2030 *Macromolecules* **2008,** *41,* 2030−2036

One-Pot Synthesis of a Novel Ladder Polymer of Calixarene via Condensation Reaction of Resorcinol and Alkanedial Based on Dynamic Covalent Chemistry

Hiroto Kudo, Kyosuke Shigematsu, Kouji Mitani, and Tadatomi Nishikubo*

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan

Noriko C. Kasuga

Department of Materials Science, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa, 259-1293, Japan

Hidehiro Uekusa and Yuji Ohashi

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan

Received September 24, 2007; Revised Manuscript Received December 14, 2007

ABSTRACT: Reaction of resorcinol and 1,4-butanedial [$(CH_2)_2(CHO)_2$] in the presence of concentrated HCl in ethanol at 80 °C for 48 h afforded a soluble polymer (CRA−polymer) in quantitative yield under thermodynamic control. Single X-ray crystal analysis revealed that the precursor product had cyclic structure, and TOF mass spectroscopy of CRA−polymer revealed a ladder structure with calixresorcinarene moieties in the main chain. The photoinduced deprotection reaction of CRA−polymer derivative (CRA−polymer−BOC) containing *tert*-butyloxycarbonyl groups were examined in the film state in the presence of photoacid generator to produce the alkaline developable CRA−polymer with release of isobutylene and carbon dioxide.

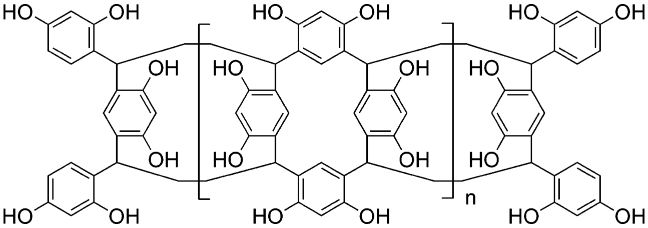
Introduction

Nonlinear polymers,[1] such as cyclic polymers, star polymers, hyperbranched polymers, dendrimers, polyrotaxanes, cyclic polymers, and ladder polymers, have much attractive attention, due to that their unique structures often induce unusual physical, optical, or mechanical properties such as thermal stabilities, solubility, viscoelastic behavior, densities, and high- or low-refractive index. Among them, ladder polymers have excellent thermal stability, chemical resistance, and high tensile strength due to their skeletons, and their application are recently expected as optoelectronics materials.[2]

There are many reports concerning the synthesis and properties of ladder polymers since 1960. Generally, ladder polymers were synthesized by Diels−Alder reaction[3] of the two different monomers, stepwise cyclization[4] of the linear polymers, and polycondensation of alkoxisilanes (polysilsesquioxane).[5] Furthermore, synthesized ladder polymers are often insoluble in common organic solvents due to that their conformational mobility is not flexible and gives entropic force for solubility.

Recently, we succeeded the synthesis of ladder cyclic oligomer by the condensation reaction of resorcinol and 1,5-pentanedial. Single-crystal X-ray analysis of this molecule showed 24 hydroxyl groups, 6 cavities in the side, and a large hydrophobic central hole, i.e., a water-wheel-like structure with ladder-type cyclic rings; we named it noria (water-wheel in Latin).[6] This reaction was performed under dynamic covalent chemistry (DCC) conditions,[7] which is similar to the method used for the synthesis of cyclic oligomer calixarene.[8] There is increasing interest in DCC system, because the products finally obtained are under equilibrium control depending on thermal stability, and a one-pot method can be used.[9] In this DCC system for the synthesis of noria, soluble oligomers or polymers can be synthesized by the reaction of resorcinol and other α,ω-alkanedials [$(CHO)_2(CH_2)_m$]. Among them, it was found that only soluble polymer was obtained by the reaction of resorcinol and 1,4-butanedial [$(CH_2)_m(CHO)_2$, $m = 2$]. In this paper, we deal with the behavior of this condensation reaction and the structure of the obtained polymer (Scheme 1).

Table 1. DATA of MALDI−TOF Mass Spectra of CRA−Polymer



	m/z (calcd)	*m/z* (found)
L₁($n = 1$)	($C_{76}H_{68}O_{20}$ + H): 1301.43	not determined
L₂ $n = 2$)	($C_{108}H_{96}O_{28}$ + H): 1841. 61	1841.69
L₃ ($n = 3$)	($C_{140}H_{124}O_{36}$ + H): 2381.79	2382.18
L₄ ($n = 4$)	($C_{172}H_{152}O_{44}$ + H): 2921.97	2921.93
L₅ ($n = 5$)	($C_{204}H_{180}O_{52}$ + H): 3462.14	3462.94
L₆ ($n = 6$)	($C_{236}H_{208}O_{60}$ + H): 4002.32	4003.52

Experimental Section

Materials. Resorcinol, 2,5-dimethoxytetrahydrofuran (DTHF), pyridine, methanol, and ethanol were used without further purification. Tetrabutylammonium bromide (TBAB) was recrystallized from dried ethyl acetate.

Measurements. Infrared (IR) spectra were measured on a Jasco model IR-420 spectrometer. The ^1H NMR spectra were recorded on JEOL model JNM α-600 (600 MHz for ^1H NMR) instruments

---

* To whom all correspondence should be addressed. E-mail: nishikubot@kanagawa-u.ac.jp.

