Introduction of a Long Alkyl Side Chain to Poly(benzimidazole)s. N-Alkylation of the Imidazole Ring and Synthesis of Novel Side Chain Polyrotaxanes

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ABSTRACT: NaH promoted deprotonation of the NH group in poly(benzimidazole)s, $(-ImC_6H_4-)_n$ (**1a**, Im = 5,5′-dibenzimidazole-2,2′-diyl), $[-Im(CH_2)_8-]_n$ (**2a**), and $[\{-Im(CH_2)_{11}O(CH_2)_{11}\}_{0.91}\{Im(CH_2)_{10}-\}_{0.09}]_n$ (**3a**) followed by addition of $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ causes substitution of the NH hydrogen of the parent polymer with the $(CH_2)_{12}OCOCH_2CPh_3$ group. The produced respective poly(benzimidazole) derivatives, **1b**, **2b**, and **3b**, contain the N-alkylated imidazole group with a high content (85−91%) in the main chain and show high solubility in organic solvents. ^{1}H NMR spectra of **1b**−**3b** reveal that 91, 91, and 85% of the respective imidazole rings are N-alkylated. When the same reaction is carried out in the presence of trimethyl-β-cyclodextrin (TMe-β-CD), the reaction gives a new type of polymer (**1c**, **2c**, and **3c**, respectively), side chain polyrotaxanes. TMe-β-CD is incorporated in 21% and 57% of the side chains of **1c** and **2c**, while every side chain of **3c** threads through two TMe-β-CDs. A GPC trace of **3c** supports the formation of the polyrotaxane. Polyrotaxanes **1c**−**3c** also show considerably higher solubility in organic solvents than the parent polymers **1a**−**3a**.

Introduction

Poly(benzimidazole)s exhibit high thermal stabilities, chemical resistance, and nonlinear optical properties owing to their rigid structures containing π-conjugated benzimidazole groups.[1] Recently Gieselman, Dang, and their respective co-workers have succeeded in functionalization of imidazole rings of poly(benzimidazole)s. Deprotonation of the N−H group of the imidazole ring of the polymer followed by reaction of the resulting polyanion with sodium 4-(bromomethyl)benzenesulfonate or 1,4-butanesultone transformed the poly(benzimidazole) into new water soluble polymer derivatives.[2,3]

On the other hand, polyrotaxanes are the subject of recent interest, and many papers have been published on synthesis of the polymers as well as on their interesting supramolecular structure and potential applicability of the polymers for electron switching, photoswitching, and sensing ions.[4−14] However, most of the research has been carried out with main chain type polyrotaxanes, and reports on side chain type polyrotaxanes have been limited.[15] On these bases, we have designed a new type of poly(benzimidazole)s with the side chain rotaxane unit by using the N-alkylation method and by choosing $-(CH_2)_{12}O(C{=}O)CH_2CPh_3$, which is expected to form stable rotaxanes with cyclodextrins, as the alkyl chain; the bulky CPh_3 group is considered to trap cyclodextrins effectively. The side chain threading through the macrocyclic molecules would cause change of the physical properties of the poly(benzimidazole)s. Here we report results of the preparation of the side chain type polyrotaxanes and properties of the polymers.

Results and Discussion

As the first step, the N-alkylation reaction of poly(benzimidazole)s by the $-(CH_2)_{12}O(C{=}O)CH_2CPh_3$ group has been examined.

N-Alkylation of Poly(*p*-phenylenebenzimidazole), 1a, and Poly(octamethylenebenzimidazole), 2a. Reaction of poly(*p*-phenylenebenzimidazole) (**1a**) and poly(octamethylenebenzimidazole) (**2a**) with sodium hydride in DMSO causes deprotonation of the imidazole NH group to give a deep red solution of polyanions. Subsequent treatment of these polyanions with $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ results in separation of N-alkylated polymers **1b** and **2b** from the solution in 66% and 58% yields, respectively, as shown in Scheme 1. The spectroscopic data of the products indicate that the polymers contain N-alkylated imidazole rings and a small amount of unreacted imidazole rings randomly in the main chain.

Results of the N-alkylation, together with those of N-alkylation in the presence of trimethyl-β-cyclodextrin (TMe-β-CD), are summarized in Table 1.

IR spectra of **1b** and **2b** in Figure 1 show peaks due to the introduced side chain of the product. New ν(C=O) and ν(C−O) peaks of the ester group in the side chain appear at about 1730 and 1145 cm^{-1}, respectively. A strong absorption peak at 698 cm^{-1} is assigned to the δ(C−H) vibration of the CPh_3 group. Although **1a** and **2a** show a ν(N−H) peak around 3300 cm^{-1} clearly, the ν(N−H) peak becomes almost negligible for the IR spectra of **1b** and **2b**.

The ^{1}H NMR spectrum of **1b** in Figure 2 reveals a high degree (91%) of the N-alkylation as estimated from the peak area of aliphatic hydrogens. It shows new peaks at δ 4.3, 3.73, and 3.72, which are assigned to the NCH_2, OCH_2 and CH_2CPh_3 hydrogens, respectively. Aromatic hydrogens of the benzimidazole group of the original **1a** show only three signals at δ 9.2, 8.3, and 8.0, while **1b** shows several peaks in the range δ 8.1−7.5. The more complicated ^{1}H NMR peak pattern of aromatic hydrogens of **1b** than that of **1a** may be ascribed to the presence of two types of N-alkylated units shown in Chart 1.

