Polymethylenes Containing [2.2]Paracyclophane in the Side Chain

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Introduction. Almost all conjugated polymers reported so far are through-bond conjugated polymers in which π-electrons are delocalized through sp and/or sp^2 carbon frameworks. Such polymers are considered to be an important class of polymers due to their potential applications in optoelectronic devices.[1] There have been a few reports on the synthesis of π-stacked polymers comprising a $\pi-\pi$ stacking of aromatic rings.[2−9] For example, Nakano and co-workers have synthesized poly(dibenzofulvene)s by the chain polymerization of dibenzofulvene derivatives.[2] The poly(dibenzofulvene) film exhibits a high hole drift mobility.[3] Recently, we have studied the synthesis of π-stacked polymers by incorporating [2.2]paracyclophane into a conjugated polymer main chain.[7] In addition, [2.2]paracyclophane-layered polymers with a π-stacked structure have been prepared using a xanthene compound as a scaffold,[8,9] which exhibited fluorescence resonance energy transfer (FRET) from the layered [2.2]paracyclophanes to the end-capping groups.[9] Thus, the formation of a successive $\pi-\pi$ stacking in the primary structure of a polymer[10,11] is of importance from the viewpoint of charge and energy transfer.

Polymethylene is a polymer in which a substituent is attached to each carbon atom in the main chain,[12,13] while polyethylene, a well-known polymer synthesized by vinyl polymerization, has a substituent attached to alternate carbon atoms. Therefore, the functional groups in the polymethylene chain are closely packed. It is expected that the introduction of bulky [2.2]paracyclophane into polymethylene as a pendent group will lead to a methodology for the construction of a $\pi-\pi$ stacking structure. There have been several studies on the incorporation of [*m.n*]cyclophanes into the side chains of polymers such as polyethylenes;[14−16] however, polymethylene has not yet been used for scaffold dangling [*m.n*]cyclophanes.

In this paper, we report the synthesis of π-stacked polymers based on a polymethylene skeleton containing [2.2]paracyclophane in the side chain by the BF_3-catalyzed polymerization of 4-diazomethyl[2.2]paracyclophane. The monosubstituted [2.2]paracyclophane exhibits planar chirality.[17] Chiral as well as racemic 4-diazomethyl[2.2]paracyclophane monomers were used to obtain optically active polymethylenes. A synthetic procedure for the preparation of polymethylenes is described; further, we discuss the optical properties of polymethylenes.

Results and Discussion. 4-Diazomethyl[2.2]paracyclophane, (*rac*)-**5**, was synthesized from commercially available [2.2]paracyclophane (**1**), as shown in Scheme 1. [2.2]Paracyclophane (**1**) was brominated by a Fe catalyst[18] and then reacted with *n*-BuLi and DMF to obtain 4-formyl[2.2]paracyclophane (**3**) in high yield. The reaction of **3** with *p*-toluenesulfonyl hydrazide resulted in the formation of 4-[2.2]paracyclophanecarboxaldehyde tosylhydrazone (**4**) in 90% yield. The treatment of **4** with NaOH in a benzene/H_2O solution containing benzyltriethylammonium chloride afforded (*rac*)-4-diazomethyl[2.2]paracyclophane, (*rac*)-**5**, in 71% yield. 4-Monosubstituted [2.2]paracyclophane is a planar chiral compound. Therefore, as shown in Scheme 1, chiral resolution was carried out according to procedure established by Rowlands and co-workers,[19] and diastereomers (R_p,*S*)-**7** and (S_p,*S*)-**7** were separated by common SiO_2 column chromatography. Thus, 4-bromo[2.2]paracyclophane **2** was converted to enantiomerically pure[20] 4-diazomethyl-[2.2]paracyclophanes (R_p)-**5** and (S_p)-**5** in moderate yields at each step. These 4-diazomethyl[2.2]paracyclophane monomers (*rac*)-**5**, (R_p)-**5**, and (S_p)-**5** could be purified by recrystallization from hexane and were relatively stable to handle under air.

