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Synthesis and properties of poly(phenylacetylene)s having dialkylamino groups

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Summary

Poly(phenylacetylene)s bearing dialkylamino groups were prepared by the polymerization of *p*-(*N,N*-dialkylamino)phenylacetylenes with $[Rh(nbd)Cl]_2$, and their electrochemical behavior was examined. Rh-catalyzed polymerization of *p*-(*N,N*-diethylamino)phenylacetylene (DEAPA) and *p*-(*N,N*-di-*n*-butylamino)phenylacetylene (DBAPA) in toluene in the presence of triethylamine gave good yields of the polymers (86 and 90%, respectively). Poly(DEAPA) was soluble in chloroform and dichloromethane, and poly(DBAPA) dissolved in various solvents such as toluene, THF, dichloromethane and chloroform. Poly(DEAPA) and poly(DBAPA) showed onset temperatures at 248 and 190°C, respectively, and absorptions around 300-400 nm. Electrochemical doping of the polymer films resulted in the shift of the absorptions to a region around 680 nm, which accompanied a color change of the polymer films from green ocher to deep blue.

Introduction

Substituted polyacetylenes have been known to exhibit characteristic properties based on the π-conjugation through alternating double bonds of the main chain [1]. Since the discoveries of excellent catalysts for acetylene polymerizations including W-, Mo-, Ta-, Nb-, and Rh-based transition metal complexes, a variety of substituted acetylenes has been designed and polymerized with the motivation of producing advanced functional materials such as nonlinear optical and electroluminescent materials, organic conductors, and so on.

We have energetically studied the synthesis and functions of a wide range of substituted polyacetylenes so far, and one of our recent interests directs to the polyacetylenes with nitrogen-containing functional groups such as amino, indolyl and carbazolyl groups [2]. The electron-donating feature of these functional groups amplifies the electron density of the polymer backbones and reduces the band-gap energy, which would stabilize the p-doped state. Therefore, these polymers are expected to show characteristic electrochemical behavior. Here, we wish to report the synthesis and

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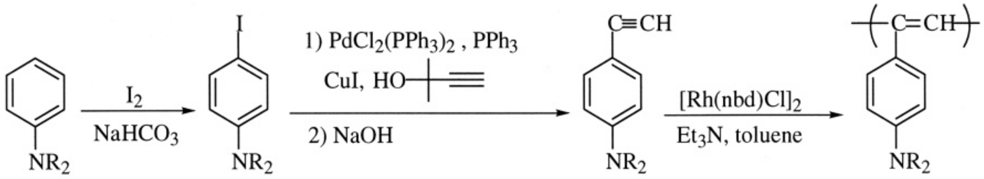
properties of new poly(phenylacetylene)s with dialkylamino functional groups (Scheme 1). We also examined the possibility of the polymers as electrochromic materials [3].

Scheme 1



DEAPA (R = Et)
DBAPA (R = *n*-Bu)

Results and Discussion

Synthesis of the polymers. The monomers employed in the present study are *p*-(*N*,*N*-diethylamino)phenylacetylene (DEAPA) and *p*-(*N*,*N*-di-*n*-butylamino)phenylacetylene (DBAPA). They were prepared by the iodination of the respective *N*,*N*-dialkylanilines and sequential palladium-catalyzed coupling with 2-methyl-3-butyn-2-ol, followed by the deprotection under alkaline conditions.

Polymerizations were carried out by adding the monomer solution into a solution of (bicyclo[2.2.1[hepta-2,5-diene)chlororhodium (I) dimer {[Rh(nbd)Cl]$_2$} containing triethylamine at 35°C. Vigorous gas evolution was observed just after the polymerization started, and the viscosity of the system rapidly increased, indicating the formation of the polymers. Gas chromatographic analyses indicated the complete conversion of the monomers. Tabata and coworkers have attempted to polymerize *p*-(*N*,*N*-dimethylamino)phenylacetylene (DMAPA) and reported that the homopolymer of DMAPA with high molecular weight is not attainable in good yield [4, 5]. However, good yields of the polymers were obtained from DEAPA and DBAPA (90 and 86%, respectively). This is probably due to the reduced basicity of DEAPA and DBAPA compared with that of DMAPA.

Gel permeation chromatographic (GPC) measurement of poly(DEAPA) showed that the major products were oligomers with molecular weights of a few thousands, however, the GPC curve of poly(DEAPA) indicated the presence of a small amount of a high molecular weight polymer. In contrast, the product from DBAPA mainly involved quite high molecular weight polymer whose molecular weight was impossible to be estimated by GPC because the molecular weight exceeded the exclusion limit. Thus, poly(DBAPA) possesses a molecular weight beyond one million. These results are probably because of the excellent solubility of poly(DBAPA). Namely, poly(DBAPA) dissolved in various solvents such as THF, toluene, chloroform and dichloromethane, whereas poly(DEAPA) was only soluble in chloroform and dichloromethane. The polymers produced were green ocher solids, and thermogravimetric analyses showed that the onset temperatures of the weight loss of poly(DEAPA) and poly(DBAPA) were 248 and 190°, respectively.