As for **1a** (R = H in Chart 1), it undergoes a rapid 1,3-shift of the N−H hydrogen,[16] the two isomeric structures are not distinguished from each other by NMR spectroscopy. However, the two N-alkylated isomeric structures give aromatic signals at δ 8.1, 7.9, 7.7, and 7.5 (Figure 2) assignable to $H^b + H^{b'}$, $H^a + H^{c'}$,

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Scheme 1. Synthesis of N-Alkylated Polymers 1b and 2b

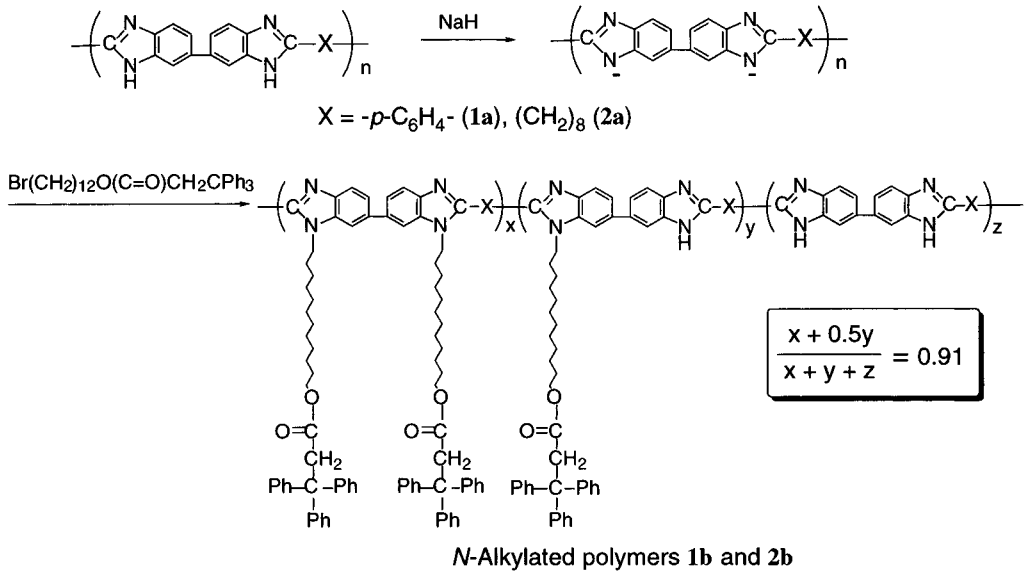


Table 1. Preparation of N-Alkylated Poly(benzimidazole)s and Side Chain Polyrotaxanes

						molar ratio of TMe-β-CD	
polymers	yield, %	$10^{-3}M_n$[a]	$10^{-3}M_w$[a]	[η], dL g^{-1} [b]	degree of N-alkylation, %[c]	TMe-β-CD/ imidazole ring, %[c]	TMe-β-CD/ side chain, %[c]
1a		*d*	*d*	0.20			
2a		*d*	*d*	0.17			
3a		2.2	4.0	0.07			
1b	66	46.7	95.3	0.38	91		
2b	58	25.4	42.1	0.34	91		
3b	53	5.7	6.5	0.10	85		
1c	95	30.8	61.1	0.08	29	6	21
2c	45	15.9	41.5	0.11	54	31	57
3c	85	7.0	9.5	0.06	62	124	200

[a] Measured by GPC (eluent: DMF containing 0.01 M LiBr; polystyrene standards). [b] Measured in DMSO (**1a**, **2a**, **3a**, **2b**, and **2c**) or $CHCl_3$ (**1b**, **3b**, **1c**, and **3c**) at 30 °C. [c] Estimated from relative peak intensities of the ^{1}H NMR spectra. [d] Not measured due to insufficient solubility.

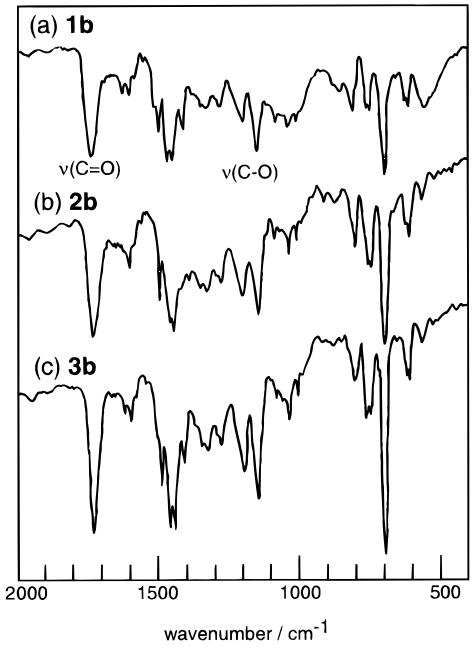


Figure 1. IR spectra of (a) **1b**, (b) **2b**, and (c) **3b** in KBr disks.

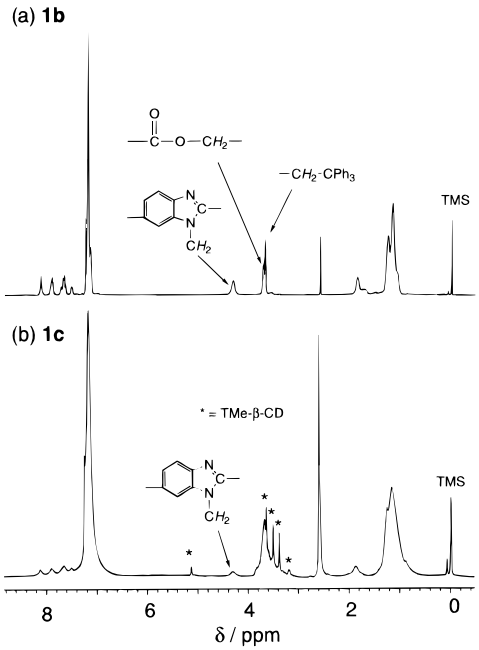


Figure 2. ^{1}H NMR spectra of (a) **1b** and (b) **1c** in $CDCl_3$ (400 MHz). Peaks with asterisks are due to TMe-β-CD.