Polymethylene **6** was synthesized by the polymerization of 4-diazomethyl[2.2]paracyclophane (**5**) in the presence of a catalytic amount (2 mol %) of $BF_3 \cdot Et_2O$ (Scheme 1).[13] The polymerization results are listed in Table 1. Entries 1 and 2 were carried out at −15 and −10 °C in toluene and CCl_4 solutions, respectively, in order to dissolve a diazomethane monomer. However, these reaction temperatures accelerated the decomposition of the monomer and resulted in low yields of the desired polymers. The best result was obtained when CH_2Cl_2 was used as a solvent at −78 °C (entry 4), and polymer (*rac*)-**6** was isolated in 20% yield with a number-average molecular weight (M_n) of 1100 ($CHCl_3$ eluent, polystyrene standards). However, the reaction temperature affected the polymerization even when the CH_2Cl_2 solvent was used, and the decomposition of the monomer resulted in the formation of polymer (*rac*)-**6** in low yields (entries 5 and 6). Chiral monomers (R_p)-**5** and (S_p)-**5** exhibited almost the same reactivities to yield the corresponding polymers (R_p)-**6** in 20% yield with M_n of 1200 and (S_p)-**6** in 13% yield with M_n of 1300 (entries 7 and 8), respectively.

The structures of polymers (*rac*)-**6**, (R_p)-**6**, and (S_p)-**6** were confirmed by ^1H and ^{13}C NMR spectra in $CDCl_3$, and their spectra were identical irrespective of the chirality.[21] In the ^1H NMR spectrum, two broad peaks were observed at around 6.5 and 3.0 ppm, which are attributed to the aromatic protons of [2.2]paracyclophanes and the aliphatic protons of bridge methylenes and methines. The integral ratio of the signals between the aromatic and aliphatic regions was found to be 7:9, suggesting the proposed polymethylene structure. The tacticity of the polymer main chain could not be determined because of the broadness of the signals due to the rigid polymer chain conformation as well as ring-current effect on the packed [2.2]paracyclophane units. Figure 1 shows the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of polymer (*rac*)-**6** obtained by entry 4. Polymer (*rac*)-**6** exhibited a major series of peaks that were regularly separated by the molar mass of a repeating unit (*m*/*z* 220). The molecular weight of each peak in the major series was almost consistent with that expected for polymethylene with hydrogen atoms at its chain ends, which is supported by the chain termination mechanism proposed by Bawn, Ledwith, and Matthies.[13]

Thermogravimetric analysis (TGA) of polymer (*rac*)-**6** revealed that its weight decreased by the following two processes in air (Figure S8 in Supporting Information).[22] In the first process, the degradation of the polymer began at around

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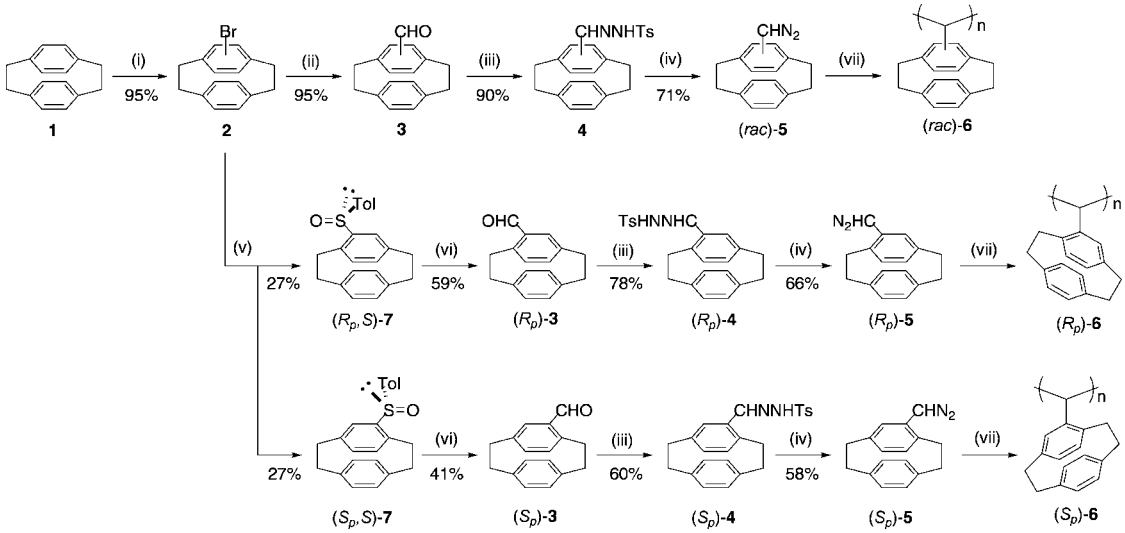
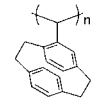
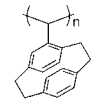
Scheme 1. Synthesis of 4-Diazomethyl[2.2]paracyclophane Monomers and Polymers



