Synthesis and Properties of Polyacetylenes Having Pendant Carbazole Groups

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ABSTRACT: Five novel carbazole-containing polymers, i.e., poly(3,6-di-*tert*-butyl-9-prop-2-ynylcarbazole) [poly(*t*-Bu_2CzPr)], poly(9-but-2-ynylcarbazole) [poly(CzBu)], poly(3,6-di-*tert*-butyl-9-but-2-ynylcarbazole) [poly(*t*-Bu_2CzBu)], poly(9-(4-ethynylphenyl)carbazole) [poly(*p*-CzPA)], and poly(9-(4-prop-1-ynylphenyl)-carbazole) [poly(*p*-CzPPr)] were synthesized by the polymerization of the corresponding carbazole-containing acetylene monomers using [(norbornadiene)RhCl]$_2$−Et_3N, WCl_6, $MoCl_5$, $TaCl_5$, and $NbCl_5$ in conjunction with Sn, Bi, Sb, and Si cocatalysts and $W(CO)_6$−$h\nu$/CCl_4 catalysts. The UV−vis absorption band edge wavelengths of poly(*t*-Bu_2CzPr) and poly(*p*-CzPA) were longer than those of the corresponding polymers substituted by methyl group at the main chain, poly(*t*-Bu_2CzBu) and poly(*p*-CzPPr), respectively. The band edge wavelengths of phenylene-spacer-containing polymers, poly(*p*-CzPA) and poly(*p*-CzPPr), were longer than those of methylene-spacer-containing polymers, poly(*t*-Bu_2CzPr) and poly(*t*-Bu_2CzBu), respectively. Poly(*p*-CzPA) obtained by WCl_6−*n*-Bu_4Sn-catalyzed polymerization exhibited UV−vis absorption apparently at a longer wavelength than the $MoCl_5$−*n*-Bu_4Sn-based counterpart did. Poly-(*t*-Bu_2CzPr) showed photoconductivity. The temperatures for 5% weight loss of the polymers were around 300−350 °C under air.

Introduction

Carbazole is a well-known hole-transporting and electroluminescent unit. Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various photonic applications such as photoconductive, electroluminescent, and photorefractive materials.[1] Recent examples of the polymers containing carbazole moieties in the main chains include poly(carbazole),[2] poly(carbazolylenevinylene),[3] and poly-(carbazolyleneethynylene).[4] 9-Phenylcarbazoleethynylene-based dendrimer has been also synthesized.[5] On the other hand, there have been many reports concerning photoconductive polymers having carbazole moieties in the side chain such as poly(*N*-vinylcarbazole) (PVK), polymethacrylate,[6] polymethacrylamide,[7] poly(*p*-phenylenevinylene),[8] poly(biphenylenevinylene),[9] and poly-(organophosphazene).[10]

Polyacetylene derivatives exhibit unique properties such as semiconductivity, high gas permeability, helix inversion, and nonlinear optical properties.[11] It is expected that incorporation of carbazole into polyacetylene will lead to the development of novel functional polymers based on synergistic actions of carbazole and main-chain conjugation. Tang et al. have synthesized acetylenic monomers containing carbazole chromophores and polymerized them with WCl_6−, $WOCl_4$−, $MoCl_5$−, $MoOCl_4$−, and $NbCl_5$−Ph_4Sn catalysts to obtain the corresponding polyacetylenes with carbazolyl side groups, which show photoluminescence and photoconductivity.[12] Advincula et al. and we have synthesized carbazole-substituted phenylacetylene monomers and polymerized them with an Rh-based catalyst to obtain the corresponding substituted poly(phenylacetylene)s.[13] Controlled electrochemical oxidation leads to oxidative polymerization−cross-linking of the carbazole units without causing decomposition of the poly(phenylacetylene) backbone. The UV−vis spectra of the cross-linked polymers show two absorption peaks at 350 and 560 nm, wherein the latter is assignable to cross-linked carbazole units. The redox potential decreases with increasing the length of the alkyl chain; i.e., longer alkyl chains tend to weaken electron-withdrawing effects. Tabata et al. have reported the synthesis and Rh-catalyzed polymerization of several *N*-alkyl-3-ethynylcarbazole monomers and found that the resulting polymers take a pseudohexagonal columnar structure in the solid phase.[14]

We have previously polymerized *N*-carbazolylacetylene (CzA) with WCl_6-based catalysts to obtain the polymer in good yields.[15] The polymers produced with W catalysts are dark purple solids and mostly soluble in toluene and chloroform. Poly(CzA) exhibits an absorption maximum around 550 nm and a band edge wavelength at 740 nm, showing a large red shift compared with that of poly(phenylacetylene) [poly(PA)]. Poly(CzA) shows a third-order susceptibility of 18×10^{-12} esu, which is 2 orders larger than that of poly-(PA). On the other hand, poly(CzA) obtained by the polymerization with $MoCl_5$, [(nbd)RhCl]$_2$ (nbd = norbornadiene), and Fe(acac)$_3$ catalysts is insoluble in any solvent. We have also polymerized 3-(*N*-carbazolyl)-1-propyne with $MoCl_5$- and WCl_6-based catalysts to obtain the polymer in high yields, but the polymer is insoluble in any solvent.[16] We have further polymerized 1-(*p*-*N*-carbazolylphenyl)-2-phenylacetylene with $TaCl_5$-based catalysts to obtain a yellowish-orange solid polymer, which is partly soluble in toluene and chloroform. This

