

Ru(0) complex catalyzed polyaddition

New synthesis of poly(alkylenebenzoxazole) and poly(alkylenebenzimidazole)

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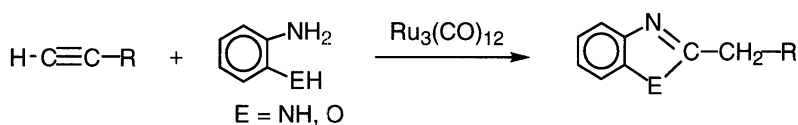
Summary

The reactions of α,ω -diyne, $\text{HC}\equiv\text{C}(\text{CH}_2)_m\text{C}\equiv\text{CH}$ ($m = 6$ and 8), with 3,3'-diaminobenzidine and with 3,3'-diamino-4,4'-dihydroxybiphenyl in the presence of $\text{Ru}_3(\text{CO})_{12}$ - PPh_3 catalyst give the corresponding poly(alkylenebenzoxazole)s and poly(alkylenebenzimidazole)s, respectively. The former polymers obtained from the equimolar reaction of the monomers are partly soluble in polar organic solvents such as DMF, DMSO, and NMP, while the poly(benzimidazole)s are soluble in these solvents. GPC measurement shows the molecular weights of the polymers, M_n of $4.8\text{--}14.1 \times 10^3$ and M_w of $6.4\text{--}19.7 \times 10^3$.

Introduction

Poly(benzimidazole) and poly(benzoxazole) show high thermal stability and resistance toward oxidation, and have potential utility as electrical and nonlinear optical devices (1). However, conventional preparation of the polymers often requires polycondensation under severe conditions. For example, the polymers were synthesized by melting polycondensation of esters of dicarboxylic acid with 3,3'-diaminobenzidine and with 3,3'-diamino-4,4'-dihydroxybiphenyl (2) or by polycondensation of aliphatic dicarboxylic acid and 3,3'-diaminobenzidine tetrahydrochloride using polyphosphoric acid as the dehydrating agent (3).

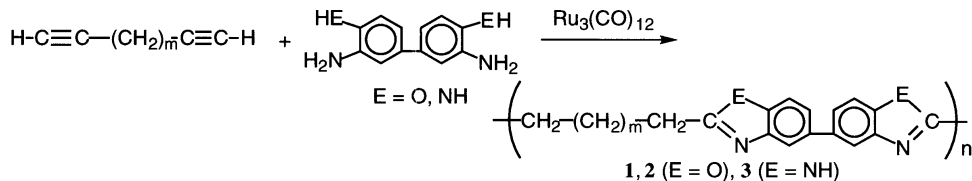
Recent progress in transition metal complex catalyzed bond forming reactions has enabled novel polyaddition and polycondensation. Ru-complex-catalyzed reaction of *o*-phenylenediamine or 2-aminophenol with primary alcohols (4) and with 1-alkynes (5) provides a unique synthetic method of 2-alkylbenzimidazole and 2-alkylbenzoxazole (Scheme 1). Some of the reactions have recently been applied to polycondensation of 3,3'-diaminobenzidine and 1, 12-dodecanediol to give poly(alkylenebenzimidazole) (6).



Scheme 1 Reaction of 1-alkyne with *o*-phenylenediamine and with 2-aminophenol.

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Further extension of the Ru-complex-catalyzed polyaddition to reaction of α,ω -diynes with 3,3'-diamino-4,4'-dihydroxybiphenyl and 3,3'-diaminobenzidine would provide a new method for synthesis of poly(benzoxazole) and poly(benzimidazole) under non-acidic conditions as shown in Scheme 2. Here we report results of the $\text{Ru}_3(\text{CO})_{12}$ catalyzed polyaddition to give poly(alkylenebenzoxazole) and poly(alkylenebenzimidazole).



Scheme 2 Polyaddition of α,ω -diynes with 3,3'-diamino-4,4'-dihydroxybiphenyl (E=O) and with 3,3'-diaminobenzidine (E = NH).