Reaction conditions: (i) Br_2/Fe in CH_2Cl_2 at rt for 24 h; (ii) 1) *n*-BuLi in Et_2O at 0°C for 20 min, 2) *N,N*-dimethylformamide (DMF) at rt for 12 h; (iii) *p*-toluenesulfonylhydrazide in EtOH at 50 °C for 12 h; (iv) NaOH in benzene/H_2O with benzyltriethylammonium chloride at 65°C for 2 h; (v) 1) *n*-BuLi in tetrahydrofurane (THF) at –78°C for 2 h, 2) (*S*)-(–)-menthyl *p*-toluenesulfinate for 12 h; (vi) 1) *t*-BuLi in THF at –78°C for 3 min, 2) DMF for 12 h; (vii) 2 mol% of $BF_3{\cdot}Et_2O$.

Table 1. Results of BF_3-Catalyzed Polymerization of (*rac*)-5, (R_p)-5, and (S_p)-5[a]

entry	monomer	temperature °C	solvent	polymer	yield %[b]	M_n[c]	M_w[c]
1	 (*rac*)-**5**	–15	toluene	 (*rac*)-**6**	5	800	1100
2	(*rac*)-**5**	–10	CCl_4	(*rac*)-**6**	trace	-	-
3	(*rac*)-**5**	–78	tetrahydrofuran	(*rac*)-**6**	trace	-	-
4	(*rac*)-**5**	–78	CH_2Cl_2	(*rac*)-**6**	20	1100	1800
5	(*rac*)-**5**	–15	CH_2Cl_2	(*rac*)-**6**	5	900	1200
6	(*rac*)-**5**	r.t.	CH_2Cl_2	(*rac*)-**6**	trace	-	-
7	 (R_p)-**5**	–78	CH_2Cl_2	 (R_p)-**6**	20	1200	1600
8	 (S_p)-**5**	–78	CH_2Cl_2	 (S_p)-**6**	13	1300	1600

[a] Reactions were carried out for 72 h using 2 mol % of $BF_3{\cdot}Et_2O$ catalyst. [b] Isolated yields after reprecipitation. [c] Estimated by gel permeation chromatography (GPC), $CHCl_3$ eluent, and polystyrene standards.

210 °C, while in the second, it began at ~500 °C. A similar degradation profile was obtained for poly(4-vinyl[2.2]paracyclophane) (**8**), which was obtained by the radical polymerization of 4-vinyl[2.2]paracyclophane.[16] The degradation temperatures of the first and second processes of poly(4-vinyl[2.2]paracyclophane) **8** (M_n = 8600) were approximately 155 and 420 °C, respectively. Thus, the degradation temperature of (*rac*)-**6** was higher than that of **8**, implying that polymethylene (*rac*)-**6** has a more rigid structure than that of polyethylene **8**. Incidentally, distinct glass transition temperatures from dif-