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polymer forms a tough film by solution casting and shows photoconductivity and redox activity.[17]

As described above, polyacetylenes with pendant carbazole are expected to show unique electronic and photonic functions. However, most of these polymers are poorly soluble, resulting in difficult elucidation of their properties. This article deals with the synthesis of novel soluble carbazole-containing polyacetylenes and their characterization.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer in chloroform-*d* ($CDCl_3$) using tetramethylsilane as an internal standard. IR and UV−vis spectra were measured on a Shimadzu FTIR-8100 and a JASCO UV-2200 spectrophotometer, respectively. Melting points (mp) were measured by a Yanaco micro melting point apparatus. Elemental analyses were carried out at the Kyoto University Elemental Analysis Center. The number-average molecular weights (M_n) of polymers were determined by gel permeation chromatography (GPC) on a JASCO GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7.

Evaluation of Photoconductivity. A 1% w/v solution of polymer in $CHCl_3$ was coated on an ITO electrode using a spin-coater at 100 rpm for a period of 30 s. The thickness of the film coated was 5−7 μm. Au was sputtered on the coated layer to prepare a counter electrode for the ITO electrode. The relationships between current and applied voltage for the ITO/poly(*t*-Bu$_2$CzPr)/Au cells (effective electrode area 0.06 cm^2, thickness 6 μm) were measured at room temperature under reduced pressure of ca. 10^{-2} Torr in the dark and under photoirradiation (2.5 mW/m^2) with a Xe lamp using a thermoabsorption filter.

Materials. Unless otherwise stated, reagents were commercially obtained and used without further purification. 3,6-Di-*tert*-butylcarbazole[18] and 9-(4-iodophenyl)carbazole[17] were synthesized according to the literature. The solvents for polymerization were purified before use by the standard methods.

3,6-Di-*tert*-butyl-9-prop-2-ynylcarbazole (*t*-Bu$_2$CzPr). A solution of 3,6-di-*tert*-butylcarbazole (3.0 g, 11 mmol) in benzene (100 mL) was added to NaH (60%, 0.56 g, 14 mmol, washed with benzene three times before use) and then dimethyl sulfoxide (DMSO) (4 mL) at room temperature. The reaction mixture was stirred for 1 h, and propargyl bromide (1.31 g, 11 mmol) was added to the mixture. The resulting mixture was stirred at 50 °C for 3 h. Ether was then added to the mixture, and the organic phase was washed with water and aqueous NaCl and dried over anhydrous Na_2SO_4. It was concentrated by rotary evaporation, and the residue was purified by silica gel column chromatography eluted with *n*-hexane/ethyl acetate = 10/1 (volume ratio). Yield 1.37 g (39%); mp 163−165 °C. ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.45 (18H, s, $-CH_3$), 2.22 (1H, s, $\equiv$CH), 4.98 (2H, s, $-CH_2-$), 7.36−7.53 (4H, m, Ar), 8.09 (2H, s, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 32.01 ($-CH_3$), 32.34 ($-CH_2-$), 34.68 ($-C(CH_3)_3$), 71.97 ($\equiv$CH), 78.17 ($-C\equiv$CH), 108.07, 116.43, 123.16, 123.51, 138.38, 142.33. IR (KBr, cm^{-1}): 3279 ($\nu_{\equiv C-H}$), 2953, 2122 ($\nu_{C\equiv C}$), 1632, 1610, 1478, 1298, 806, 677, 613. Anal. Calcd for $C_{23}H_{27}N$: C, 87.02; H, 8.57; N, 4.41. Found: C, 86.73; H, 8.42; N, 4.39.

9-But-2-ynylcarbazole (CzBu). The title compound was synthesized from carbazole and 1-bromo-2-butyne in 31% yield in a manner similar to *t*-Bu$_2$CzPr. Mp 84−87 °C. ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.74 (3H, s, $-CH_3$), 4.99 (2H, s, $-CH_2-$), 7.20−8.15 (8H, m, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 3.48 ($-CH_3$), 32.62 ($-CH_2-$), 73.25 ($\equiv C-CH_3$), 79.91 ($-C\equiv C-CH_3$), 108.80, 119.26, 120.34, 123.10, 125.74, 139. 93. IR (KBr, cm^{-1}): 3049, 2918, 2210 ($\nu_{C\equiv C}$), 1597, 1453, 1325, 1325, 1211, 1055, 722. Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.85; H, 6.25; N, 6.37.