10.1021/ma7019573 CCC: $40.75

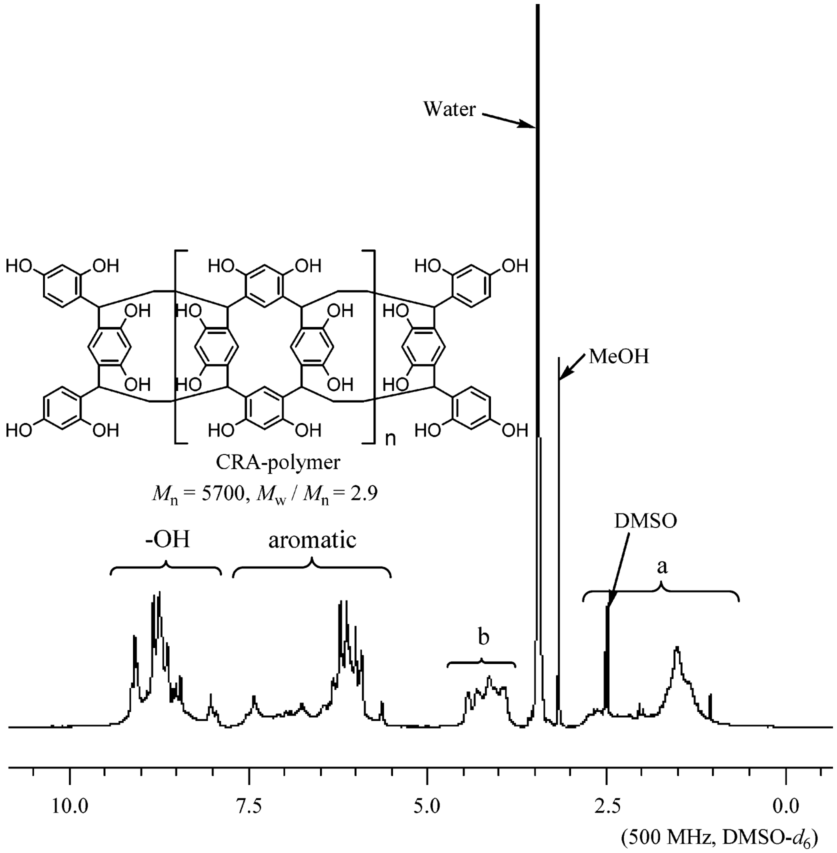
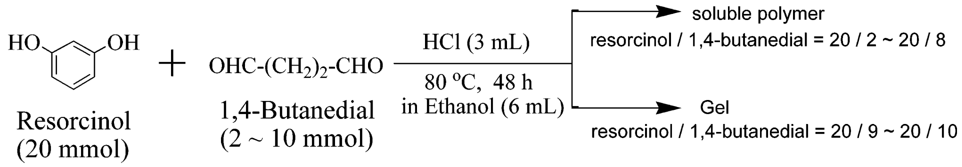


Figure 1. ^{1}H NMR spectrum of CRA−polymer (M_n = 5700, M_w/M_n = 2.9). a = methylene proton, b = methine proton.

Scheme 1. Condensation Reaction Resorcinol and 1,4-Butanedial



in $CDCl_3$ and DMSO-d_6 using Me_4Si (TMS) as an internal standard reagent for ^{1}H NMR. The glass transition temperatures (T_g's) were measured on a Seiko Instruments differential scanning calorimeter (DSC) model EXSTAR6000/DSC6200 at a heating rate of 10 °C/min under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analysis (TGA) model EXSTAR6000/TG/DTA6200 at a heating rate of 10 °C/min under nitrogen. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) with the use of a TOSO HLC-8220 SEC equipped with refractive index and ultraviolet detectors using TSK gel columns [eluent: solution of LiBr and phosphoric acid (20 mM) in DMF]; calibrated with narrow molecular weight polystyrene standards.

Synthesis of CRA—Polymer. The reaction mixture of resorcinol (20 mmol) and 2,5-dimethoxytetrahydrofuran (6.0 mmol) in the presence of conc. HCl (3.0 mL) in ethanol (6.0 mL) was stirred at 80 °C for 24 h, then poured into a large amount of ethyl ether to precipitate a solid. The solid was washed with ethyl ether several times and dried *in vacuo* at 60 °C for 12 h. Yield 99% (2.07 g). M_n = 5700, M_w/M_n = 2.9. IR (film, cm^{-1}): 3367 (ν(O−H)), 2935, 1863 (ν(C−H)), 1616, 1504 (ν(C═C aromatic)). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ (ppm) = 1.00−2.69 (m, $-CH_2-CH_2-$), 3.96 − 4.44 (m, >CH−), 5.64−7.43 (m, aromatic H), 7.95−9.13 (m, −OH).

Preparation of Single-Crystal X-ray Analysis. Di-*tert*-butyldicarbonate (DiBOC) (0.41 g) was added slowly to a solution of $\mathbf{L_0}$ (0.8 g) and TBAB (0.015 g) in pyridine (3 mL) at room temperature, and the mixture was stirred at 25 °C for 48 h. $CHCl_3$ (100 mL) was added, and the resulting mixture was washed with saturated aqueous sodium hydrogen carbonate, 1 N hydrogen chloride solution, and water. The organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The resulting residue was purified by recrystallization from a mixture of chloroform and *n*-hexane to obtain colorless blocklike crystals of the $\mathbf{L_0}$ derivative. IR (film, cm^{-1}): 2981 (ν(CH_3)), 2935 (ν($-CH_2-$)), 1761 (ν(>C═O)), 1371 (ν($-C(CH_3)_3$)), 1140 (ν(C−O−C)). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ (ppm) = 1.25−1.55 (m, 108 H, $-C(CH_3)_3$), 1.83−2.12 (m, 8 H, $-CH_2-CH_2-$), 4.39 (d, J = 12.5 Hz, 4 H, >CH−), 6.82−7.05 (m, 16 H, aromatic H). A single crystal was mounted on a glass fiber and cooled rapidly to 133 K in a stream of cold N_2. Diffraction data were measured using an RAXIS−RAPID IP diffractometer with the rotating anode X-ray generator (graphite-monochromated Cu Kα radiation, λ = 1.5418 Å). Intensity data were processed using the RAPID-AUTO package and an empirical absorption correction was applied, which resulted in transmission factors ranging from 0.927 to 0.977. Structure was solved using the direct methods program SHELXS-97. Subsequent full-matrix, least-squares refinement was carried out on F^2 using the SHELXL-97 program.

