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Preparation and characterization of poly(9-hexylcarbazole-3,6-diylbutadiynylene)

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Summary

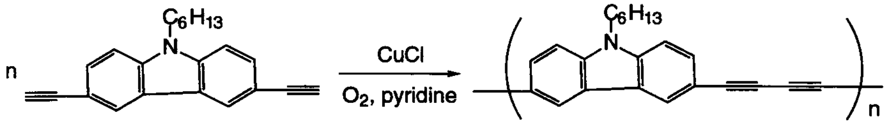
Oxidative polymerization of 3,6-diethynyl-9-hexylcarbazole with oxygen in the presence of copper complex affords soluble poly(9-hexylcarbazole-3,6-diylbutadiynylene) in good yield. Irradiation with UV-vis. light and annealing under nitrogen lead to photochemical and thermal cross-linking and insolubilization of the polymer film.

Introduction

Poly(arylenebutadiynylene)s have been considered to be useful in photochemical and optoelectronic applications such as nonlinear optical materials and photoresists (1-5). However, the solubility of the polymers so far prepared in common organic solvents has been low. Recently, Rutherford et al. (3) and Mangel et al. (4) have prepared soluble poly(arylenebutadiynylene)s by incorporating soluble aliphatic side groups on the aromatic units. Miller et al. have demonstrated syntheses of soluble poly(arylenebutadiynylene) copolymers by varying the quantity of the end cap, and applied the polymers to photodefinable materials (5).

On the other hand, polymers containing a carbazole structure in the main chains as well as in pendant groups are known to exhibit interesting optoelectronic properties such as photoconductivity. Poly(N-vinylcarbazole) and the related polymers are used in photocopies, laser printers, electrophotographic printing plates, and microfilming (6).

These informations prompted us to design new soluble poly(arylenebutadiynylene) containing the carbazole units in the main chain. Herein we report preparation of poly(9-hexylcarbazole-3,6-diylbutadiynylene), PHCzB, and its properties.



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Experimental

Synthesis

3,6-diethynyl-9-hexylcarbazole, **1**, was prepared by modifying the reported method (7).

Oxygen was bubbled through a rigorously stirred solution of copper (I) chloride (34 mg, 0.34 mmol) in 5 ml of freshly distilled pyridine at 40 °C for 10 min. Then a pyridine (5 ml) solution of 1 (360 mg, 1.2 mmol) was added and stirred at 40 °C for 1 h, and a brown precipitate formed. The mixture was then diluted with 100 ml of methanol, and the precipitate was washed thoroughly with HCl-acidic methanol, methanol, and acetone. Yellow powder of PHCzB was purified by reprecipitation from 1,1,2,2-tetrachloroethane (TCE) / acetone (335 mg, 94% yield). Anal. Found: C, 88.7%, H, 6.3%, N, 4.3%. Calcd for $(C_{22}H_{19}N)_n$: C, 88.9%, H, 6.4%, N, 4.7%. IR (KBr, cm^{-1}): 3070, 2925, 2853, 2208, 2136, 1626, 1594, 1480, 1382, 1351, 1285, 1240, 1194, 1149, 1131, 880, 804, 735, 652, 589. ^1H NMR (TCE + $CDCl_3$ (9:1), ppm): 0.8 (3H), 1.2 (6H), 1.7 (2H), 4.1 (2H), 7.2 (2H), 7.6 (2H), 8.1 (2H). ^{13}C NMR (TCE + $CDCl_3$ (9:1), ppm): 13.9, 22.4, 26.7, 28.7, 31.2, 43.2, 79.6, 82.4, 109.1, 112.3, 121.9, 124.9, 130.5, 140.4.

Photochemical Studies

Polymer films were formed by spin-casting from TCE solutions of PHCzB on quartz slides. The film thickness was ca. 20-30 nm. The cast films were irradiated using a 400 W high pressure mercury lamp with a Pyrex water jacket at a distance of 25 cm. The wave length of incident light was longer than 290 nm. Following exposure to the light, UV-vis. absorption spectra and fluorescence spectra were recorded on a Shimadzu UV-265 FS spectrometer and Hitachi 650-10S spectrometer, respectively.