3,6-Di-*tert*-butyl-9-but-2-ynylcarbazole (*t*-Bu$_2$CzBu). The title compound was synthesized from 3,6-di-*tert*-butylcarbazole and 1-bromo-2-butyne in 40% yield in a manner similar to *t*-Bu$_2$CzPr. Mp 170−173 °C. ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.45 (18H, s, $-C(CH_3)_3$), 1.73 (3H, s, $\equiv C-CH_3$), 4.93 (2H, s, $-CH_2-$), 7.37−7.54 (4H, m, Ar), 8.09 (2H, s, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 3.50 ($\equiv C-CH_3$), 32.03 ($-C(CH_3)_3$), 32.63 ($-CH_2-N\langle$), 34.66 ($-C(CH_3)_3$), 73.60 ($\equiv C-CH_3$), 79.60 ($-C\equiv C-CH_3$), 108.14, 116.30, 122.97, 123.38, 138.47, 141.98. IR (KBr, cm^{-1}): 3049, 2957, 2226 ($\nu_{C\equiv C}$), 1632, 1611, 1478, 1298, 804, 613. Anal. Calcd for $C_{24}H_{29}N$: C, 86.96; H, 8.82; N, 4.23. Found: C, 86.71; H, 8.82; N, 4.23.

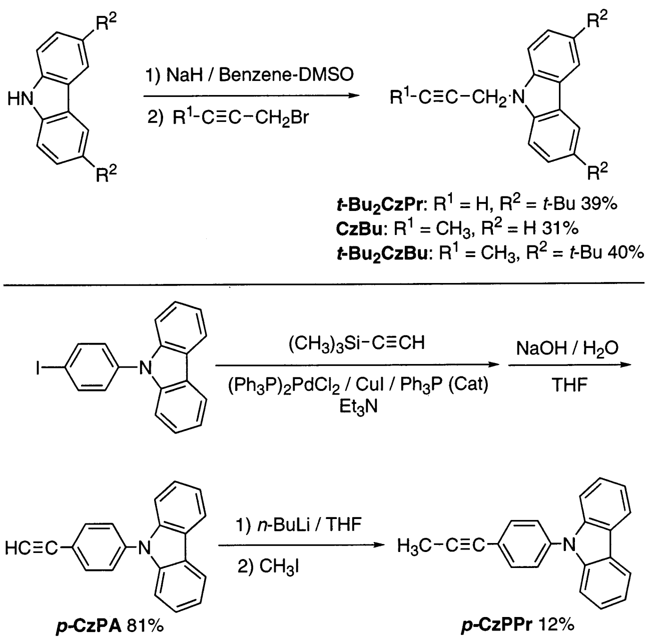
9-(4-Ethynylphenyl)carbazole (*p*-CzPA). A solution of (trimethylsilyl)acetylene (3.14 g, 32 mmol), $(Ph_3P)_2PdCl_2$ (56 mg, 0.08 mmol), CuI (92 mg, 0.40 mmol), Ph_3P (84 mg, 0.32 mmol), and Et_3N (40 mL) was stirred at 50 °C for 1 h. A solution of 9-(4-iodophenyl)carbazole (10 g, 27 mmol) in Et_3N (50 mL) was added, and the resulting solution was stirred at room temperature overnight. Et_3N was removed from the solution by evaporation to obtain yellow powder. THF (200 mL) and aqueous 0.5 mol/L NaOH (200 mL) were added to the residue, and the resulting mixture was stirred at room temperature overnight. The mixture was concentrated by rotary evaporation, and ether was added to the residue. The ether solution was washed subsequently with 5% HCl and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation to obtain orange powder. It was purified by silica gel column chromatography eluted with *n*-hexane/ethyl acetate = 40/1 (volume ratio) and recrystallization from *n*-hexane. Yield 5.84 g (81%); mp 102−103 °C. ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 3.17 (1H, s, $\equiv$CH), 7.26−8.19 (12H, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 78.10 ($\equiv$CH), 82.91 ($-C\equiv$CH), 109.68, 120.25, 120.36, 121.02, 123.54, 126.07, 126.80, 133.68, 138.10, 140.46. IR (KBr, cm^{-1}): 3264 ($\nu_{\equiv C-H}$), 2100 ($\nu_{C\equiv C}$), 1603, 1559, 1451, 1227, 837, 754, 723. Anal. Calcd for $C_{20}H_{13}N$: C, 89.86; H, 4.90; N, 5.24. Found: C, 89.77; H, 5.06; N, 4.94.

