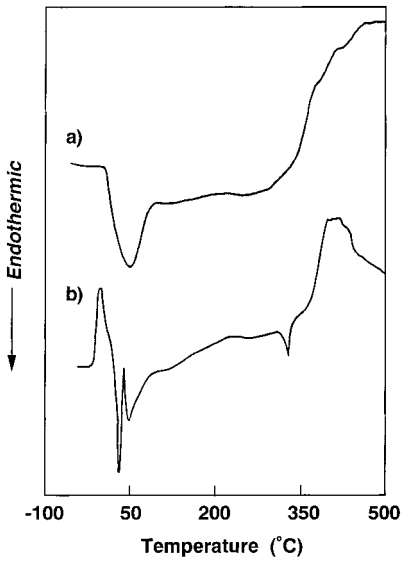


Figure 5. DSC thermograms of (a) the blend of the *p-tert*-butylphenol resin with PEG1000 and (b) the complex using PEG1000.

phenolic PEG components. On the other hand, the DSC curve of the blend showed the broad endothermic peak at 51 °C, indicating the compatibility of the phenolic resin and PEG1000. From the figure, it was obvious that thermal properties of the complex were different from that of the blend. In addition, the enthalpy of melting (ΔH_m) of the PEG1000 phase in the complex was equal to that of the original PEG1000. This indicates that the crystallinity of PEG in the complex is equal to that of the original PEG in the complex and calixarenes will be located in the amorphous parts of PEG. The complex showed independently thermal properties corresponding to PEG1000 phase and calixarene phase because the phase separation occurs. From these results it was found that the structure of the complex is completely different from that of the blend.

Dethreading of Calixarenes. It is well understood that threaded cyclic molecules readily move along the backbone polymer, and they can slip off the backbone in polypseudorotaxanes. The complex obtained by the polycondensation of BP in the presence of PEG must be a polypseudrotaxane type. So, we attempted to dethread calixarenes off the PEG backbone, and the kind of the calixarene was determined. The dethreading was carried out by heating the complex in ethylene glycol (EG) at 180 °C. The dethreading behavior was monitored by GPC. Figure 6 shows GPC chromatograms of the complex obtained from PEG1000 before heating and the complex and dethreaded compounds with a 2 h heating period. In the latter chromatogram new peaks appeared in the lower molecular weight region by heating the complex, and each peak position fitted in that of *p-tert*-butylcalix[8]rene and *p-tert*-butylcalix[4]-arene. The ^1H NMR spectrum of the dethreaded compounds is shown in Figure 7. The position of the singlet arising from the OH protons in ^1H NMR varies with the ring size of the calixarene.[9] The ^1H NMR spectrum shows peaks due to the O−*H* hydrogen of *p-tert*-butylcalix[8]arene at 9.62 ppm and that of *p-tert*-butylcalix[4]arene at 10.31 ppm. Thus, it is found that the complex was composed of *p-tert*-butylcalix[8]rene and *p-tert*-butylcalix[4]arene. On the other hand, by using both ends blocked PEG1000 by a bulky "trityl group", a complex could be also obtained under similar

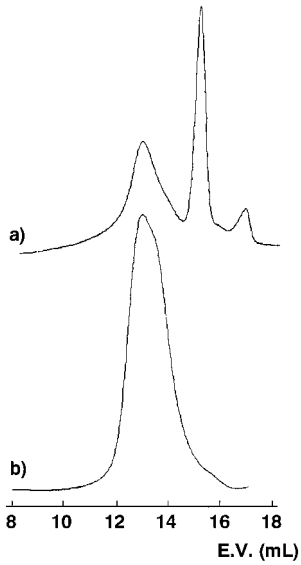


Figure 6. GPC chromatograms of (a) the complex before heating and (b) the complex and dethreaded compounds with a 2 h heating in ethylene glycol at 180 °C.

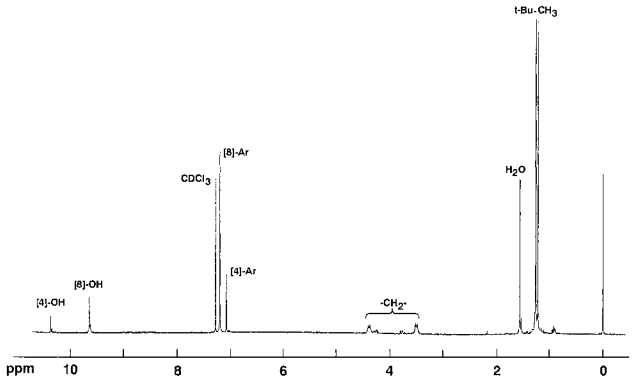


Figure 7. ^{1}H NMR spectrum of the calixarenes dethreaded off the complex with a 2 h heating in ethylene glycol at 180 °C. The peaks corresponding to *p-tert*-butylcalix[8]arene and *p-tert*-butylcalix[4]arene are marked with "[8]" and "[4]", respectively. The peaks corresponding to methylene protons between phenolic units, and methyl protons of the *p-tert*-butyl group in both *p-tert*-butylcalix[8]arene and *p-tert*-butylcalix-[4]arene are marked with "$-CH_2-$" and "*t*-Bu$-CH_3$", respectively.