Spectroscopic Data of 1,1,4,4-Tetra(2,4-dihydroxyphenyl)-butane (TDPB). Mp = 163.6−164.1 °C.^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ = 1.64 (s, 4.0 H, $-CH_2-CH_2-$), 4.26 (s, 2.0H, >CH−), 6.07 (d, J = 8.5 Hz, 4.0 H, aromatic H), 6.17 (s, 4.0 H, aromatic H), 6.70 (d, J = 8.5 Hz, 4.0 H, aromatic H), 8.86 (s, 8.0 H, −OH). ^{13}C NMR (150.92 MHz, DMSO-d_6, TMS) δ = 18.90

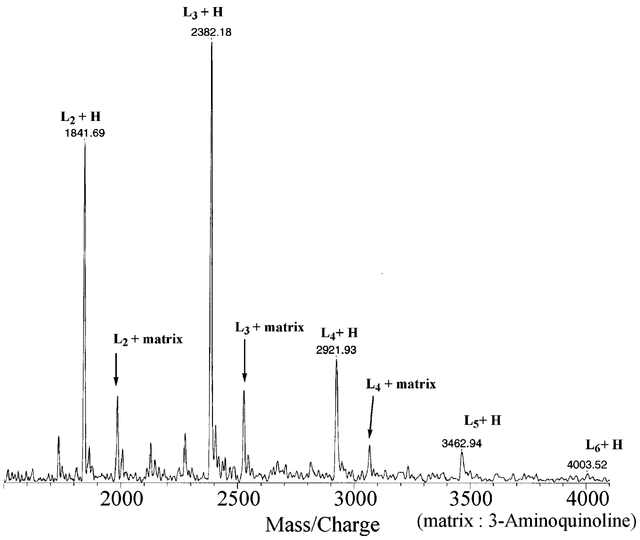


Figure 2. MADI-TOF Mass spectra of CRA−polymer ($M_n = 5700$, $M_w/M_n = 2.9$).

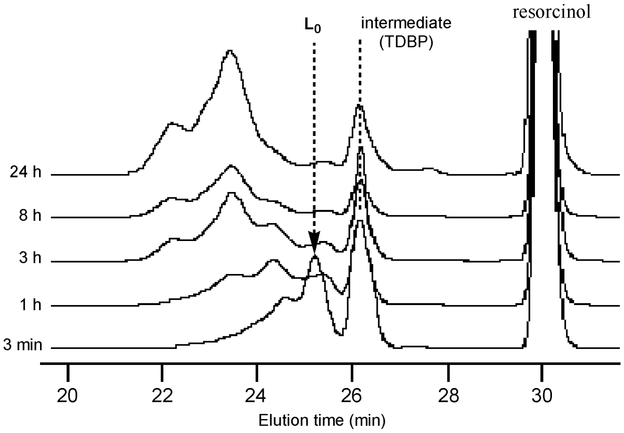


Figure 3. SEC profiles of the products obtained by the reaction of resorcinol (20 mmol) and 1,4-butanedial (6 mmol) in the presences of conc. HCl (3 mL) in ethanol (6 mL) at 80 °C.

Table 2. Effect of Feed Ratio on the Polycondensation of Resorcinol and 1,4-Butanedial[a]

run	feed ratio resorcinol/1,4-butanedial	M_n[b]	M_w/M_n[b]	yield[c] (%)
1	20/2	3700	1.2	99
2	20/4	5000	1.4	99
3	20/6	5700	2.9	99
5	20/8	10 100	3.1	94
6	20/9	*d*	*d*	gel
7	20/10	*d*	*d*	gel

[a] The reaction of conditions: resorcinol (20 mmol), 1,4-butanedials (1−10 mmol), EtOH (6 mL), concentrated HCl (3 mL), for 24 h. [b] Estimated by SEC (DMF) based on polystyrene standards. [c] Insoluble part of ethyl ether. [d] Not determined.

Table 3. Effect of Reaction Temperatures on the Polycondensation of Resorcinol and 1,4-Butanedial[a]

run	temp (°C)	M_n[b]	M_w/M_n[b]	yield[c] (%)
1	−20	4800	4.5	>99
2	0	3400	6.3	>99
3	rt	3500	6.1	83
4	40	4200	3.9	>99
5	60	11 400	2.5	84
6	80	5700	2.9	99

[a] The reaction of conditions: resorcinol (20 mmol), 1,4-butanedial (6 mmol), EtOH (6 mL), concentrated HCl (3 mL), for 24 h. [b] Estimated by SEC (DMF) based on polystyrene standards. [c] Insoluble part of ethyl ether.

($-CH_2-$), 35.53 ($>CH-$), 102.66, 106.02, 122.73, 128.60, 155.62, and 156.00 (aromatic C). IR (film, cm^{-1}): 3298 (ν(OH)), 2946 ($\nu(-CH_2-)$), 1604 (ν(C=C of aromatic)).

Reaction of CRA—Polymer with Di-*tert*-butyloxydicarbonate. The reaction mixture of CRA−polymer (0.1 g, $M_n = 9500$) and TBAB (0.025 g, 0.075 mmol) in pyridine (3 mL) was stirred at 25 °C for 4 h. Di-*tert*-butyloxycarbonate (DiBOC) was added to the resulting mixture, which was stirred at 25 °C for 48 h.

After that, $CHCl_3$ (100 mL) was added, and the resulting mixture was washed with saturated aqueous sodium hydrogen carbonate, 1 N hydrogen chloride solution, and water. The organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The resulting residue was dissolved in chloroform and poured into large amount of *n*-hexane to precipitate the solid. The solid was dried *in vacuo* at 60 °C for 24 h. The degree of introduction of BOC group was calculated to be 100% by ^{1}H NMR integration of the signal for the aromatic protons at 5.50 − 7.50 ppm and methyl protons at 0.70−2.50 ppm. Yield = 0.194 g (77%). IR (film, cm^{-1}): 2981 ($\nu(CH_3)$), 2937 ($\nu(-CH_2-)$), 1758 (ν(>C=O)), 1496 (ν(C=C of aromatic)), 1370 ($\nu(-C(CH_3)_3)$), 1145 (ν(C−O−C)). ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ (ppm) = 0.70−2.50 (br m, $-CH_2-$ and $-C(CH_3)_3$), 3.80−4.90 (br m, $>CH-$), 5.50−7.50 (br m, aromatic H).