9-(4-Prop-1-ynylphenyl)carbazole (*p*-CzPPr). *n*-BuLi (1.59 M solution in *n*-hexane, 7.98 mL, 12.6 mmol) was added slowly to a solution of *p*-CzPA (2.80 g, 10.5 mmol) in THF (10 mL) at −78 °C under nitrogen, and the resulting solution was stirred at the temperature for 1 h. A solution of MeI (0.76 mL, 12.6 mmol) in THF (10 mL) was slowly added to the solution at −78 °C, and the resulting mixture was stirred at room temperature overnight. Water was added to the mixture to quench the reaction, and the mixture was extracted with ether. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated by rotary evaporation to obtain a viscous brown liquid. The liquid was purified by silica gel column chromatography eluted with *n*-hexane and recrystallization from *n*-hexane. Yield 350 mg (12%); mp 107−111 °C. ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 2.10 (3H, s, $-CH_3$), 7.27−8.13 (12H, m, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 4.43 ($-CH_3$), 77.20 ($\equiv C-CH_3$), 86.93 ($-C\equiv C-CH_3$), 109.74, 120.07, 120.25, 120.31, 123.45, 125.98, 126.80, 123.96, 137.10, 140.62. IR (KBr, cm^{-1}): 2250 ($\nu_{C\equiv C}$), 1601, 1512, 1451, 1231, 835, 749, 723. Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.85; H, 5.63; N, 4.94.

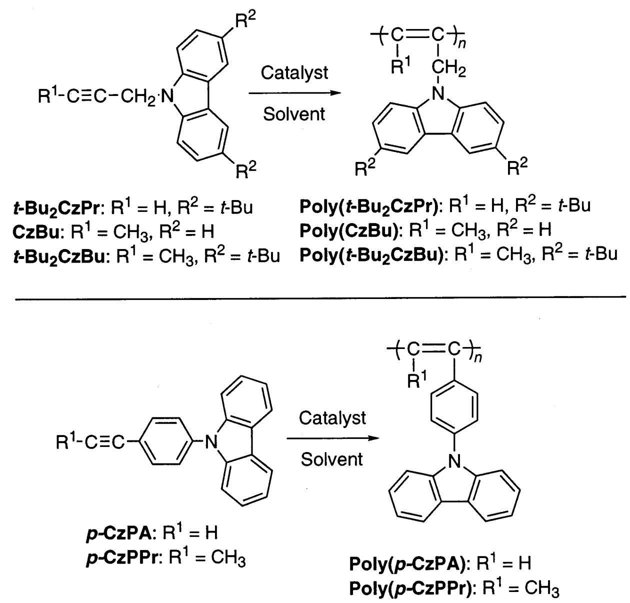
Polymerization. All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. The polymerization mixture was poured into a large amount of methanol to precipitate a polymer. It was separated from the supernatant by filtration and dried under reduced pressure.

Spectroscopic Data of the Polymers. Poly(*t*-Bu$_2$CzPr) ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.99 (18H, broad s, $-CH_3$), 3.16 (2H, broad s, $-CH_2-$), 4.71 (1H, broad s, $-CH=C\langle$), 7.02 (2H, broad s, Ar), 7.40 (4H, broad s, Ar). IR (KBr, cm^{-1}): 2959, 1717, 1534. Poly(CzBu) IR (KBr, cm^{-1}): 3050, 1485, 1325, 1211, 1154, 1121, 747, 722. Poly(*t*-Bu$_2$CzBu) ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.43 (9H, broad s, $-C(CH_3)_3$), 2.29 (3H, broad s, CH_3), 5.52 (2H, broad s, $-CH_2-$), 6.87−7.41 (4H,

Scheme 1



Scheme 2



m, Ar), 8.07−8.11 (2H, m, Ar). IR (KBr, cm^{-1}): 2963, 2867, 1492, 1296, 880, 803, 612. Poly(*p*-CzPA) ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 6.0−8.2 (broad m). IR (KBr, cm^{-1}): 1509, 1451, 747, 722. Poly(*p*-CzPPr) ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.4−2.4 (3H, broad m, CH3), 6.4−8.2 (broad m, 12H, Ar). IR (KBr, cm^{-1}): 1509, 1453, 1316, 747, 723.

Results and Discussion

Monomer Synthesis. Scheme 1 illustrates the synthetic routes for the substituted carbazole-containing acetylene monomers. *t*-Bu_2CzPr, CzBu, and *t*-Bu_2CzBu were prepared by alkylation of 3,6-di-*tert*-butylcarbazole or carbazole with propargyl bromide or 1-bromo-2-butyne in 31−40% yields. *p*-CzPA was synthesized by Pd−Cu-catalyzed coupling of 9-(4-iodophenyl)carbazole with (trimethylsilyl)acetylene, followed by desilylation using aqueous NaOH in 81% yield. *p*-CzPPr was synthesized by methylation of *p*-CzPA in 12% yield. All the monomers were obtained as yellowish-orange powder after purification by silica gel column chromatography and successive recrystallization. The structures were confirmed by ^{1}H and ^{13}C NMR and IR besides elemental analysis.