Experimental

General considerations, materials, and measurements

All the polymerization and model reaction were carried out under nitrogen using standard Schlenk techniques. NMP (*N*-methyl-2-pyrrolidone) was distilled prior to use and stored under nitrogen. $\text{Ru}_3(\text{CO})_{12}$, PCy_3 (Cy = cyclohexyl), PPh_3 , 1,9-decadiyne, 1,11-dodecadiyne, 3,3'-diamino-4,4'-dihydroxybiphenyl, 3,3'-diaminobenzidine and other common organic chemicals were purchased and used without further purification. IR spectra were obtained on a JASCO-IR 810 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL EX-400 and GX-270 spectrometers. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder. GPC traces were obtained on a Tosoh HLC-8020 using a DMF solution of LiBr (0.006 M) as the eluent and polystyrene as the standards.

Polyaddition of 3,3'-diamino-4,4'-dihydroxybiphenyl and 1,9-decadiyne

To an NMP (5 mL) solution of $\text{Ru}_3(\text{CO})_{12}$ (70 mg, 0.15 mmol) and PPh_3 (60 mg, 0.22 mmol) was added 3,3'-diamino-4,4'-dihydroxybiphenyl (0.41 g, 3.0 mmol) and 1,9-decadiyne (0.65 g, 3.0 mmol) at room temperature. After the reaction mixture was stirred at 180 °C for 15 h, the solution was poured into acetone (*ca.* 400 mL) to give a light-green solid. The solid product was collected by filtration and dried in vacuo to give **1a** (0.64 g, 61%). Anal. Calcd for $(\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2)_n$: C = 76.28%, H = 6.40%, N = 8.09%. Found: C = 76.56%, H = 8.06%, N = 8.15%. ^1H NMR (400 MHz in $\text{DMSO}-d_6$): δ 6.55-7.49 (aromatic), 2.80 (br, CH_2 bonded to oxazole rings), 1.32 (br, $(\text{CH}_2)_6$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz in $\text{DMSO}-d_6$): δ 160.3 (N=C-O), 146.1, 140.0, 137.5, 128.3, 113.9 (aromatic carbons), 28.9 ($(\text{CH}_2)_8$). IR (KBr, cm^{-1}): 3300 (w), 3040 (w), 2925 (s), 2851 (s), 1623 (m), 1478 (s), 1280 (m), 805 (m). Reaction with a 1:2 ratio gave **1b**. Data of **1b**: Found: C = 77.34%, H = 8.73%, N = 8.10%.

Reactions of 1,11-dodecadiyne with 3,3'-diamino-4,4'-dihydroxybiphenyl and with 3,3'-diaminobenzidine were carried out in a similar manner. Data of **2** (cf. Table): Anal. Calcd for $(\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_2)_n$: C = 70.22%, H = 7.37%, N = 6.82%. Found: C = 70.31%, H = 7.24%, N = 6.47%. Data of **3a**: Anal. Calcd for $(\text{C}_{22}\text{H}_{24}\text{N}_4 \cdot 1.5\text{H}_2\text{O})_n$: C = 71.13%, H = 7.33%, N = 15.08%. Found: C = 70.16%, H = 7.28%, N = 14.18%. Data of **3b**: Found: C = 70.65%, H = 7.39%, N = 14.82%. ^1H NMR (400 MHz in