The Refractive-Index Property of CRA—Polymer—BOC. CRA−polymer−BOC was dissolved in THF, followed by spin-coating on a silicon-wafer and dried *in vacuo* at 25 °C for 24 h. The refractive index (n_D) of CRA−polymer−BOC film with about 0.1 μm spin-coated on silicon-wafer was determined at 632.8 nm by ellipsometry.

Photoinduced Deprotection of CRA—Polymer—BOC. CRA−polymer−BOC (0.05 g) and bis({[4-(2-hydroxy)ethoxy]-diphenylsulfonoiophenyl}hexafluorophosphate)sulfide (sp-150) (5 mg) were dissolved in $CHCl_3$ (1.0 mL). The solution was cast on a KBr plate and dried into a film state on the plate *in vacuo* at 25 °C for 24 h. The film containing the photoacid generator was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co.) without a filter under nitrogen and followed by the heat at 130 °C for 1 h. The rate of decrease of the *tert*-butyl group at 1370 cm^{-1} was measured by FT-IR spectroscopy.

Results and Discussion

The Reaction of Resorcinol and 1,4-Butanedial. The reaction of resorcinol (1.1 g, 10 mmol) and DTHF (0.396 g, 3.0 mmol) was carried out in the presence of conc. HCl (1.0 mL) in ethanol (3.0 mL) at 80 °C, in which DTHF is decomposed in the presence of HCl to produce 1,4-butanedial (Scheme 1). The initially homogeneous reaction mixture afforded an insoluble product after 2 h. After 24 h, the reaction mixture was poured into ethyl ether to precipitate the product, which was then dried *in vacuo* at 60 °C for 12 h. The obtained product (0.80 g) was soluble in aprotic, highly polar solvents, such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO), and its number-average molecular weight (M_n) and polydispersity ratio (M_w/M_n) were 5700 and 2.9, respectively. The ^{1}H NMR spectrum showed that the product contained methine and methylene moieties in a ratio of 1:2 based on integration of the signals at 3.96−4.44 ppm and 1.00−2.69 ppm, respectively. Furthermore, aromatic and hydroxyl proton signals were seen at 5.64−7.43 ppm and 7.95−9.13 ppm, respectively (Figure 1). These results indicated that the obtained polymer was formed by condensation reaction of resorcinol and 1,4-butanedial.

Figure 2 depicts the MALDI−TOF mass spectrum of the obtained polymer. Mass difference patterns corresponded to the molecular mass of calixarene, $M = 540$. $\mathbf{L_2}$ was the ladderlike polymer derived from 14 molecules of resorcinol and 6

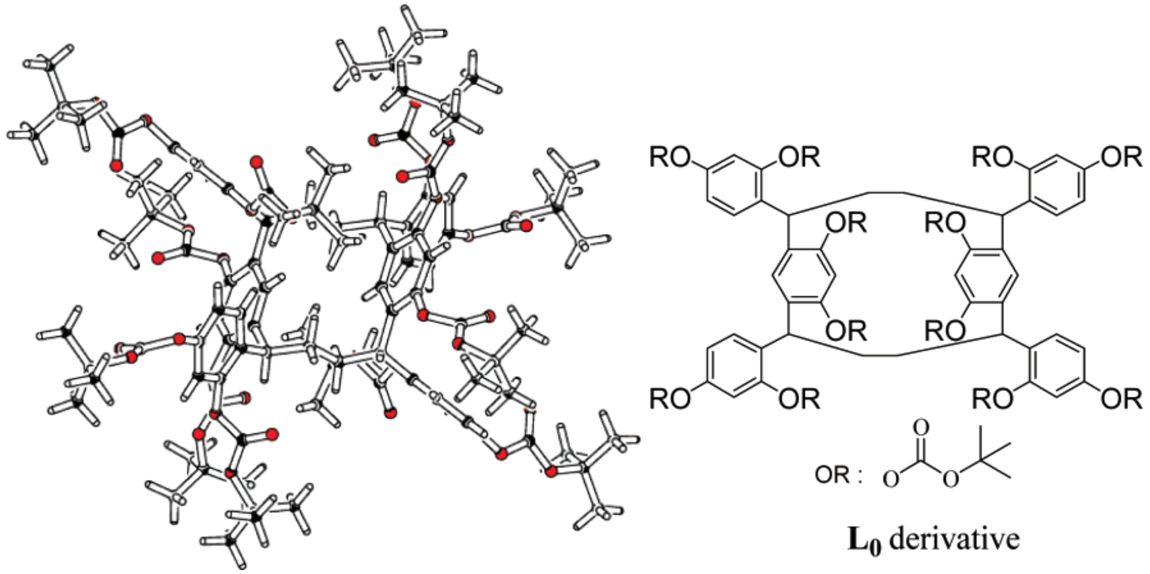
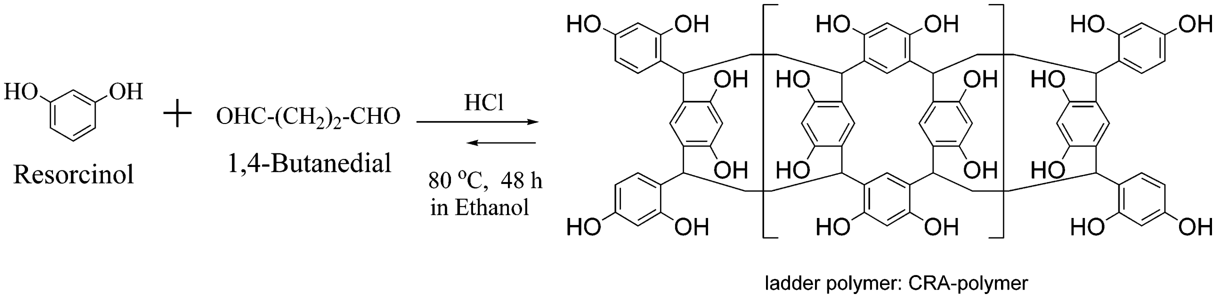
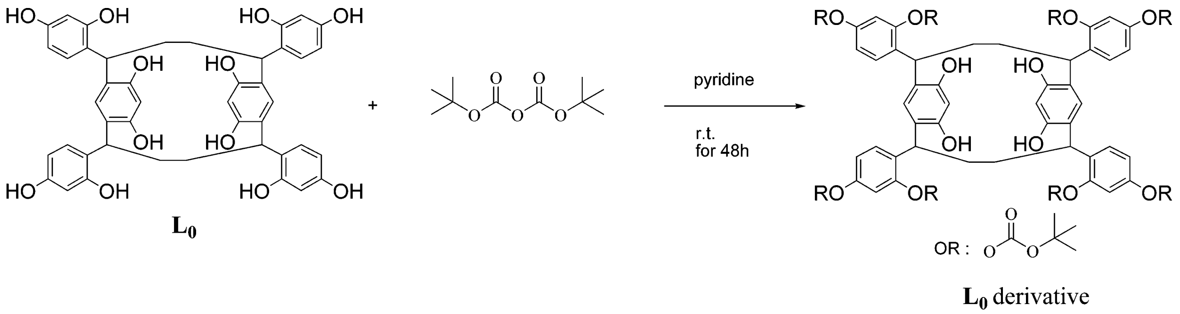