Polymerization. Scheme 2 and Table 1 summarize the conditions and results of the polymerization of the carbazole-containing novel acetylene monomers, catalyzed by $[(nbd)RhCl]_2$, WCl_6, $MoCl_5$, $TaCl_5$, $NbCl_5$, and $W(CO)_6-h\nu$ in toluene, chlorobenzene (PhCl), 1,4-dioxane, cyclohexane, and CCl_4 at 30−80 °C for 24 h. The polymerization of *t*-Bu_2CzPr proceeded homogeneously to afford the corresponding polymer with M_n ranging from 1600 to 163 000, except in the case when CCl_4 was used as the solvent (runs 1−12). When $[(nbd)RhCl]_2$-Et_3N was used as the catalyst (run 1), the M_w/M_n ratio was larger than the values with WCl_6 and $MoCl_5$ (runs 2−11). The yield and M_n of the polymer obtained by WCl_6-catalyzed polymerization were very low (run 2). The addition of *n*-Bu_4Sn was effective to increase the yield and M_n of the polymer formed (run 3) in a fashion similar to monosubstituted acetylene polymerization.[16,19] The yield and M_n of the polymer obtained by $MoCl_5$-catalyzed polymerization tended to be high (runs 4−11) compared with those of the polymer obtained with Rh and W catalysts (runs 1−3). The addition of cocatalysts, Ph_3SiH, *n*-Bu_4Sn, Ph_4Sn, Ph_3Bi, and Ph_3Sb, was also effective to increase the yield and M_n, when toluene and PhCl were used as the solvents (runs 5−10). Combination of $MoCl_5$ with Ph_4Sn and Ph_3Bi was the most satisfactory to form high-molecular-weight polymers (runs 7 and 8), but it exhibited multimodal GPC. This may be due to incomplete solubility of the cocatalysts in toluene, which may cause formation of plural active species. Use of 1,4-dioxane as solvent resulted in the decrease of polymer yield (run 11), presumably because the monomer was partly insoluble in the solvent under the condition and/or because the catalyst was deactivated by donor effect of the oxygen of 1,4-dioxane. No polymer was obtained when cyclohexane was used as solvent (run 12).

The polymerization of CzBu and *t*-Bu_2CzBu was carried out with $TaCl_5$ and $NbCl_5$ using *n*-Bu_4Sn as cocatalyst (runs 13−15), because it has been reported that these metal halides effectively catalyze the polymerization of disubstituted acetylenes such as internal octynes, 1-phenyl-1-propyne, and 1,2-diphenylacetylene derivatives to give the corresponding polymers with M_n of ca. 1 000 000.[20] The polymer of CzBu was insoluble in common organic solvents such as MeOH, *n*-hexane, toluene, benzene, acetone, ether, THF, $CHCl_3$, DMSO, and DMF (run 13). On the other hand, the polymer of *t*-Bu_2CzBu obtained by the polymerization with $TaCl_5$−*n*-Bu_4Sn was soluble in toluene, benzene, THF, and $CHCl_3$ (run 14). Incorporation of *tert*-butyl groups onto the carbazole ring effectively increased the polymer solubility as expected. However, no MeOH-insoluble polymer could be obtained when $NbCl_5$−*n*-Bu_4Sn (run 15) and WCl_6−*n*-Bu_4Sn were used as catalyst (run 16).

The polymerization of *p*-CzPA was carried out with $[(nbd)RhCl]_2$−Et_3N, $MoCl_5$, and WCl_6 in conjunction with Sn cocatalysts and $W(CO)_6-h\nu/CCl_4$[21] (runs 17−22). It is quite interesting that the polymer obtained with $[(nbd)RhCl]_2$−Et_3N catalyst was insoluble in toluene, benzene, THF, and $CHCl_3$ (run 17), while the polymers formed with Mo and W catalysts were soluble in these solvents (runs 18−22). This is probably due to the difference of the cis−trans configuration of the polyacetylene main chains based on the catalysts used.

Table 1. Polymerization of Carbazole-Containing Acetylene Monomers[a]