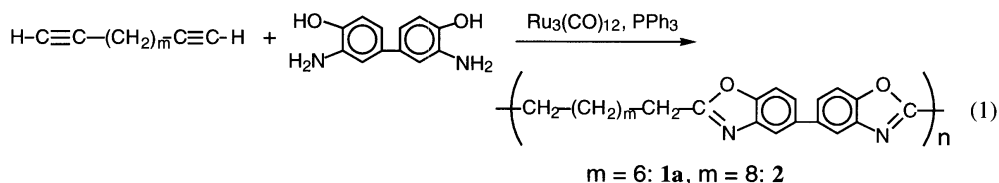
DMSO- d_6): δ 12.10 (br, NH), 6.51-8.10 (br, aromatic), 2.80 (br, CH_2 bonded to imidazole rings), 2.05 and 1.32 (br, $(\text{CH}_2)_6$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz in DMSO- d_6): δ 155.2 (N=C-N), 131.4, 130.6, 124.7, 123.7, 122.1, 122.0 (aromatic carbons), 32.4, 29.4, 29.2, 28.8, 28.2, 17.9 ($(\text{CH}_2)_8$). IR (KBr, cm^{-1}): 3270 (m), 3050 (w), 2926 (s), 2854 (m), 1622 (s), 1499 (s), 1277 (s), 807 (m). Data of **4**: Anal. Calcd for $(\text{C}_{24}\text{H}_{28}\text{N}_4 \cdot 1.5\text{H}_2\text{O})_n$: C = 72.15%, H = 7.82%, N = 14.02%. Found: C = 72.43%, H = 8.05%, N = 14.51%.

Reaction of *o*-phenylenediamine and 1,9-decadiyne

Reaction was carried out in a similar manner of preparation of **1a** to give **5** (30%). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4$: C = 76.27%, H = 7.56%, N = 16.17%. Found: C = 75.55%, H = 7.74%, N = 16.00%. ^1H NMR (400 MHz in DMSO- d_6): δ 12.10 (br, NH), 7.39 (br, aromatic hydrogens at H^4 and H^7 positions), 7.12 (dd, $J = 2.9$ and 5.6 Hz, aromatic hydrogens at H^5 and H^6 positions), 2.81 (t, $J = 7.3$ Hz, CH_2 bonded to imidazole rings), 1.75 and 1.32 (s, $(\text{CH}_2)_6$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz in DMSO- d_6): δ 155.1 (N=C-N), 143.3, 134.3, 121.0, 117.8, 110.5 (aromatic carbons), 28.6, 28.5, 27.5 ($(\text{CH}_2)_6$). IR (KBr, cm^{-1}): 3090 (w), 2930 (m), 2852 (m), 1623 (s), 1540 (w), 1454 (s), 1422 (s), 1270 (s), 744 (s). MS (FAB, m/z): 347 ($\text{M}+\text{H}^+$).

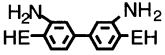
Results and discussion

The reactions of 3,3'-diamino-4,4'-dihydroxybiphenyl with 1,9-decadiyne and with 1,11-dodecadiyne in the presence of $\text{Ru}_3(\text{CO})_{12}$ - PPh_3 catalyst give poly(2,2'-octamethylene-5,5'-bibenzoxazole) (**1a**) and poly(2,2'-decamethylene-5,5'-bibenzoxazole) (**2**), respectively (eq. 1). Table summarizes results of the polyaddition.



The IR spectrum of **1a** shows a peak due to $\nu(\text{C-N})$ vibration of the oxazole group at 805 cm^{-1} . The ^1H NMR spectrum (soluble part in DMSO- d_6) shows a broad signal due to the CH_2 group bonded to the oxazole ring at δ 2.80 in addition to the other CH_2 hydrogens (δ 1.32). **1a** is partially soluble in organic solvents, however its ^{13}C NMR spectrum obtained in the solid state with a CP-MAS technique has provided useful information for characterization of the polymer as shown in Figure 1. The spectrum gives rise to a peak at δ 160.3 due to the oxazole carbon and peaks due to aromatic and aliphatic carbons at reasonable positions. Polymers **1a** and **2** are partially soluble in polar organic solvents such as DMF, DMSO, and NMP. GPC measurement of the polymers **1a** and **2** (soluble part) shows M_n of 4,800 and 5,700 and M_w of 6,400 and 8,300, respectively.