H^c, and $H^{a'}$, respectively. **1b** is considered to contain the form A and form B units in about a 6:4 ratio as estimated from the ^{1}H NMR analysis. The ^{1}H NMR spectrum of **2b** gives an analogous result (cf. Experimental) and the degree of N-alkylation of **2b** is also high (91%, Table 1).

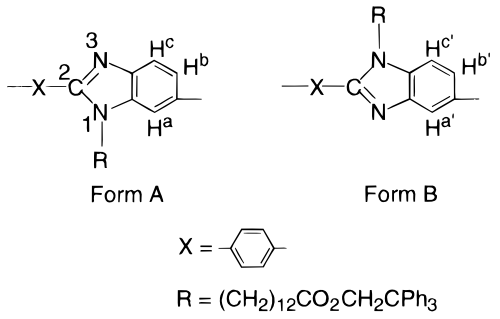
GPC measurement shows that **1b** and **2b** have molecular weights M_n of 46 700 and 25 400 and M_w of 95 300 and 42 100, respectively. Inherent viscosities of

Table 2. Solubility of the Polymers[a]

	poly(benzimidazole)			N-alkylated polymer			polyrotaxane		
solvent	**1a**	**2a**	**3a**	**1b**	**2b**	**3b**	**1c**	**2c**	**3c**
DMF	−	−	++	+	+	++	±	++	++
DMSO	+	+	++	+	−	++	+	−	++
NMP	+	+	++	+	+	++	+	+	++
acetone	−	−	−	±	±	±	−	−	±
chloroform	−	−	−	++	++	++	+	++	++
THF	−	−	−	±	±	±	−	−	±

[a] Solubility (ca. 2 mg mL^{-1}); ++, soluble at room temperature; +, soluble at 80 °C; ±, partially soluble at 80 °C; −, insoluble.

Chart 1. Isomeric Structures of the Benzimidazole Group



1b and **2b**, [η], are 0.38 and 0.34 dL g^{-1} (30 °C, in DMSO (**1b**) and $CHCl_3$ (**2b**)), respectively. Table 2 summarizes the solubility of the polymers. The N-alkylated **1b** and **2b** are soluble in common organic solvents such as $CHCl_3$, THF, and acetone, while the original **1a** and **2a** show a limited solubility in highly polar solvents such as DMSO and NMP and are practically insoluble in less polar solvents.

N-Alkylation of Poly(alkylenebenzimidazole), 3a. $RuCl_2(PPh_3)_3$-catalyzed polycondensation of 3,3′-diaminobenzidine and 1,12-dodecanediol gives poly(alkylenebenzimidazole), **3a**, whose main chain consists of $[Im(CH_2)_{11}O(CH_2)_{11}]$ and $[Im(CH_2)_{10}]$ (Im = 5,5′-dibenzimidazole-2,2′-diyl) units.[12] Reaction of $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ with the corresponding polyanion of **3a** gives N-alkylated polymer **3b** in 53% yield (Scheme 2).

The ^1H NMR spectrum of **3b** in Figure 3a shows peaks due to CH_2N, CH_2OCO, and CH_2CPh_3 hydrogens at δ 4.1, 3.76, and 3.74, respectively. The main chain CH_2 hydrogens adjacent to the imidazole ring and to the oxygen atom of **3b** show peaks at δ 2.82 and 3.64, respectively, which are shifted to lower magnetic field compared with those of **3a**. The degree of N-alkylation is 85% as determined by relative peak intensities. Figure 1c shows the IR spectrum of **3b**.

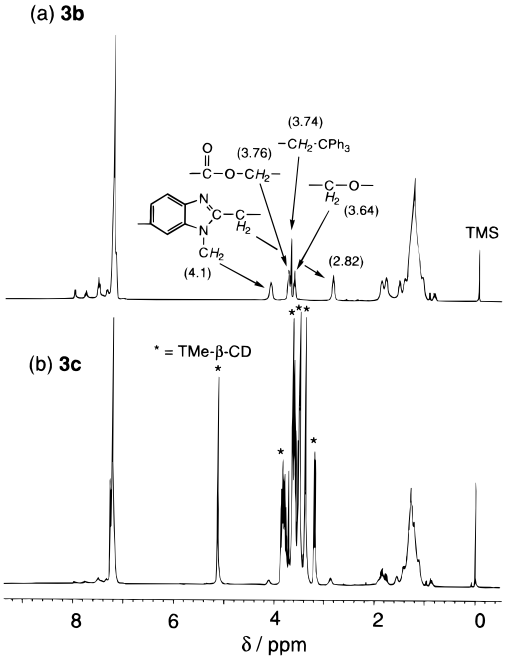


Figure 3. ^1H NMR spectra of (a) **3b** and (b) **3c** in $CDCl_3$ (400 MHz). Peaks with asterisks are due to TMe-β-CD.

Synthesis of Side Chain Polyrotaxanes. Ritter and his co-workers reported the preparation of side chain polyrotaxanes by using poly(ether sulfone) and β-cyclodextrins (β-CDs).[18] In their research, they found

Scheme 2. Synthesis of N-Alkylated Polymer 3b.