run	monomer	cat.	cocat.	solvent	temp (°C)	yield[b] (%)	M_n[c]	M_w/M_n[c]
1	t-Bu_2CzPr	$[(nbd)RhCl]_2$[d]	Et_3N[d]	toluene	30	47	9 100	3.20
2	t-Bu_2CzPr	WCl_6		toluene	30	13	1 600	1.93
3	t-Bu_2CzPr	WCl_6	n-Bu_4Sn	toluene	30	66	8 400	1.72
4	t-Bu_2CzPr	$MoCl_5$		toluene	30	46	51 200	1.76
5	t-Bu_2CzPr	$MoCl_5$	Ph_3SiH	toluene	30	68	92 800	1.69
6	t-Bu_2CzPr	$MoCl_5$	n-Bu_4Sn	toluene	30	68	69 400	1.81
7	t-Bu_2CzPr	$MoCl_5$	Ph_4Sn	toluene	30	68	148 000[e]	1.46
8	t-Bu_2CzPr	$MoCl_5$	Ph_3Bi	toluene	30	63	163 000[e]	1.37
9	t-Bu_2CzPr	$MoCl_5$	Ph_3Sb	toluene	30	71	95 200	1.99
10	t-Bu_2CzPr	$MoCl_5$	Ph_3Sb	PhCl	30	70	67 800	1.77
11	t-Bu_2CzPr	$MoCl_5$	Ph_3Sb	1,4-dioxane	30	24	33 600	2.04
12	t-Bu_2CzPr	$MoCl_5$	Ph_3Sb	cyclohexane	30	0		
13	CzBu	$TaCl_5$	n-Bu_4Sn	toluene	80	60	f	f
14	t-Bu_2CzBu	$TaCl_5$	n-Bu_4Sn	toluene	80	54	30 000	1.78
15	t-Bu_2CzBu	$NbCl_5$	n-Bu_4Sn	toluene	80	0		
16	t-Bu_2CzBu	WCl_6	n-Bu_4Sn	toluene	60	0		
17	p-CzPA	$[(nbd)RhCl]_2$[d]	Et_3N[d]	toluene	30	92	f	f
18	p-CzPA	$MoCl_5$	n-Bu_4Sn	toluene	30	27	10 600	1.78
19	p-CzPA	WCl_6	n-Bu_4Sn	toluene	30	46	67 600	2.17
20[g]	p-CzPA	WCl_6	n-Bu_4Sn	toluene	30	23	104 000	2.13
21[h]	p-CzPA	WCl_6	Ph_4Sn	1,4-dioxane	30	86	62 300	4.21
22[i]	p-CzPA	$W(CO)_6-h\nu$		CCl_4	30	10	10 000	2.11
23	p-CzPPr	$TaCl_5$	n-Bu_4Sn	toluene	30	78	123 000	2.48
24	p-CzPPr	$NbCl_5$	n-Bu_4Sn	toluene	30	39	101 000	1.48
25	p-CzPPr	WCl_6	n-Bu_4Sn	toluene	60	0		

[a] $[M]_0$ = 0.2 M, [cat.] = [cocat.] = 10 mM, time 24 h. [b] MeOH-insoluble part. [c] Determined by GPC eluted with THF, polystyrene calibration. [d] [Cat.] = 2 mM, $[Et_3N]$ = 20 mM. [e] Main peak (area ratio 70%) of multimodal GPC traces. The others were low-molecular-weight oligomer peaks [M_n 4000−5000 (25%) and M_n 900 (5%)]. [f] Insoluble in THF. [g] $[M]_0$ = 0.5 M, time 6 h. [h] $[M]_0$ = 0.5 M, [cat.] = [cocat.] = 20 mM. [i] $[M]_0$ = 0.5 M, [cat.] = 20 mM, catalytic solution was irradiated by a UV lamp for 1 h before polymerization.

In fact, it has been reported that $[(nbd)RhCl]_2-Et_3N$ catalysts afford substituted polyacetylenes with *cis*-C=C backbone, while Mo and W catalysts yield trans C=C-rich polyacetylenes.[20] The polymerization of *p*-CzPPr provided the polymer with M_n over 100 000 in the presence of mixtures of $TaCl_5$ and $NbCl_5$ with *n*-Bu_4Sn (runs 23 and 24) but gave no polymer with WCl_6 (run 25).

Polymer Structure. The polymer structures were examined by ^{1}H NMR and IR spectroscopies. The ^{1}H NMR spectrum of $[RhCl(nbd)]_2-Et_3N$-based poly(*t*-Bu_2CzPr) (run 1 in Table 1) clearly exhibited a signal assignable to the main-chain cis olefinic proton at 4.71 ppm, indicating cis−transoidal structure.[22] The cis content of the polymer was determined to be quantitative from the integrated peak ratio between the cis vinyl proton and the methylene protons adjacent to the nitrogen atom. When W and Mo catalysts were used, the ^{1}H NMR signals of the formed polymers were very broad, and no signal assignable to the cis olefinic proton was observed at 4−6 ppm. It is assumed that the W- and Mo-based polymers take the trans structure, and the trans olefinic proton signal overlaps the aromatic proton signals around 7 ppm. The IR spectra of the polymers exhibited no absorption due to $\nu_{C\equiv C}$ at 2100−2250 cm^{-1}, which were observed in the monomers. In a similar fashion, poly(*t*-Bu_2CzPr) and poly(*p*-CzPA) exhibited no IR absorption due to $\nu_{\equiv C-H}$ at 3279 cm^{-1} [poly(*t*-Bu_2CzPr)] and 3264 cm^{-1} [poly(*p*-CzPA)]. Otherwise, the spectroscopic patterns of the polymers were similar to those of the corresponding monomers.