Table Results of the polyaddition

run	conditions ^a		products			
	HC≡C(CH ₂) _m C≡CH		polymer	yield (%)	M _n , M _w X 10 ⁻³ ^b	[η]/ dL g ⁻¹ ^c
1	m = 6 (3 mmol)	E = O (3 mmol)	1a	61	4.8, 6.4 ^e	
2	8 (3 mmol)	O (3 mmol)	2	51	5.7, 8.3 ^e	
3	6 (3 mmol)	NH (3 mmol)	3a	55	8.6, 9.4	
4	8 (3 mmol)	NH (3 mmol)	4	60	11.7, 18.2	
5	6 (4 mmol)	O (2 mmol)	1b	59	14.1, 19.7	0.18
6	6 (4 mmol)	NH (2 mmol)	3b	41	9.2, 9.9	
7 ^d	6 (4 mmol)	NH (2 mmol)	3c	34	8.9, 9.8	0.07

^a Amounts of the substrates are shown in parentheses. The reaction for 15 h at 180 °C in NMP. Catalyst = 0.15 mmol (run 1-4), 0.013 mmol (run 5-7). ^b Measured by GPC (eluent: DMF containing 0.006 M LiBr; polystyrene standards). ^c Measured in DMSO at 30 °C. ^d PCy₃ was used instead of PPh₃. ^e DMF soluble part.

The reactions of 3,3'-diaminobenzidine with 1,9-decadiyne and with 1,11-dodecadiyne in the presence of Ru₃(CO)₁₂ and PPh₃ give poly(2,2'-octamethylene-5,5'-bibenzimidazole) (**3a**) and poly(2,2'-decamethylene-5,5'-bibenzimidazole) (**4**) in 55% and 60% yields (run 3 and 4), respectively, as shown in eq. 2.

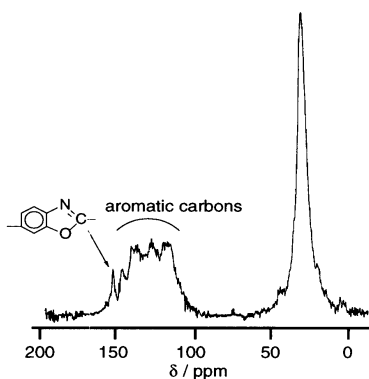
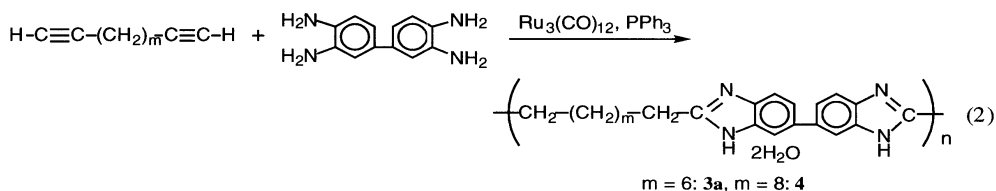


Figure 1 The solid state ¹³C{¹H} NMR spectrum of **1a** (67.5 MHz with a CP-MAS technique).

Spectroscopic data of the polymers were compared with those of **3d** which was prepared from polyphosphoric acid promoted polycondensation of sebacic acid and 3,3'-diaminobenzidine tetrahydrochloride. The IR spectra of **3a-3c** show a peak due to $\nu(\text{N-H})$ vibration of the imidazole ring at 3270 cm^{-1} . The peak position as well as absorption pattern of other region of the IR spectra are similar to those of **3d** (3). The ^1H NMR spectrum of **3b** depicted in Figure 2a shows signals due to NH of the imidazole group at δ 11.60 whose low magnetic field position is ascribed to $\text{N-H}\cdots\text{O}$ hydrogen bond between the imidazole group and the solvent. A broad signal at δ 2.80 is assigned to CH_2 group bonded to the imidazole group based on similarity of the positions to the corresponding signal of alkylbenzimidazoles. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3b** shows the signal due to the $\text{N}=\text{C}-\text{NH}$ carbon of the imidazole ring at δ 155.2. The NMR peak positions are similar to those of **3d** as well as a model compound of the polymer, 1,8-bis(2-benzimidazolyl)octane (**5**) (Chart 1), prepared from the Ru complex catalyzed reaction of *o*-phenylenediamine and 1,9-decadiyne in a 2:1 molar ratio.