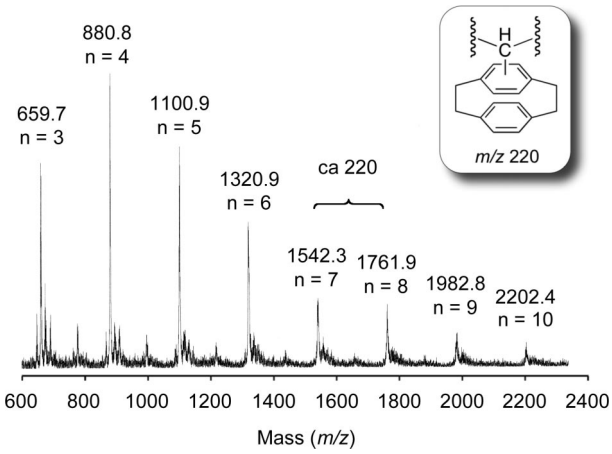
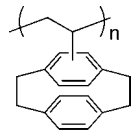


Figure 1. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of polymer (*rac*)-**6**. Dithranol was used as a matrix. Solution of $CHCl_3$ with 1 mg/mL of dithranol and an analyte/matrix weight ratio of $\sim 10^{-3}$ was prepared. The solution was directly cast on the stainless steel sample holder of the MALDI instrument.

ferential scanning calorimetry (DSC) were not observed before decomposition of the polymers.



M_n = 8600

polymer **8**

The optical properties of the polymers were examined. Figure 2 shows the UV−vis absorption spectra of [2.2]paracyclophane (**1**), polyethylene **8**, and polymethylene (*rac*)-**6** in dilute $CHCl_3$ solution. The absorption spectrum of **8** was similar to that of [2.2]paracyclophane (**1**), suggesting that no electronic interactions occurred among the [2.2]paracyclophane units in the polyethylene side chain. On the other hand, the absorption maxima of polymethylene (*rac*)-**6** exhibited a remarkable bathochromic shift as compared to those of **1** and **8**, and

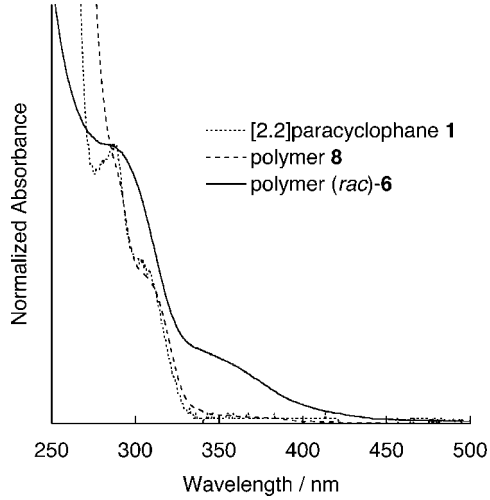


Figure 2. Normalized absorption spectra of [2.2]paracyclophane (**1**), polymer **8**, and polymer (*rac*)-**6** in $CHCl_3$. Solutions of $CHCl_3$ (10 mL, 90−200 μM/repeating unit of the polymer) were prepared. The UV measurements of these solutions were carried out at room temperature using a cell of length 1 cm.

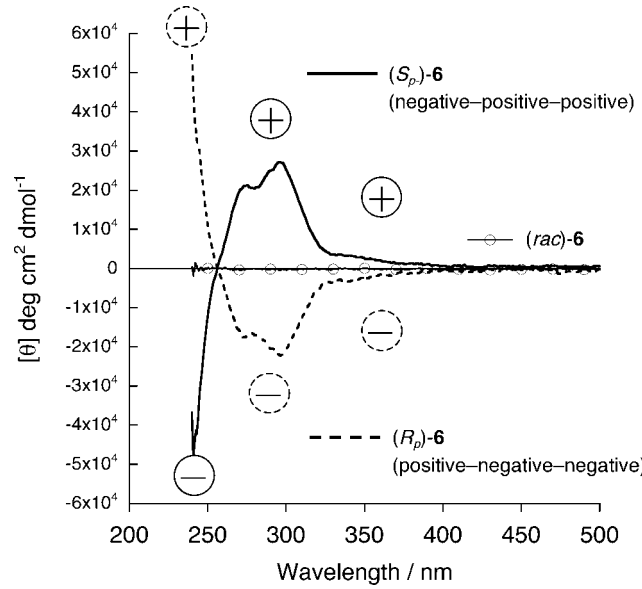


Figure 3. Circular dichroism (CD) spectra of polymers (R_p)-**6**, (S_p)-**6**, and (*rac*)-**6** in $CHCl_3$. Solutions of $CHCl_3$ (10 mL, 60−90 μM/repeating unit of the polymer) were prepared. The CD measurements of these solutions were carried out at room temperature using a cell of length 1 cm.