Polymer Properties. Figure 1 depicts the UV−vis spectra of poly(*t*-Bu_2CzPr), poly(*t*-Bu_2CzBu), poly(*p*-CzPA), and poly(*p*-CzPPr). All the polymers exhibited absorption peaks at 300 and 350 nm, which are assignable to the carbazole moiety. The absorption bands of poly(*t*-Bu_2CzPr) and poly(*p*-CzPA) extend toward longer wavelength region as compared to those of poly(*t*-Bu_2CzBu) and poly(*p*-CzPPr), respectively. This indicates that the methyl group substituted on the main chain decreases the conjugation. Poly(*p*-CzPA) and poly(*p*-CzPPr) exhibited absorption at longer wavelengths than poly(*t*-Bu_2CzPr) and poly(*t*-Bu_2CzBu) did, because the phenylene spacer participates in the main-chain conjugation. Interestingly, poly(*p*-CzPA) obtained by WCl_6−*n*-Bu_4Sn-catalyzed polymerization exhibited UV−vis absorption band edge apparently at a longer wavelength than the one obtained by $MoCl_5$−*n*-Bu_4Sn-catalyzed

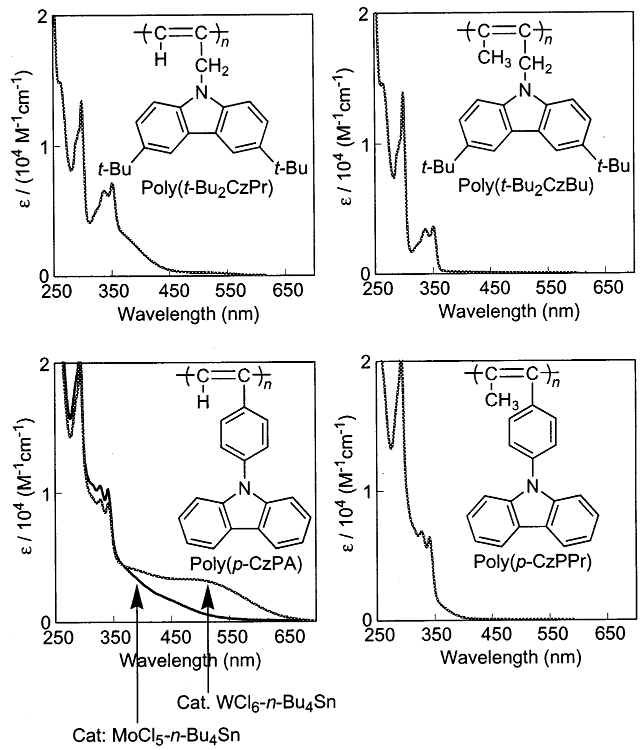


Figure 1. UV−vis spectra of poly(*t*-Bu_2CzPr), poly(*t*-Bu_2CzBu), poly(*p*-CzPA), and poly(*p*-CzPPr) measured in THF.

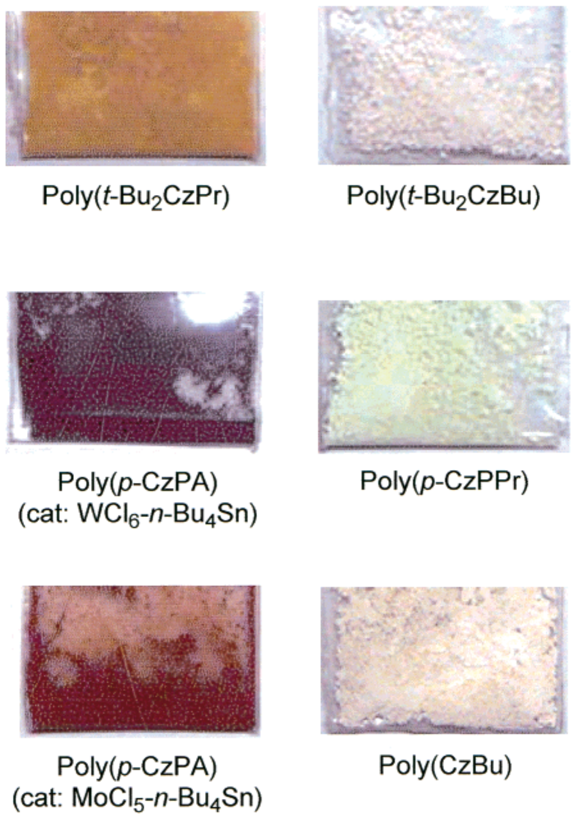


Figure 2. Appearance of the polymer samples.

polymerization, which may indicate the former polymer has a main-chain conjugation longer than that of the latter. The UV−vis spectrum of poly(CzBu) could not be measured because of the insolubility of the polymer.

Figure 2 summarizes the appearance of the polymer samples. Clearly the polymer color becomes darker as the UV−vis absorption expands toward longer wavelengths as shown in Figure 1, including the difference between the two poly(*p*-CzPA) samples obtained by W- and Mo-catalyzed polymerizations. It seems that the extent of main-chain conjugation of poly(CzBu) is nearly the same as that of poly(*t*-Bu_2CzBu) judging from the color of the polymer samples. Although introduction of *tert*-butyl groups onto the carbazole ring is effective in increasing the polymer solubility, it is likely that the *tert*-butyl groups hardly affect the main-chain conjugation, because the *tert*-butyl groups are located at the 3- and 6-positions of the carbazoyl group, which are distant from the main chain.