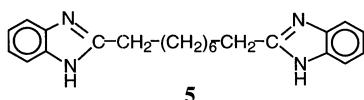


Chart 1

Polymers **3a-3c** and **4** are soluble in polar solvents such as DMF and DMSO at room temperature. GPC measurement of **3a** and **4** shows M_n and M_w of 8,600-11,700 and 9,400-18,200, respectively.

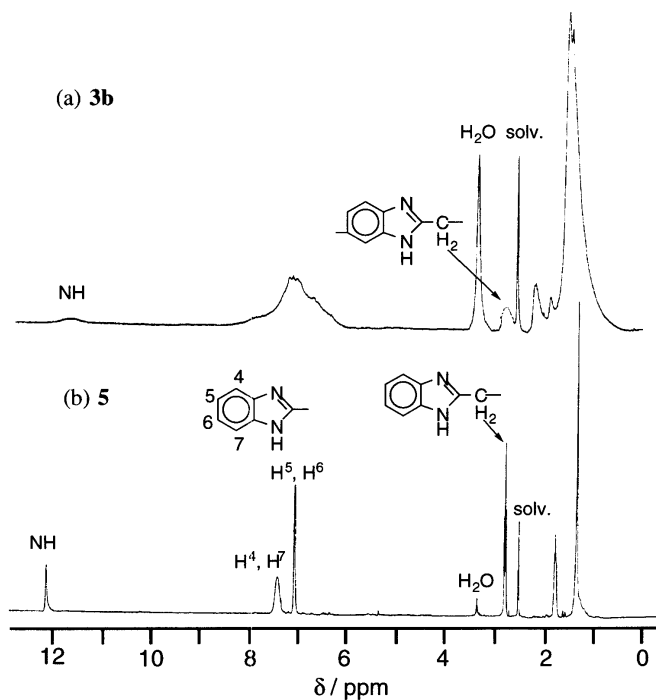
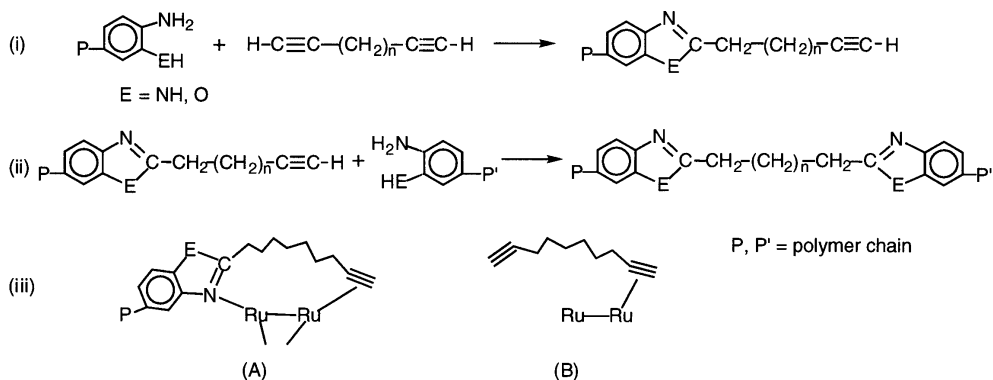


Figure 2 ^1H NMR spectra of **3b** (a) and **5** (b) (400 MHz in $\text{DMSO}-d_6$).