Figure 4. Left: Molecular structure of the *L_0* derivative determined by single-crystal X-ray analysis. Right: Schematic representation of the **L_0** derivative.

Scheme 2. Synthesis of Ladder Polymer by the Condensation Reaction of Resorcinol and 1,4-Butanedial



Scheme 3. Synthesis of L_o Derivative by the Reaction of L_o with Di-*t*-butyloxy Dicarbonate



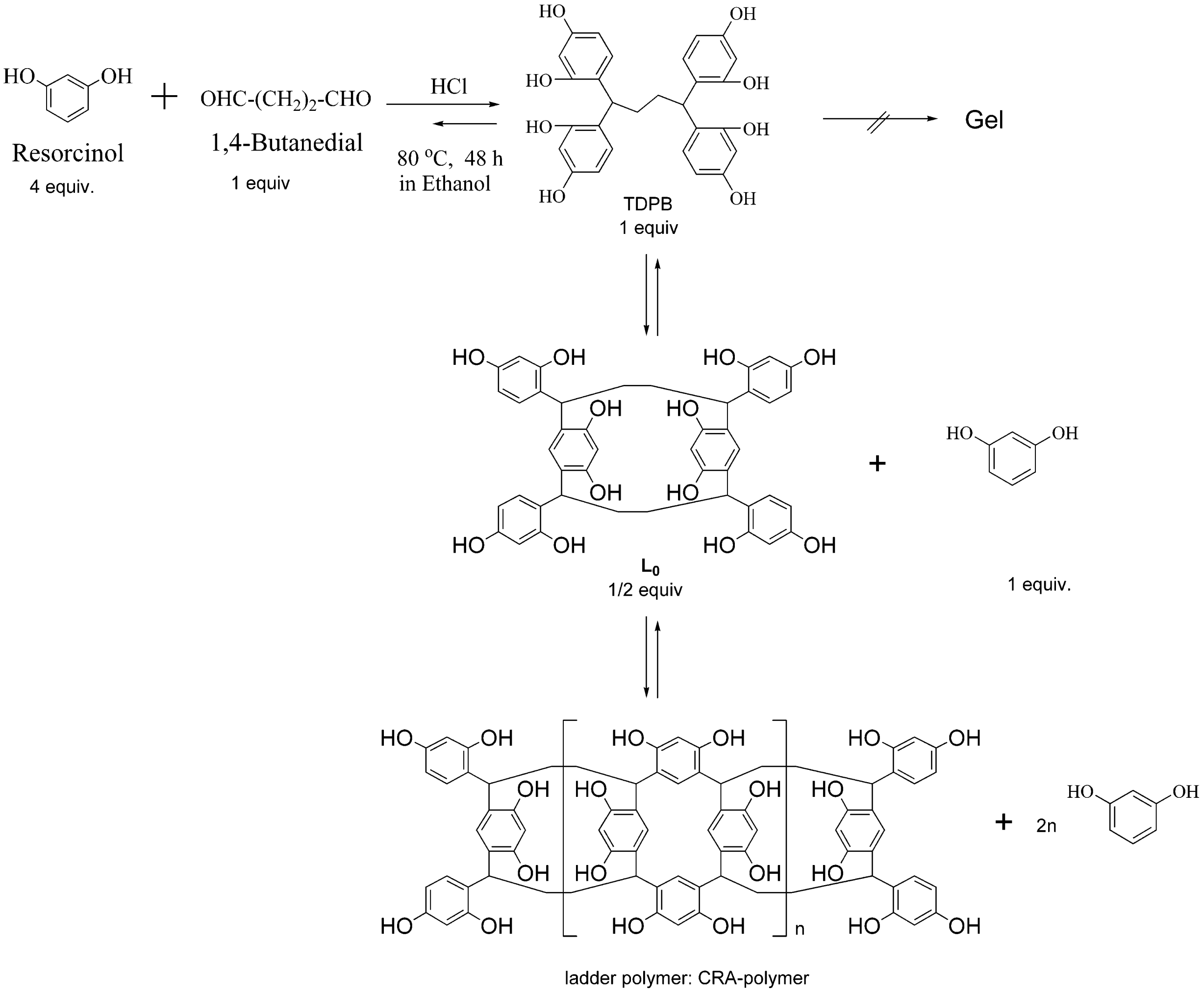
molecules of 1,4-butanedial (*M* = 1841.69). A series of ladderlike polymers, **L_3−L_6**, was found. These results are summarized in Table 1, and indicate that the polycondensation of resorcinol and 1,4-butanedial afforded a ladder polymer (CRA−polymer; yield 99%) containing calixarene moieties, as shown in Scheme 2. However, the SEC profiles showed bimodal peaks (Figure 3). This means that the synthesized polymer contains some branch architectures in part.