Measurement

IR spectra and NMR spectra were recorded on a JASCO FT/IR-230 spectrometer and a JEOL JNM-A400 NMR spectrometer, respectively. Elemental analyses were carried out with a Yanaco CHN Corder MT-5. GPC analyses were performed with a JASCO 880 system using a Shodex K-804L column using $CHCl_3$ as an eluent (polystyrene standards). Measurement of weight average molecular weight was carried out with a Photal DLS-7000DH/DL light scattering spectrophotometer. TGA curve was recorded on a Rigaku Thermal analysis Station TAS100.

Results and Discussion

PHCzB was prepared by Hay's oxidative coupling reaction (1-5). Oxidative polymerization of **1** in the presence of CuCl and O_2 in pyridine gives PHCzB in 94% yield. The reaction in a mixture of *o*-dichlorobenzene and N,N,N',N'-tetramethylethylenediamine (10:1, v/v) also affords the polymer in good yield (80%). Elemental analysis data of PHCzB is reasonable for the polymer.

PHCzB is soluble in TCE, *o*-dichlorobenzene, NMP, DMAc, *o*-dichlorobenzene, and pyridine, and partially soluble in $CHCl_3$ and THF. The light scattering technique applied for the TCE solution of PHCzB indicates that the polymer has molecular weight of 47000 (degree of polymerization ≒ ca. 160). GPC measurement of $CHCl_3$ soluble fraction of PHCzB shows the molecular weight of $M_n = 6300$ and $M_w = 9000$, respectively.

IR spectrum of PHCzB is essentially the same as that of **1**, except for the disappearance of ν(≡C-H) band (3270 cm^{-1} for **1**), and two peaks assignable to butadiynylene (-C≡C-C≡C-) are observed at 2208 and 2136 cm^{-1}. Figure 1 shows ^1H and ^{13}C NMR spectra of PHCzB in TCE + $CDCl_3$ (9:1).