The Ru complex catalyzed reactions of 3,3'-diamino-4,4'-dihydroxybiphenyl and of 3,3'-diaminobenzidine with α,ω -diyne in a 1:2 molar ratio were examined with expectation of formation of the linear heteroaromatic molecule containing $-C\equiv CH$ groups at the both ends. The 1:2 reaction of 3,3'-diamino-4,4'-dihydroxybiphenyl with 1,9-decadiyne, however, gives poly(2,2'-octamethylene-5,5'-bibenzoxazole) (**1b**) in 59% yield when a much smaller amount of the catalyst than the equimolar polyaddition is used ($[\text{catalyst}]/[\text{substrate}] = \text{ca. } 0.006$, run 5 in Table). The product **1b** gives satisfactory analytical results and $^1\text{H NMR}$ signals at similar positions to those of **1a**. An acetone soluble fraction of the product of the reaction (run 5), separated from the product during reprecipitation, was analyzed by $^1\text{H NMR}$ and GPC in order to obtain the reason for insufficient yield (59%) of the relatively high molecular weight product ($M_n = 14,100$, $M_w = 19,700$). Results of the analyses of the fraction indicates the presence of a small amount of unreacted 3,3'-diamino-4,4'-dihydroxybiphenyl and oligomers with lower molecular weights ($M_n = 3,500$, $M_w = 3,800$) than the isolated polymer.

The reactions of 3,3'-diaminobenzidine with 1,9-decadiyne in a 1:2 molar ratio in the presence of PPh_3 and PCy_3 (Cy = cyclohexyl) also give poly(2,2'-octamethylene-5,5'-bibenzimidazole) (**3b** and **3c**) in 41% and 34% yields, respectively (run 6 and 7). Polymers **1b**, **3b**, and **3c** are soluble in highly polar organic solvents such as DMF and DMSO. Inherent viscosities of **1b** and **3c** are 0.18 and 0.07 dL g^{-1} , respectively. The equimolar reaction of 3,3'-diamino-4,4'-dihydroxybiphenyl in the presence of the small amount of the catalyst ($[\text{catalyst}]/[\text{substrate}] < 0.01$) does not give any polymer product. Polymer **1a** (run 1 in Table) has a lower solubility in DMF and lower molecular weight of a *soluble* fraction than **1b** which is soluble in DMF (run 5). Different solubility of the polymers suggests occurrence of possible side reactions such as cyclotrimerization of the $\text{C}\equiv\text{C}$ triple bonds during the polymerization of run 1 with a high catalyst/monomer ratio leading to branched partial structure in **1a**.

The Ru complex catalyzed polyaddition of 3,3'-diamino-4,4'-dihydroxybiphenyl and of 3,3'-diaminobenzidine to α,ω -diyne shown above proceeds via repetition of the stepwise reaction of two $\text{C}\equiv\text{CH}$ groups of the diyne toward diamino or hydroxy and amino groups of the aromatic substrates ((i) and (ii) in Scheme 3). Under the conditions with the low catalyst/substrate ratio, the mixture of α,ω -diyne and 3,3'-diamino-4,4'-dihydroxybiphenyl (or 3,3'-diaminobenzidine) in a 2:1 molar ratio gave the polymer products, whereas polyaddition of the equimolar mixture was not observed. These results suggest that the reaction (ii) occurs much faster than (i) in the presence of a small amount of the ruthenium catalyst.



Scheme 3 Schematic drawing of the polymer growth.

Ru-complex-catalyzed addition of the N-H bond to the C≡C bond of the monomer or growing polymer seems to involve nucleophilic addition of NH₂ group to C≡C bond π-coordinated to the Ru center as the crucial step. The ligation of alkynyl group of the polymer is assisted by strong coordination of the imidazole or oxazole group to a Ru center ((A) in Scheme 3 (iii)), and affinity of the C≡C triple bond to Ru center is much higher than that of α,ω-diyne ((B) in Scheme 3 (iii)). Thus, the reaction of alkynyl group of the polymer end is enhanced significantly by the catalyst and occurs more readily than that of the α,ω-diyne.

In summary, the carbonyltriruthenium (0) complex has been disclosed to catalyze polyaddition of the α,ω-diyne with bifunctional aromatic polyamine and bisaminoalcohol to give the corresponding poly(benzimidazole) and poly(benzoxazole), respectively. The polyaddition under non-acidic conditions would be extended to synthesis of further functionalized polymer having the heterocycles in the main chain.

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