The reaction conditions for the synthesis of CRA−polymer were examined with various feed ratios of resorcinol and 1,4-butanedial at 80 °C for 24 h. The reaction with the feed ratio of resorcinol/1,4-butanedial of 20/10 or 20/9 afforded a gel in quantitative yield. At feed ratios of 20/2 to 20/8, soluble CRA−polymers were obtained in almost quantitative yields (Table 2). This result indicates that structure of the polymer is determined by the feed ratio.

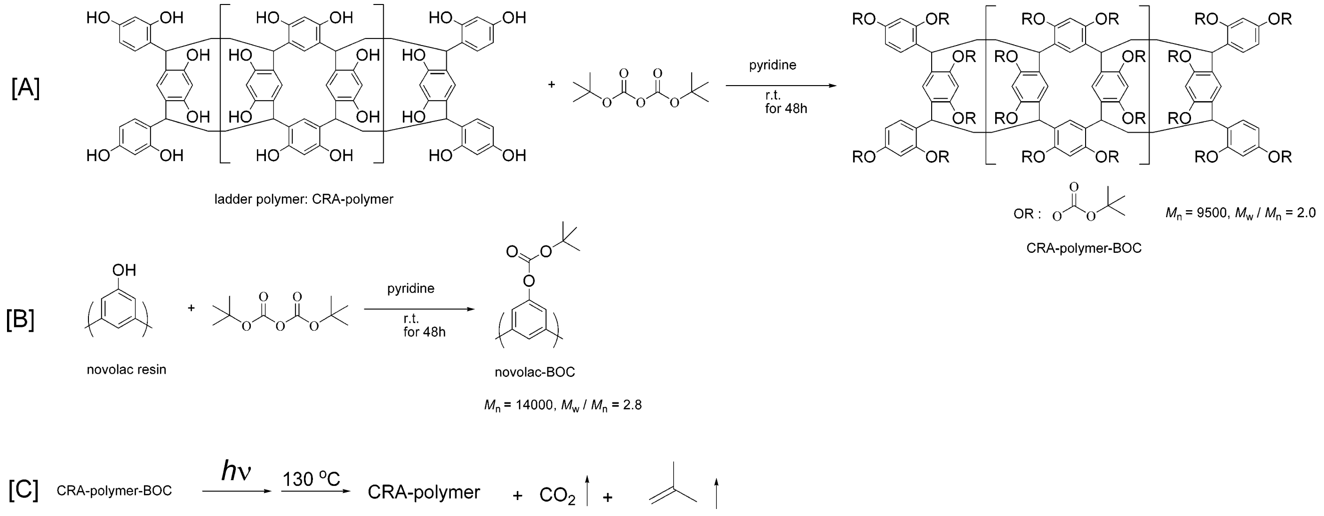
Furthermore, when the temperature was varied in the range between −20 and +80 °C with the fixed feed ratio of resorcinol/1,4-butanedial = 20/6, CRA−polymers with M_n = 2500−11400 were obtained in satisfactory yields (Table 3). The value of M_w/M_n decreased with increasing reaction temperature, i.e., the amount of lower-molecular-weight polymers increased at lower reaction temperatures. It is noteworthy that no gel product was obtained under these reaction conditions.

To examine the mechanism of the reaction of resorcinol and 1,4-butanedial leading to CRA−polymer, we traced the size exclusion chromatography (SEC) profiles of the obtained products with reaction time (Figure 3). After 3 min, peaks of oligomers were observed at retention times of around 25 min and 26 min. Subsequently, a decrease of molecular weight of oligomers and an increase in the amount of CRA−polymers were observed as the reaction time increased. The oligomer of retention time 26.2 min was present at all reaction times. This oligomer appeared to be the key intermediate leading to CRA−polymers. It was separated by silica gel column chromatography, and determined by means of ^{1}H NMR, ^{13}C NMR, and IR

Scheme 4. Plausible Mechanism of the Reaction of Resorcinol and 1,4-Butanedial for the Synthesis of CRA−Polymer



Scheme 5



spectroscopic analyses to be 1,1,4,4-tetra(2,4-dihydroxyphenyl)-butane (TDPB), which would have been formed by the condensation reaction of 4 equiv of resorcinol with 1,4-butanedial. Furthermore, an oligomer with the retention time of 25.3 min was also separated by HPLC and reacted with di-*t*-butyl dicarbonate (DiBOC) in an attempt to increase its solubility (Scheme 3). A single block-like crystal of this derivative was obtained from chloroform/hexane. X-ray analysis showed that this derivative is a cyclic compound (**L_0**) formed by the condensation of 6 equiv of resorcinol and 2 equiv of 1,4-butanedial, as shown in Figure 4.[10] This shows that a cyclic ring is consisted by two resorcinols and two 1,5-pentanedials, and their aromatic moieties are located in apposite positions, respectively.