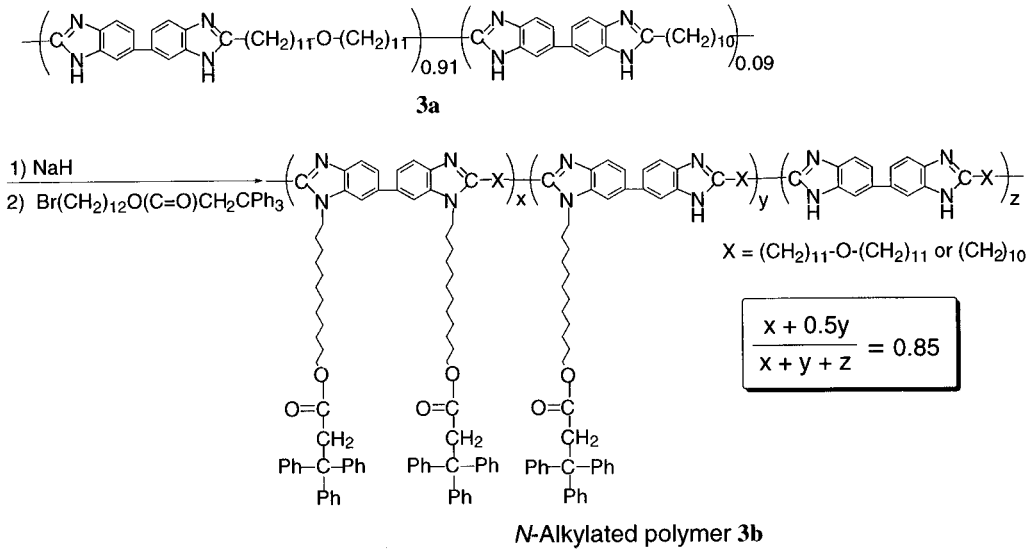
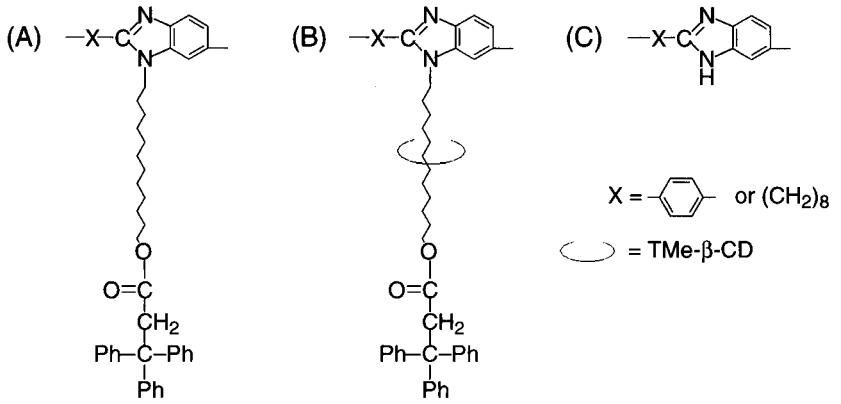


Chart 2. Benzimidazole Units in Polyrotaxanes 1c and 2c



that protection of two or three OH hydrogens of β-CD with Me or acetyl groups was effective to avoid undesirable side reactions. In our present study, the N-alkylation reaction proceeds through the polyanion; therefore, protection of the OH groups of β-CD also seems inevitable. Actually, reactions of the polyanions obtained from **1a**, **2a**, and **3a** with $Br(CH_2)_{12}O(C{=}O)CH_2$-$CPh_3$ in the presence of trimethyl-β-cyclodextrin (TMe-β-CD) give analogous side chain-type polyrotaxanes (**1c**, **2c**, and **3c**) successfully. On the other hand, similar reactions using unprotected β-CD gives products that are not characterizable.

1a, **2a**, **3a** $\xrightarrow{\text{NaH}}$ $\xrightarrow{CPh_3CH_2CO_2(CH_2)_{12}Br + \text{TMe-}\beta\text{-CD}}$ **1c**, **2c**, **3c**

IR spectra of polyrotaxanes **1c**, **2c**, and **3c** are similar to those of N-alkylated polymers **1b**, **2b**, and **3b**, except for an additional absorption band around 1040 cm^{-1} due to a ν(C−O) peak of TMe-β-CD. The ^1H NMR spectrum of **1c** (Figure 2b) shows peaks due to CH_3 hydrogens of TMe-β-CD at δ 3.64, 3.60, and 3.50. Similar to cases of polyrotaxanes of poly(ethylene oxide) and cyclodextrins,[5e,f] the CH_3 peaks of TMe-β-CD appear at the same position as those of free TMe-β-CD. The relative peak area ratios among CH_2N, TMe-β-CD, and the benzimidazole group show that **1c** and **2c** contain the imidazole units A, B, and C in ratios of 23:6:71 and 23:31:46, respectively (Chart 2).[17]

On the other hand, the ^1H NMR spectrum indicates that the degree of N-alkylation in **3c** is 0.62 and that the every side chain threads through two TMe-β-CD rings (Chart 3). The $(CH_2)_{12}O(C{=}O)CH_2$ part of the side chain has a length of ca 17 Å, corresponding to double the thickness of TMe-β-CD (7.8 Å),[18] and seems to be capable to accept two TMe-β-CDs. The ^1H NMR spectra of **1c**−**3c** before and after reprecipitation from $CHCl_3$−MeOH do not show any change in the peak area ratio between the hydrogens of poly(benzimidazole)s and TMe-β-CD. Although solid evidence for the formation of polyrotaxane **3c** has not been obtained from the NMR spectroscopy, comparison of a GPC trace of **3c** with that of a mixture of N-alkylated poly(benzimidazole) and TMe-β-CD clearly supports the formation of the expected rotaxanes. Figure 4 shows GPC traces of **3c** (top), a mixture of **3b** and TMe-β-CD (middle), and TMe-β-CD (bottom). The unimodal elution pattern of **3c** indicates that all the TMe-β-CD is incorporated in the