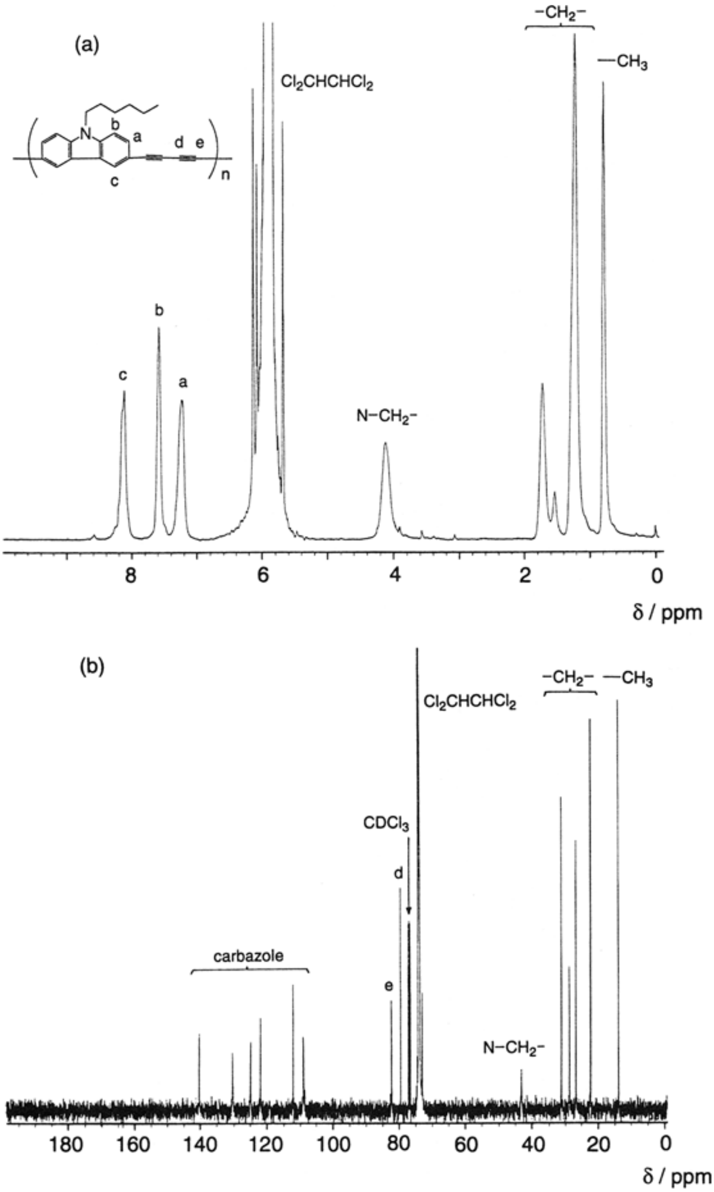


Figure 1. ^1H (a) and ^{13}C (b) NMR spectra of PHCzB in a mixture of 1,1,2,2-tetrachloroethane and $CDCl_3$.

Assignment of the peaks was carried out by comparison of the peak positions of PHCzB with those of monomer 1. In Figure 1(a), no peak assignable to the ≡C-H (δ 3.0 ppm for 1) group is observed. The ratios of the peak area assist the structure for PHCzB. The ^{13}C NMR spectrum of PHCzB shows 14 peaks, and two peaks at δ 79.6 and 82.4 ppm are due to the carbons of butadiynylene group. Thus, the elemental analysis, molecular weight, and IR and NMR data indicate the proposed structure of PHCzB.

Thermal stability of PHCzB was measured by TGA under nitrogen. Detectable weight loss was not observed below 250 °C, and temperature for 10% weight loss (T_{d10}) of the polymer is 468 °C. The UV-vis. spectrum of PHCzB in TCE exhibits four absorption peaks at 257, 318, 358, and 387 nm presumably based on π-π^* transition. The TCE solution of PHCzB shows strong fluorescence with peaks at 431 nm with a shoulder at 465 nm when excited at 385 nm.

Figure 2 shows change in absorption spectrum of a cast film of PHCzB during irradiation of light. The absorption peaks gradually decrease with light irradiation time. The decrease in fluorescence peaks of the polymer was more sensitive than that of the absorption peaks. Similar changes in the absorption and fluorescence spectra of the polymer film were also observed, when the film was annealed at 150 °C under nitrogen. The photo-irradiated and annealed films were insoluble in common organic solvents.

We tentatively assume that these changes in absorption and fluorescence spectra and solubility of the films originate from change in conjugation system in the polymer chain. A number of reports on topochemical polymerization of diacetylene derivatives by UV-irradiation and annealing have been published (2,8), and photochemical and thermal cross-linking reactions of poly(arylenebutadiynylene)s have also been reported (2,3,5). These results suggest that photochemically and thermally cross-linking reactions related to the topochemical polymerization of diacetylenes occur partially in the polymer chain by light irradiation or annealing as expressed by Scheme 1.