When TDPB was heated in ethanol in the presence of concentrated HCl at 80 °C for 48 h, interestingly, soluble CRA−polymer was obtained in quantitative yield, accompanied by the formation of resorcinol. These results suggest that TDPB

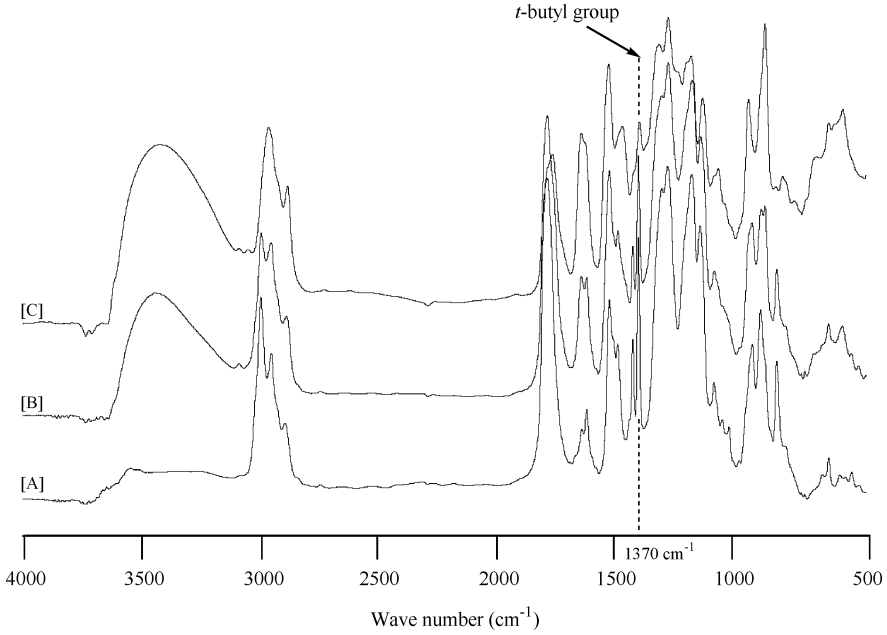


Figure 5. FT-IR spectra of photoinduced deprotection reactionj of CRA−polymer−BOC. UV-irradiation (8.0 mW/cm^2 at 254 nm) for 30 min using 5 mol % SP-150 and heating at 130 °C. [A] before heating; [B] after 10 min; [C] after 30 min.

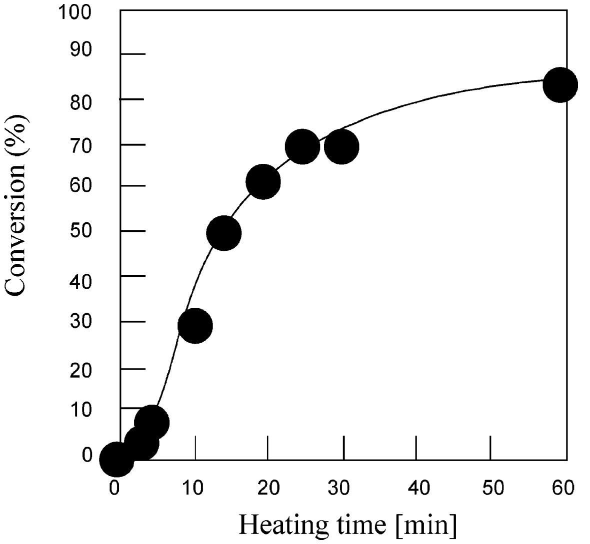


Figure 6. Relationships between the conversion (%) and heating time (min) at 130 °C on the photoinduced deprotection reaction of CRA−polymer−BOC.

was formed by reversible condensation reaction between polymers, oligomers, resorcinol, and 1,4-butanedial, followed by the elimination reaction of resorcinol with TDPB in the presence of HCl as a catalyst to produce CRA−polymer under complete thermodynamic control (Scheme 4).

The thermal properties of the CRA−polymer ($M_n = 5700$, $M_w/M_n = 2.9$) were examined by DSC and TGA. No apparent T_g was observed up to 250 °C and thermal decomposition occurred at more than 300 °C. Their 5% weight loss temperature ($T_d{}^5$) and 10% weight loss temperature ($T_d{}^{10}$) were 343 and 363 °C, respectively.

The Synthesis, Refractive-Index Property, and Photoinduced Deprotection of CRA—Polymer—BOC. Wilson et al. reported the photoinduced deprotection reaction of the polymers bearing *tert*-butyloxycarbonyl (BOC) groups using photoacid generator (PAG) as a chemical amplified photoresist systems.[11] In our previous reports, we also examined the photoinduced deprotection of the calixarene[12] derivatives and noria[13] derivative with BOC groups affording the calixarene and noria, respectively, releasing carbon dioxide and isobutylene. In this time, we examined the synthesis, refractive-index property, and photoinduced deprotection of CRA−polymer−BOC (Scheme 5). In this reaction system, it is expected that novel alkaline-developable hydroxyl groups of CRA−polymer is produced to release isobutylene and carbon dioxide by the deprotection reaction of CRA−polymer−BOC. All the hydroxyl groups of polymer−CRA were converted to BOC groups, affording the corresponding polymer CRA−polymer−BOC in 77% yield. The structure of CRA−polymer−BOC was confirmed by IR and ^{1}H NMR spectroscopy.

The value of refractive-index (n_D) of the CRA−polymer−BOC film with about 0.1 μm spin-coated on silicon-wafer was measured at 632.8 nm by ellipsometry (Scheme 5A). The n_D of novolac resin containing BOC groups (novolac−BOC) which structure is similar to that of CRA−polymer−BOC was also determined (Scheme 5B). It was found that the n_D of CRA−polymer−BOC (1.489) was smaller than that of novolac-BOC (1.517). This result might be caused that CRA−polymer−BOC had many cavities in the main chain due to its ladder skeletons.

Next, the photoinduced deprotection reaction was examined under UV irradiation with a 250-W high-pressure mercury lamp in the film state prepared with 5 mol % of sp-150 as a photoacid generator for 30 min, followed by heating at 130 °C (Scheme 5C). Figure 5 depicts the IR spectra of the before and after the photoinduced deprotection of CRA−polymer−BOC. Before the deprotection reaction, a peak around at 1700 cm^{-1} was assignable to the stretching vibration of BOC group (Figure 5A). After 10 and 30 min heating, the new broad peaks appeared at around at 3500 cm^{-1}, which were assignable to the stretching vibration of hydroxyl groups (Figure 5, parts B and C). This means that the deprotection reaction of BOC groups proceeded to produce the hydroxyl groups with releasing CO$_2$ and isobutylene. The peak at 1370 cm^{-1} was assignable to the deformation vibration of *tert*-butyl moieties, and its decrease was observed with increasing the heating time. From this peak, the values of conversion of the photoinduced deprotection reaction of CRA−polymer−BOC can be calculated by the FT-IR spectroscopy. After 60 min heating, the conversion of its photoinduced deprotection reaction reached to be 88% (Figure 6). These results indicate that the application of CRA−polymer−BOC is expected as a useful positive working photoresists.