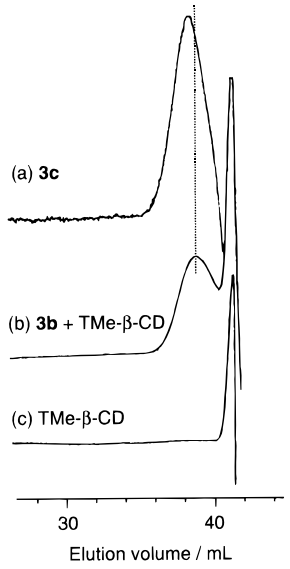
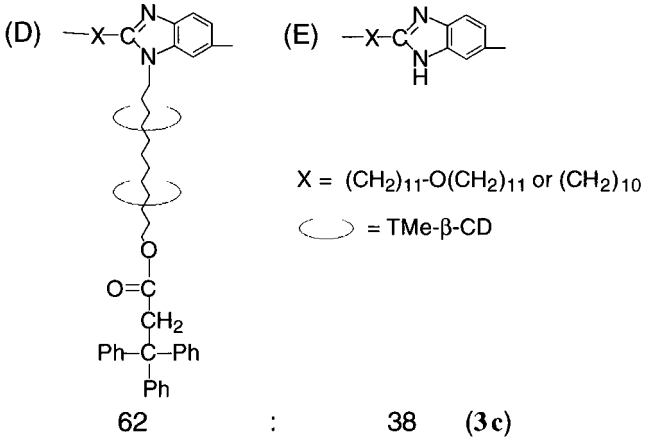


Figure 4. GPC traces of **3c**; mixture of **3b** and TMe-β-CD; and TMe-β-CD.

Chart 3. Benzimidazole Units in Polyrotaxane 3c



side chains. As described above and shown in Table 1, the degree of N-alkylation and content of TMe-β-CD in **1c**−**3c** depends on the spacing group between the imidazole rings in the main chain. The short *p*-phenylene spacing group of **1a** retards introduction of the bulky side chains. On the other hand, the long $(CH_2)_{11}O(CH_2)_{11}$ spacing group in **3a** seems to make it possible to form **3c** with a higher degree of N-alkylation

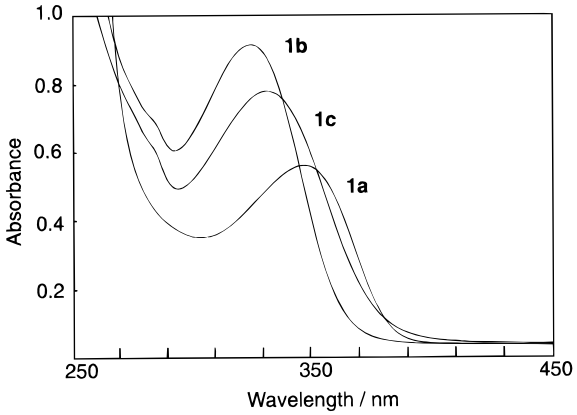


Figure 5. UV−visible spectra of **1a** (1.0×10^{-5} mol L^{-1}), **1b** (5.0×10^{-5} mol L^{-1}), and **1c** (4.0×10^{-5} mol L^{-1}) in DMSO at 25 °C.

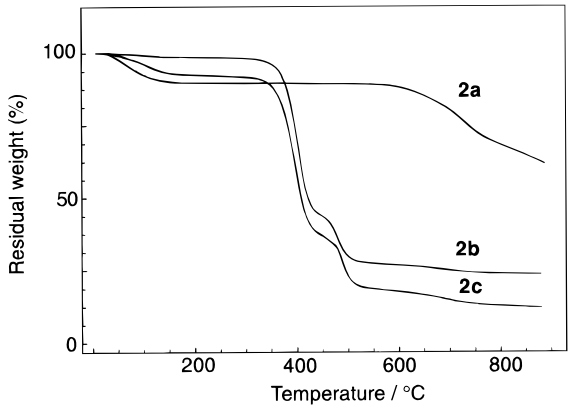


Figure 6. TG curves of **2a**, **2b**, and **2c** at a heating rate of 10 °C/min under nitrogen.

and the high content of TMe-β-CD.

UV−visible spectra of **1b** and **1c** show $\pi-\pi^*$ absorption peaks at 324 and 331 nm, respectively, while **1a** shows the corresponding peak at 347 nm as shown in Figure 5. The hypsochromic shift of the $\pi-\pi^*$ absorption peak of **1b** and **1c** is attributed to a decrease in coplanarity of the main chain by increasing the steric repulsion. Polyrotaxane **3c** shows solubility similar to that of **3b** as shown in Table 2, whereas polyrotaxanes **1c** and **2c** are less soluble in THF or $CHCl_3$ than the corresponding N-alkylated polymers.

Thermal Properties of the Polymers. Figure 6 shows thermogravimetric (TG) curves of **2a**, **2b**, and **2c**. Polymers **2a** and **2c** include solvated water, and show an initial weight loss of 12−15% on heating at 140 °C. **2b** is hydrated to a small extent and shows a negligible weight loss up to 360 °C. Gradual thermal decomposition of **2a** starts at 462 °C, while decomposition of **2b** and **2c** begins at much lower temperatures. Polyrotaxane **3c** shows quite different DSC results from **3b** and from a mixture of **3b** and TMe-β-CD. A T_m transition is not observed in the DSC curve of **3c** at all, while that of a physical mixture of **3b** and TMe-β-CD shows a significant T_m transition peak due to TMe-β-CD.