Figure 3 depicts the conductivity of ITO/poly(*t*-Bu_2CzPr)/Au. The current was 1 order higher under photoirradiation than that without. This proves that poly(*t*-Bu_2CzPr) exhibits photoconductivity. The dark conductivity of poly(*t*-Bu_2CzPr) was calculated to be ca. 5×10^{-15} S/cm under the electric field of 10^3−10^4 V/cm. This value is 2 orders higher than that of PVK,[23] presumably due to π-conjugation of the poly(*t*-Bu_2CzPr) main chain. It has been reported that the photocurrent/dark current ratio of PVK is less than 100.[24] This value depends on several factors including light intensity, illumination wavelength, and electric field. It is impossible to directly compare the photoconductivity of poly(*t*-Bu_2CzPr) with that of PVK. However, the results in Figure 3 clearly indicate that the designed polymer works as an optoelectronic functional polymer. We hoped that poly(*p*-CzPA) showed superior electrical properties than that of poly(*t*-Bu_2CzPr), because the former polymer exhibits absorption band edge at a longer wavelength than the latter dose. This is spectral sensitization due to the effect of the phenylene spacer. Poly(*p*-CzPA) may also exhibit higher photoconductivity than that of poly(*t*-Bu_2CzPr). Unfortunately, however, the photoconductivity of poly(*p*-CzPA) could not be measured because the film prepared by solution casting was too brittle.

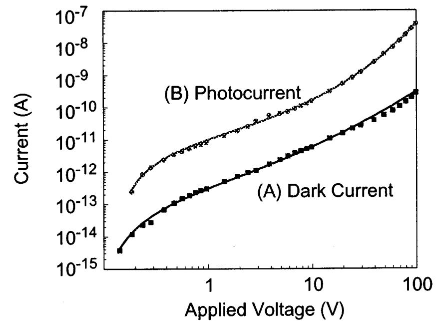


Figure 3. Relationships between current and applied voltage for ITO/poly(*t*-Bu_2CzPr)/Au cells (effective electrode area 0.06 cm^2, thickness 6 μm) measured at room temperature under reduced pressure of ca. 10^{-2} Torr: (A) without photoirradiation; (B) under photoirradiation (2.5 mW/m^2) with a Xe lamp using a thermoabsorption filter.

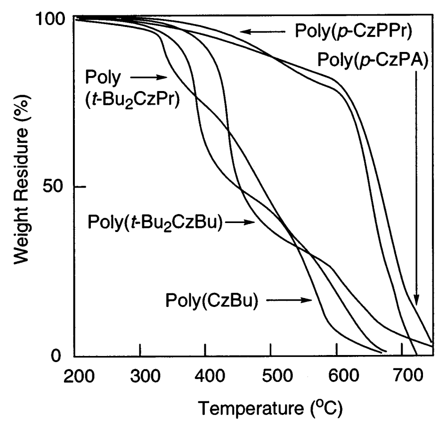


Figure 4. TGA curves of poly(*t*-Bu_2CzPr), poly(CzBu), poly(*t*-Bu_2CzBu), poly(*p*-CzPA), and poly(*p*-CzPPr) measured in air with a heating rate of 10 °C/min.

Figure 4 depicts the TGA traces of the polymers. The temperatures for 5% weight loss of the polymers were around 300−350 °C under air, which are somewhat higher than that of poly(PA).[25] The weight loss of the present polymers proceeded more slowly than that of poly(PA), which may be attributable to the bulky carbazolyl side chains. The polymers completely lost their weights around 700 °C.

Summary

In this article, we have demonstrated the synthesis of carbazole-containing novel polyacetylenes. Poly(*t*-Bu_2CzPr) and poly(*p*-CzPA) exhibited band edge wavelengths longer than those of the corresponding polymers substituted with a methyl group on the main chain, i.e., poly(*t*-Bu_2CzBu) and poly(*p*-CzPPr), respectively. Poly(*p*-CzPA) and poly(*p*-CzPPr) exhibited band edge wavelengths longer than those of poly(*t*-Bu_2CzPr) and poly(*t*-Bu_2CzBu), presumably because the phenylene spacer participates in the main-chain conjugation. The UV−vis spectroscopic pattern of poly(*p*-CzPA) depended on the catalysts used; i.e., W-based poly(*p*-CzPA) exhibited a UV–vis absorption band edge apparently at a longer wavelength than the Mo-based counterpart, which indicates that the former polymer has main-chain conjugation longer than the latter. This finding may lead to catalytic control of conjugation of polyacetylene main chain. Poly(*t*-Bu_2CzPr) showed photoconductivity.

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