absorption bands appeared at around 280 and 350 nm. It has been previously reported that the electronic spectra of multilayered cyclophanes comprising several layers of benzene rings exhibited a bathochromic shift.[11] In addition, it has been reported that the absorption maxima of multilayered cyclophanes possessing more than two benzene rings are at around 360 nm.[11] These facts indicate that the bathochromic shift of the absorption spectrum of polymethylene (*rac*)-**6** results from transannular $\pi-\pi$ interactions among the [2.2]paracyclophane units in the ground state due to their closely packed structure.[23,24] As shown in Figure S10, the bathochromic shift of the emission spectrum of polymethylene (*rac*)-**6** was compared to that of [2.2]paracyclophane,[11] which implies transannular interaction of **6** in the excited state.

In $CHCl_3$ solution, optically active polymethylenes (R_p)-**6** and (S_p)-**6** exhibited an intense and mirror-image Cotton effect, while the optically inactive polymer (*rac*)-**6** did not exhibit any peaks, as expected, as shown in Figure 3. The circular dichroism (CD) spectra of (R_p)- and (S_p)-4-methyl[2.2]paracyclophane were reported,[25,26] and they are similar to those of polymers (R_p)-**6** and (S_p)-**6** (Figure 3). The CD spectra of these polymers also exhibited a bathochromic shift as compared to that of 4-methyl[2.2]paracyclophane. These polymers differ in terms of their patterns of the Cotton effect. For example, the CD spectrum of (S_p)-4-methyl[2.2]paracyclophane exhibits three bands in different absorption ranges, i.e., 185−210, 210−270, and 270−320 nm,[26] and these bands exhibit a negative−positive−negative Cotton effect pattern. Rosini and co-workers studied the CD spectra of a series of (R_p)-4-substituted [2.2]paracyclohpanes.[27] The spectra generally exhibited a positive−negative−positive pattern in three ranges.[27] On the other hand, as shown in Figure 3, positive−negative−negative and negative−positive−positive Cotton effect patterns were observed for polymers (R_p)-**6** and (S_p)-**6**, respectively. An effort to elucidate the relation between a CD spectrum and a higher-ordered structure of a polymer is currently underway by preparing optically active dimer, trimer, and tetramer.

In summary, polymethylenes containing [2.2]paracyclophane as a pendent group have been synthesized by the BF_3-catalyzed polymerization of 4-diazamethyl[2.2]paracyclophanes. Optically

active polymethylenes have also been prepared by taking advantage of the planar chirality of 4-substituted [2.2]paracyclophanes. The absorption and emission spectra revealed the π-stacked structure of polymethylene. The CD profiles of polymethylenes containing a planar chiral [2.2]paracyclophane unit exhibited a strong Cotton effect, which is attributed to the optically active higher-ordered structure of the polymethylene chain. Incorporation of emissive aromatic groups into the optically active polymethylene chain by copolymerization has potential application to circularly polarized luminescent materials. Future studies will focus on the synthesis of cyclophane-containing polymethylenes with electron- or energy-accepting aromatic groups in order to construct an electron or energy transfer system.

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Supporting Information Available: Synthetic details, ^{1}H and ^{13}C NMR spectra, TGA profiles, and absorption and photoluminescence spectra (Figures S1−10). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) In the present system, aromatic rings are not layered due to interaction each other, but they interact each other because they are layered. The polymerization of monomers with electron-rich and -poor aromatic rings would proceed more smoothly; for example, see:Pugh, C.; Tang, C. N.; Paz-Pazos, M.; Samtani, O.; Dao, A. H. *Macromolecules* **2007**, *40*, 8178–8188.

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