Conclusion

Three kinds of N-alkylated poly(benzimidazole)s have been prepared *via* polyanions generated by treatment with NaH. The N-alkylated polymers have considerably higher solubility than the parent polymers. Addition of TMe-β-CD in the reaction mixture affords the side chain type polyrotaxane from the original poly(benzimidazole) directly. The degree of N-alkylation and content of TMe-β-CD are strongly affected by the length of the spacing group (p-C_6H_4, $(CH_2)_8$, or $(CH_2)_{11}O(CH_2)_{11}$); thus, the poly(benzimidazole) with the $(CH_2)_{11}O(CH_2)_{11}$ spacing group gives a polyrotaxane with 62% N-alkylation and with two TMe-β-CDs on each of the side chains.

Experimental Section

General Data, Materials, and Measurement. All the manipulations in preparation of the side chain reagent and polymerization were carried out under nitrogen using standard Schlenk techniques. Solvents were dried by the usual method, distilled, and stored under nitrogen. Poly(octamethylenebenzimidazole) (**2a**) and poly(alkylenebenzimidazole) (**3a**) were prepared according to the literature.[1c,10] Trimethyl-β-cyclodextrin was prepared from β-cyclodextrin according to the literature.[19] Poly(p-phenylenebenzimidazole) (**1a**) and the other organic chemicals were purchased and used as received. IR and NMR spectra were obtained on a JASCO-IR 810 spectrometer and on a JEOL EX-400 spectrometer, respectively. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder. GPC traces were obtained on a Toso HLC-8020 using a DMF solution of LiBr (0.01 M) as the eluent and polystyrene as the standard and RI detector. UV−visible spectra were obtained on a Shimadzu UV-3100PC. TG measurement was carried out on a Shimadzu TGA-50.

Synthesis of $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$. An $SOCl_2$ (54 mL) solution of $Ph_3CCH_2(C{=}O)OH$ (5.0 g, 17 mmol) was refluxed for 4 h. Evaporation of $SOCl_2$ and recrystallization of the product from a mixture of ethyl acetate and hexane (v/v = 1/1) gave $Ph_3CCH_2(C{=}O)Cl$ as colorless crystals (2.4 g, 45%). Mp: 109−110 °C.

$Ph_3CCH_2(C{=}O)Cl$ (0.96 g, 3.0 mmol) and pyridine (0.28 mL, 3.0 mmol) were dissolved in THF (3 mL) by stirring them together at room temperature for 2 min, and then a THF (5 mL) solution of 12-bromo-1-dodecanol (0.80 g, 3.0 mmol) was added portionwise at 0 °C. After the reaction mixture was stirred for 15 h, the resulting pyridinium chloride was removed by filtration. The solvent of the filtrate was evaporated to dryness to give $BrCH^c_2CH^d_2(CH_2)_9CH^a_2O(C{=}O)CH^b_2CPh_3$ (1.3 g, 79%). The product was further purified by column chromatography (SiO_2, $CHCl_3$). Anal. Calcd for $C_{33}H_{41}BrO_2$: C, 72.1; H, 7.5; Br, 14.5. Found: C, 72.0; H, 7.5; N, 14.5. ^{1}H NMR (400 MHz in $CDCl_3$): δ 3.76 (t, H^a, J = 6.4 Hz), 3.71 (s, H^b), 3.4 (t, H^c, J = 6.8 Hz), 1.8 (m, H^d), 1.1−1.4 (m, $(CH_2)_9$). ^{13}C NMR (100 MHz in $CDCl_3$): δ 171.0 ($C{=}O$), 146.6, 129.2, 127.7, 126.1 (C_6H_5), 64.4 (CH_2O), 55.7 (CPh_3), 46.5 ($CH_2C{=}O$), 34.0 (CH_2Br), 32.8 (CH_2CH_2Br), 29.5, 29.4, 29.1, 28.7, 28.3, 28.1, 25.8 ($(CH_2)_9$).

N-Alkylation of Poly(*p*-phenylenebenzimidazole) and of Poly(octamethylenebenzimidazole). To a DMSO (3 mL) solution of NaH (32 mg, 1.3 mmol) stirred at 40 °C for 30 min and then at 75 °C for 1 h was added a DMSO (3 mL) solution of poly(p-phenylenebenzimidazole) (**1a**) (94 mg, 0.30 mmol) at 40 °C. After the mixture was stirred for 24 h at 40 °C, $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ (0.49 g, 0.90 mmol) was added. Stirring for 24 h at 30 °C caused precipitation of a dark red solid, which was collected by filtration, washed with methanol, and reprecipitated from methanol to give the N-alkylated polymer **1b** as a light brown solid (0.23 g, 66%). IR (KBr, cm^{-1}): 3056 (w), 2924 (m), 2852 (m), 1733 (s), 1445 (s), 1145 (s), 698 (s). ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.1, 7.9, 7.7, and 7.5 (aromatic hydrogens of benzimidazole ring), 7.2 (C_6H_5 and C_6H_4), 4.3 (CH_2N), 3.73 ($CH_2O(C{=}O)$, 3.72 ($C(=O)CH_2CPh_3$), 2.6, 1.9, and 1.2 ($(CH_2)_{10}$). ^{13}C NMR (100 MHz in $CDCl_3$): δ 171.0 ($C{=}O$), 153.4 ($C{=}N$), 146.5, 143.8, 142.5, 136.9, 136.3, 134.9, 134.4, 130.2, 129.2, 127.7, 126.1 (aromatic carbons), 64.4 (CH_2O), 55.7 (CPh_3), 46.4 ($CH_2C{=}O$), 32.8 (CH_2N), 29.9, 29.8, 29.7, 29.5, 29.1, 28.3, 26.8, 25.8 ($(CH_2)_9$). Anal. Calcd for $(C_{80}H_{92}N_4O_4)_{0.91}(C_{20}H_{10}N_4)_{0.09}\cdot 0.5H_2O$: C, 80.6; H, 7.9; N, 5.0. Found: C, 80.3; H, 7.5; N, 4.4.