In summary, we have synthesized a ladder polymer (CRA−polymer) using a one-pot method by the condensation reaction of resorcinol and 1,4-butanedial. The CRA−polymer contains calixarene moieties in the main chain and has many hydroxyl groups in the side chains. CRA−polymer derivative (CRA−polymer−BOC) containing *tert*-butyloxycarbonyl groups had lower refractive-index value due to its ladder structure containing many cavities. The photoinduced deprotection reaction of CRA−polymer−BOC proceeded in the film state in the presence of photoacid generator to produce the alkaline developable CRA−polymer with releasing isobutylene and carbon dioxide. We are currently examining the reaction of resorcinol and other α,ω-alkanedials $[(CHO)_2(CH_2)_m, m \geq 4]$.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research in Japan (No. 18681015) from the Ministry of Education, Culture, Sports, Science, and Technology and was partly supported by Nanospace Chemistry for the Creation of Functional Materials on Kanagawa University, which are gratefully acknowledgment.

References and Notes

(1) Tezuka, Y.; Oike, H. *Prog. Polym. Sci.* **2002**, *27*, 1069.

(2) For example: (a) Abdelaal, M. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3909−3915. (b) Oyaizu, K.; Iwasaki, T.; Tsukahara, Y.; Tsuchida, E. *Macromolecules* **2004**, *37*, 1257−1270. (c) Jacob, J.; Sax, S.; Gaal, M.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *Macromolecules* **2005**, *38*, 9933−9938. (d) Xu. C.; Yamada, H.; Wakamiya, A.; Yamaguchi, S.; Tamao, K. *Macromolecules* **2005**, *37*, 8978−8983. (e) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922−6928. (f) Quinto, M.; Jenekhe, S. A.; Bard, A. J. *Chem. Mater.* **2001**, *13*, 2824−2832. Jacob, J.; Sax. S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6978−6995.

(3) For example: (a) Chen, Z.; Amara, J. P.; Thomas, S. W.; Swager, T. M. *Macromolecules* **2006**, *39*, 3202−3209. (b) Wegener, S.; Mullen, K. *Macromolecules* **1993**, *26*, 3037−3040. (c) Godt, A.; Enkelmann, V.; Schluter, A. *Angew. Chem.* **1989**, *101*, 1704.

(4) For example: (a) Krichekdorf, H. R.; Lomadze, N.; Fritsch, D.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5344−5352. (b) Nehls, B.; Galbrecht, F.; Brauer, D.; Lehmann, C. W.; Scherf, U.; Farrell, T. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5533−5545. (c) Norman, G. G.; Ivo. K.; Milan. S.; Josef. V. *J. Am. Chem. Soc.* **1963**, *85*, 641−642.

(5) For example; (a) Roy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431. (b) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.

(6) Kudo, H.; Hayashi, R.; Mitani, K.; Yokozawa, T.; Kasuga, N. C.; Nishikubo, T. *Angew, Chem. Int. Ed.* **2006**, *45*, 7948.

(7) (a) Rowan, S. J.; Cantyrill, S. J.; Cousin, G. R. L.; Sanders, J. K. M.; Stoddart. J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898. (b) Otto, S.; Kubik, S. *J. Am. Chem. Soc.* **2003**, *125*, 7804. (c) Otto, S.; Furlan, R. L. E.; Sanders, J. K. M. *Science* **2005**, *297*, 590. (d) R. T. S. Lam, A. Belenguer, S. L. Roberts, C. Naumann, T. Jarrosson, S. Otto, J. K. M. Sanders, *Science* **2005**, *308*, 667.

(8) Gutsche, C. D.; Johnston, D. E., Jr.; Stewart, D. R. *J. Org. Chem.* **1999**, *64*, 3747.

(9) Reviews: (a) Rowan, S. J.; Cantyrill, S. J.; Cousin, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew, Chem. Int. Ed.* **2002**, *41*, 898. (b) Ramstrom, O.; Bunyapaiboonsri, T.; Lohmann, S.; Lehn, J.-M. *Biochim. Biophys. Acta* **2002**, *1572*, 178.

(10) Crystal data for the $\mathbf{L_o}$ derivative:$C_{104}H_{136}O_{36}$, $M_r = 1962.13$, triclinic, space group *P*-1, $Z = 1$, $a = 11.1662(8)$ Å, $b = 15.6990(10)$ Å, $c = 17.4920(12)$ Å, $\alpha = 66.290(4)°$, $\beta = 76.450(4)°$, $\gamma = 70.869(5)°$, $V = 2633.7(3)$ Å^3, $T = 133(2)$ K, μ(Cu Kα)= 0.774 mm^{-1}, 29968 reflections measured, 9123 unique reflections ($R_{int} = 0.0867$), $R1$ ($I > 2\sigma(I)$) = 0.0541, $wR2 = 0.110$ (all data), $S = 0.723$. CCDC641135 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(11) Wilson, C. G.; Ito, H.; Frechet, J. M. J.; Tessier, T. G.; Houlihan, F. M. J. *J. Electrochem. Soc.*, **1986**, *133*, 181.

(12) (a) Nishikubo, T.; Kameyama, A.; Tsutsui, K.; Kishimoto, S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1481. (b) Kudo, H.; Mitani, K.; Nishikubo, T.; Mitsuishi, M.; Miyashita, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 819. (c) Kudo, H.; Mitani, K.; Koyama, S.; Nishikubo, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2109.

(13) André, X.; Lee, J. K.; DeSilva, A.; Ober, C. K.; Cao, H. B.; Deng, H.; Kudo, H.; Watanabe, D.; Nishikubo, T. *SPIE* **2007**, *6519*, 65194B.

MA7019573