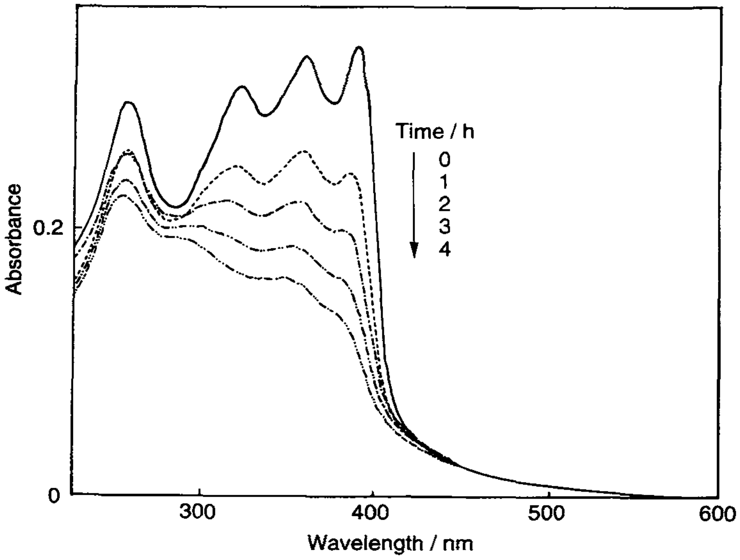
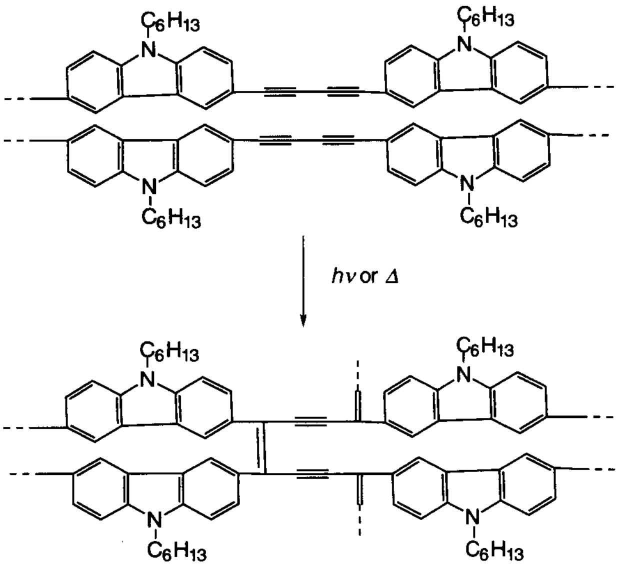


Figure 2. Change in absorption spectrum of a film of PHCzB during irradiation of light.

Scheme 1



IR spectrum of light irradiated film for 10 h was not measurably different from that of the pristine film, suggesting photolytic decomposition of the polymer backbone did not occur during 10 h irradiation. Figure 3 shows IR spectra of PHCzB before and after light irradiation for 19 h. In Figure 3(b), the peaks attributable to butadiynylene group (-C≡C-C≡C-) decrease, and a new peak, which is presumably attributable to ene-yne structure (=C-C≡C-C=) (8), is observed at 2175 cm^{-1}. These results support PHCzB would serve as photochemically and thermally cross-linkable polymer.

As described above, new soluble poly(arylenebutadiynylene) containing carbazole units in the main chain is obtained. The films of the polymer undergo photoinduced cross-linking and insolubilization upon exposure to light and heat. Although the electrical properties of the polymer are not clear in the present study, the polymer is expected to provide photochemical patterns with hole transporting and photoconducting properties. Further studies including the application of the polymer are in progress.

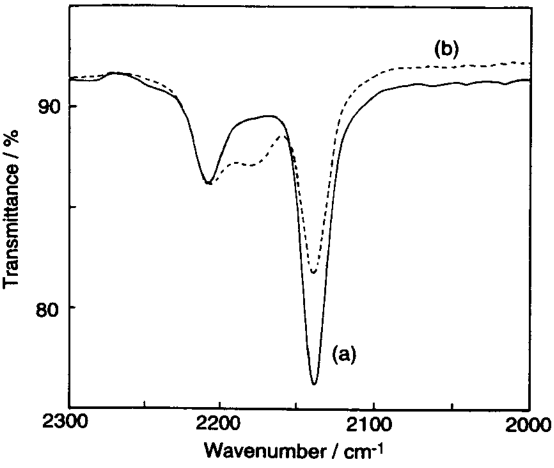


Figure 3. IR spectra of a film of PHCzB before (a) and after (b) light irradiation for 19 h.

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