N-alkylation of poly(octamethylenebenzimidazole) (**2a**) was carried out in a similar manner (58%). IR (KBr, cm^{-1}): 3054

(w), 2922 (m), 2852 (m), 1730 (s), 1446 (s), 1146 (s), 698 (s). ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.0, 7.8, 7.5, and 7.4 (aromatic hydrogens of benzimidazole ring), 7.2 (C_6H_5), 4.1 (CH_2N), 3.76 ($CH_2O(C{=}O)$), 3.74 ($C({=}O)CH_2CPh_3$), 2.8 (CH_2 bonded to imidazole carbon), and 1.2−1.6 (($CH_2)_8$ of main chain and ($CH_2)_{10}$ of side chain). ^{13}C NMR (100 MHz in $CDCl_3$): δ 170.9 ($C{=}O$), 155.5 ($C{=}N$), 146.5, 143.3, 136.6, 136.5, 136.3, 134.3, 134.3, 129.4, 129.2, 127.7, 126.1 (aromatic carbons), 64.4 (CH_2O), 55.7 (CPh_3), 46.4 ($CH_2C{=}O$), 32.8 (CH_2N), 30.1, 30.0, 29.8, 29.6, 29.5, 29.4, 29.3, 29.1, 28.2, 27.8, 27.6, 25.8 (($CH_2)_8$ of main chain and ($CH_2)_9$ of side chain).

N-Alkylation of Poly(alkylenebenzimidazole). To a DMSO (4 mL) solution of NaH (30 mg, 1.3 mmol) stirred at 40 °C for 30 min and then at 75 °C for 1 h was added poly(alkylenebenzimidazole) (**3a**) (160 mg, 0.29 mmol). The resulting deep red solution was heated for 24 h at 40 °C. Addition of $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ (0.61 g, 1.1 mmol) and ensuing stirring for 24 h at 40 °C gave a brown reaction mixture. Evaporation of the solvent under high vacuum gave a dark brown paste, which was washed with methanol and then water and reprecipitated from hexane to give **3b** as a black solid (0.23 g, 53%). IR (KBr, cm^{-1}): 3028 (w), 2850 (m), 1948 (m), 1711 (s), 1595 (m), 1145 (s), 696 (s). ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.0, 7.8, 7.5, and 7.4 (aromatic hydrogens of benzimidazole ring), 7.2 (C_6H_5), 4.1 (CH_2N), 3.76 ($CH_2O(C{=}O)$), 3.74 ($C(=O)CH_2CPh_3$), 3.64 (CH_2OCH_2), 2.82 (CH_2 bonded to imidazole carbon), 1.9 and 1.3 (($CH_2)_9$ group of main chain and ($CH_2)_{10}$ of side chain). ^{13}C NMR (100 MHz in $CDCl_3$): δ 171.0 ($C{=}O$), 155.8 ($C{=}N$), 146.6, 143.8, 142.5, 136.6, 135.7, 129.5, 129.2, 127.7, 126.2, 122.0, 119.2 (aromatic carbons), 64.5 ($CH_2O(C{=}O)$), 55.8 (CPh_3), 46.6 (CH_2CPh_3), 35.0 (CH_2N), 32.8 (CH_2CH_2N), 30.0, 29.6, 29.5, 29.4, 29.1, 28.3, 27.9, 27.0, 25.8 (($CH_2)_{11}$ of main chain and ($CH_2)_9$ of side chain).

Preparation of Poly(*p*-phenylenebenzimidazole) Rotaxane. To a DMSO (3 mL) solution of NaH (31 mg, 1.3 mmol) stirred at 40 °C for 30 min and then at 75 °C for 1 h was added a DMSO (3 mL) solution of poly(*p*-phenylenebenzimidazole) (**1a**) (92 mg, 0.30 mmol). The resulting deep red solution was heated for 24 h at 40 °C. A mixture of trimethyl-β-cyclodextrin (TMe-β-CD) (0.86 g, 0.60 mmol) and $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ (0.49 g, 0.90 mmol) was added in one portion to the reaction mixture. Stirring the mixture at 30 °C for 22 h gave a dark red precipitate which was collected by filtration, washed with methanol, and reprecipitated from methanol to give **1c** as a light brown solid (0.20 g, 95%). IR (KBr, cm^{-1}): 3056 (w), 2924 (m), 2852 (m), 1733 (s), 1445 (s), 1145 (s), 1040 (s), 698 (s). ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.1, 7.9, 7.6, and 7.5 (aromatic hydrogens of benzimidazole ring), 7.2 (C_6H_5), 5.1 (TMe-β-CD), 4.3 (CH_2N), 3.7 ($CH_2O(C{=}O)$ and $C(=O)CH_2CPh_3$), 3.64, 3.60, 3.50 (CH_3 of TMe-β-CD), 3.2 (TMe-β-CD), 2.6, 1.9, and 1.2 (($CH_2)_{10}$). ^{13}C NMR (100 MHz in $CDCl_3$): δ 171.0 ($C{=}O$), 146.5, 129.1, 127.7, 126.1 (aromatic carbons), 98.9, 82.0, 81.8, 80.3, 71.4, 70.9, 61.4, 58.9 (TMe-β-CD), 64.4 (CH_2O), 55.7 (CPh_3), 46.4 (CH_2CPh_3), 29.9, 29.6, 29.4, 29.1, 29.0, 28.2, 26.8, 25.8, 25.7 (($CH_2)_{11}$). Anal. Calcd for $(C_{206}H_{316}N_4O_{60})_{0.06}(C_{80}H_{92}N_4O_4)_{0.23}(C_{20}H_{10}N_4)_{0.71}\cdot 0.5H_2O$: C, 74.5; H, 6.7; N, 7.7. Found: C, 74.6; H, 7.2; N, 5.2.