conditions for the preparation of the polypseudrotaxane. Despite the complex was heated in EG at 180 °C for 10 h, few calixarenes were dethreaded off the blocked PEG1000. Calixarenes will be restricted between stoppers and cannot slip off the blocked PEG. This complex will be a true polyrotaxane.[16] These results strongly support that the complex obtained by the polycondensation of BP in the presence of PEG is a calixarene-based polypseudorotaxane. The weight ratio of *p-tert*-butylcalix[8]arene to *p-tert*-butylcalix[4]arene in the calixarenes dethreaded off PEG1000 in the polypseudorotaxane with a 36 h heating period was given to be 9:1. In the polypseudorotaxane, *p-tert*-butylcalix[8]-arenes are penetrated by PEG1000 and a few *p-tert*-butylcalix[4]arenes may be capped at a part of the ends of the PEG chain. Although the longer thermal treatment of the PEG1000−polypseudorotaxane was done in EG at 180 °C, all *p-tert*-butylcalix[8]arenes were not dethreaded. Calixarenes near the ends of the PEG chain dethread rapidly and readily, while those located in the interior parts of the PEG chain dethread very slowly or cannot dethread due to the distance they must move.

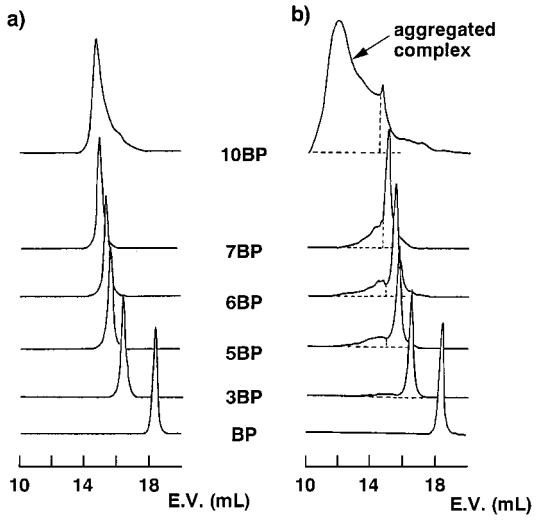
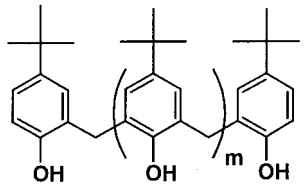


Figure 8. GPC chromatograms of (a) the standard linear oligomers of *p-tert*-butylphenol, *n*BP (*n* is the degree of polymerization = 1, 3, 5, 6, 7, and 10), and (b) the blends of the oligomers with PEG1000.

Scheme 2. Structure of BP Standard Oligomers



2BP (m= 0), 3BP (m= 1), 4BP (m= 2), 5BP (m= 3)
6BP (m= 4), 7BP (m= 5), 10BP (m= 8)

Formation Mechanism of Polypseudorotaxane Complex. The polypseudorotaxane is formed when clipping reactions (cyclizations) of BP linear oligomers templated around a PEG chain occur. In the polypseudorotaxane formation, the interaction between BP oligomers and a PEG chain plays an important role. To determine the interaction of BP oligomers with PEG chain, the aggregation formation of standard BP oligomers (BP, 3BP, 5BP, 6BP, 7BP, and 10BP: the number is the degree of polymerization (DP) in Scheme 2) with PEG1000 was tried by mixing them in molten at 130 °C for 4 h. The GPC chromatograms of the mixing crude products are shown in Figure 8. Obviously, the aggregated complex was formed when the standard oligomers 7BP and 10BP were used. This indicates that the suitable length of BP oligomer is needed to interact with PEG chain. The chain length of the oligomers, 7BP or 10BP, is close to the circle of *p-tert*-butylcalix[8]arene. This result strongly supports the formation of polypseudorotaxane composed of *p-tert*-butylcalix[8]arenes penetrated by a PEG chain. In the clipping reaction, larger *p-tert*-butylcalix[n]arenes ($n > 8$) may be formed. However, it will dethread more than *p-tert*-butylcalix-[8]arene in the polycondensation. The cavity of *p-tert*-butylcalix[8]arene fits the diameter of a PEG chain, so that *p-tert*-butylcalix[8]arene did not easily dethread on a PEG chain. Thus, the larger *p-tert*-butylcalix[*n*]arene was not found in dethreaded compounds from the polyrotaxanes.

The clipping efficiency x (the molar ratio of *p-tert*-butylcalix[8]arene to the repeating unit of PEG) was calculated from the BP/OE unit ratios; $x = 0.04$ for PEG1000, $x = 0.02$ for PEG3000, and $x = 0.01$ for PEG10000. The efficiency was less than the threading efficiency for the formation of cyclodextrin-based or crown ether-based polypseudorotaxanes. Thus far, the clipping method has been applied to low mass rotaxanes but not to polyrotaxanes. If the clipping efficiency will be higher, the clipping method is useful for preparation of polyrotaxane. In this study, the clipping efficiency will increase by using BP oligomers with hydroxymethyl groups at the ends, instead of BP. This method is under consideration in our laboratory.

From these results and discussions, we concluded that the polypseudorotaxane consisting of *p-tert*-butylcalix-[8]arenes penetrated by a PEG chain was formed by the polycondensation of BP with paraformaldehyde in the presence of PEGs. More details of the preparation of calixarene-based polyrotaxanes will be described in a future report.

References and Notes

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