Preparation of Poly(octamethylenebenzimidazole) Rotaxane. To a DMSO (3 mL) solution of NaH (32 mg, 1.3 mmol) stirred at 40 °C for 30 min and then at 75 °C for 1 h was added a DMSO (3 mL) solution of poly(octamethylenebenzimidazole) (**2a**) (0.11 g, 0.31 mmol). After the reaction for 24 h at 40 °C, TMe-β-CD (0.86 g, 0.60 mmol) and $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ (0.49 g, 0.90 mmol) were added in one portion. The resulting mixture was stirred at 30 °C for 24 h. The solvent was evaporated under high vacuum to give a light brown solid, which was washed with methanol and water to give **2c** (0.20 g, 45%). IR (KBr, cm^{-1}): 3056 (w), 2924 (s), 2850 (m), 1717 (s), 1447 (s), 1145 (s), 1037 (s), 698 (s). ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.0, 7.8, 7.7, and 7.3 (aromatic hydrogens of benzimidazole ring), 7.2 (C_6H_5), 5.1 (TMe-β-CD), 4.1 (CH_2N), 3.7 ($CH_2O(C{=}O)$ and $C(=O)CH_2CPh_3$), 3.8 and 3.75 (TMe-β-CD), 3.6, 3.5, 3.4 (CH_3 of TMe-β-CD), 3.2 (TMe-β-CD), 2.8 (CH_2 bonded to imidazole carbon), 1.0−1.5 (($CH_2)_6$ of main chain and ($CH_2)_{10}$ of side chain).

Preparation of Poly(alkylenebenzimidazole) Rotaxane. To a DMSO (4 mL) solution of NaH (16 mg, 0.67 mmol) stirred at 40 °C for 30 min and then at 75 °C for 1 h was added poly(alkylenebenzimidazole) (**3a**) (93 mg, 0.15 mmol). Stirring was continued for 24 h at 40 °C. TMe-β-CD (0.86 g, 0.60 mmol) and $Br(CH_2)_{12}O(C{=}O)CH_2CPh_3$ (0.33 g, 0.60 mmol) were added in one portion, and the resulting reaction mixture was stirred at 30 °C for 24 h. After the solvent was reduced to half of the original volume by evaporation, water (40 mL) was added into the solution to cause precipitation of a brown solid, which was collected by filtration, washed with methanol, and reprecipitated from water to give **3c** (0.71 g, 85%). IR (KBr, cm^{-1}): 3050 (w), 2928 (s), 2852 (m), 1734 (m), 1448 (s), 1143 (s), 1108 (s), 1073 (s), 1037 (s), 971 (s), 700 (s), 556 (m). ^{1}H NMR (400 MHz in $CDCl_3$): δ 8.0, 7.8, 7.5, and 7.3 (aromatic hydrogens of benzimidazole ring), 7.2 (C_6H_5), 5.1 (TMe-β-CD), 4.1 (CH_2N), 3.8, 3.72 and 3.2 (TMe-β-CD), 3.7 ($CH_2O(C{=}O)$ and $C(=O)CH_2CPh_3$), 3.64, 3.60, 3.50 (CH_3 of TMe-β-CD), 2.9 (CH_2 bonded to imidazole carbon), 1.9 and 1.3 (($CH_2)_{10}$ of side chain, ($CH_2)_8$ and ($CH_2)_9$ of main chain). ^{13}C NMR (100 MHz in $CDCl_3$): δ 170.7 ($C{=}O$), 146.3, 128.9, 127.4, 125.8 (aromatic carbons), 98.6, 81.8, 81.5, 71.1, 70.9, 62.3, 58.6, 58.2 (TMe-β-CD), 64.1 ($CH_2O(C{=}O)$), 63.2 (CH_2OCH_2 of main chain), 55.4 (CPh_3), 46.2 (CH_2CPh_3), 33.5 (CH_2N), 32.5 (CH_2CH_2N), 29.1, 29.6, 29.1, 29.0, 28.8, 28.5, 28.0, 27.8, 26.5, 25.5 (($CH_2)_{10}$ of main chain and ($CH_2)_9$ of side chain).

Similar reaction of **3a**, TMe-β-CD, and $Br(CH_2)_{12}OCOCH_2CPh_3$ in a 1:2:3 molar ratio results in formation of polyrotaxane **3c′** whose imidazole ring is N-alkylated in a 93% yield. The ratio of the side chain and TMe-β-CD is 1:1.4, indicating that almost all the macrocyclic molecules in the reaction mixture form the rotaxane with the side chain of the poly(benzimidazole).

Polyrotaxanes **1c**−**3c** obtained as above were reprecipitated by pouring the $CHCl_3$ solution into MeOH on stirring. The ^{1}H NMR peak area ratios between the main chain and TMe-β-CD hydrogens do not change by this purification process.

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(16) ^{13}C NMR spectrum of the original nonalkylated polymer (R = H in Chart 1) shows only three aromatic peaks of the benzimidazole group due to the rapid 1,3-hydrogen shift on the NMR time scale. On the contrary, the N-alkylated polymers give rise to six aromatic signals of benzimidazole group in the ^{13}C NMR spectrum due to the presence of the two isomeric structures shown in Chart 1. The 1,3-shift may take place by a direct exchange of hydrogen between N^1 or N^3 or involve interunit exchange of hydrogen.

(17) These ratios are calculated by assuming that one side chain includes TMe-β-CD, although a part of TMe-β-CD seems to be included as a 1:2 rotaxane.

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