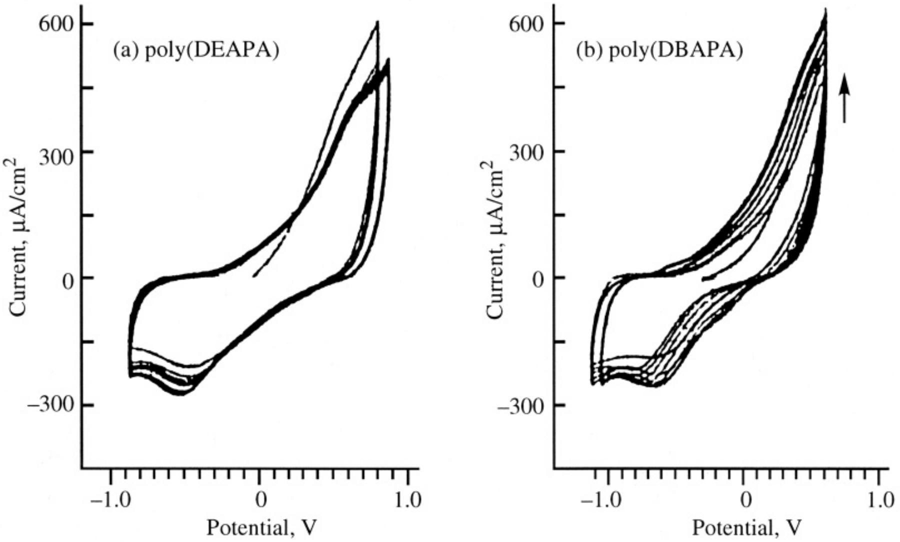


Figure 1. Cyclic voltammograms of (a) poly(DEAPA) and (b) poly(DBAPA) on an ITO electrode (v = 100 mV/s) (propylene carbonate + $LiClO_4$). Potentials are given vs. the Ag/Ag+ reference electrode.

Electrochemical behavior of the polymers. The films of the polymers were prepared by casting the solutions of poly(DEAPA) and poly(DBAPA) in dichloromethane and toluene, respectively, on In-Sn oxide (ITO)-coated quartz plates. Electrochemical doping was carried out by the common three-electrode method using propylene carbonate solution containing lithium perchlorate as an electrolyte.

Figure 1 shows cyclic voltammograms of the produced polymers. The polymers were cycled electrochemically between doped and undoped states. The current response gradually increased with repeating doping-undoping process in the case of poly(DBAPA), and after several cycles, stable doped-undoped waves were obtained. A similar phenomenon is also observed in the case of poly[o-(trimethylsilyl)phenylacetylene] [poly(TMSPA)] [3]. Although a sharp p-doping peak was not detected in the case of poly(DBAPA), the cyclic voltammogram of poly(DEAPA) exhibited a p-doping peak at 0.9 V (vs. Ag/AgCl). Both polymers showed undoping peak around -0.6 V.

The polymers produced in the present study exhibited characteristic properties as electrochromic materials [6]. For example, upon the electrochemical doping, the color of the poly(DEAPA) film changed from green ocher to deep blue. The original color of poly(DEAPA) was recovered when the voltage was applied in the reduction region. Similarly, reversible color changes of poly(DBAPA) occurred between pale green ocher and dark blue upon the electrochemical doping at the range of +1.2 - -1.2 V (vs. Ag/AgCl). This color change is in contrast to that of poly(TMSPA); poly(TMSPA) loses its color (red) upon doping [3]. Figure 2 represents the absorption spectra of poly(DEAPA) and poly(DBAPA). Both polymers possess absorptions around 300-400 nm, and small or no absorptions were detected between 500-1000 nm in the

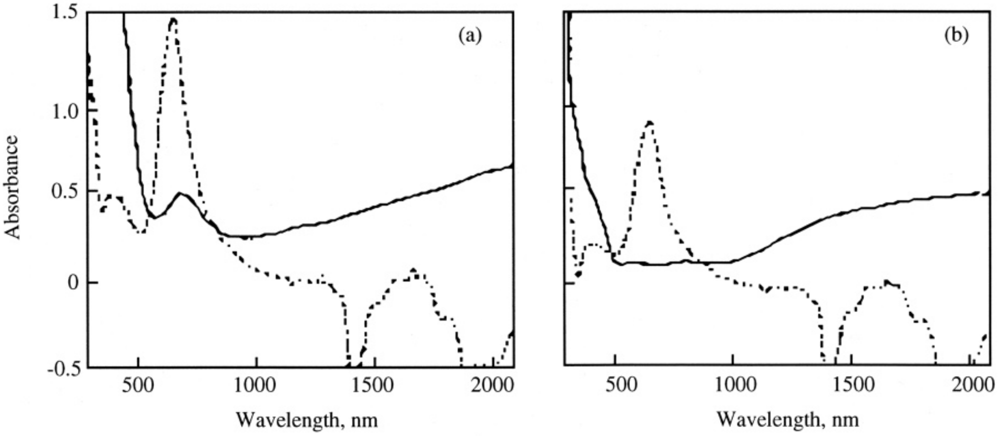


Figure 2. Absorption spectra of (a) poly(DEAPA) and (b) poly(DBAPA) in propylene carbonate (----- doped ; —— undoped).

undoped states. The electrochemical p-doping resulted in the decrease in the absorptions around 300 nm and appearance of new absorptions at 680 nm.

In summary, we have demonstrated the synthesis of novel substituted polyacetylenes from *p*-(*N*,*N*-dialkylamino)phenylacetylenes. They are obtained in good yields when the alkyl chains are longer than ethyl groups, and the polymers with very high molecular weight are accessible if long alkyl chains are incorporated onto nitrogen atom. The resulting polymers exhibited characteristics as electrochromic materials, which indicates that they may be useful as devices for display.

Experimental

Materials. All the solvents used were distilled by the standard procedures. $[Rh(nbd)Cl)]_2$ was used as received. All the reagents in monomer synthesis were used as purchased without further purification unless specified.

Measurements. The molecular weights of the polymers were estimated by GPC on a Toyo Soda HLC 8000 system with polystyrene gel columns using $CHCl_3$ as an eluent after calibration with polystyrene standards. IR spectra and UV-visible spectra were recorded on Hitachi 270-30 and Hitachi U-3400 spectrophotometers. NMR spectra were obtained by JEOL NM-GSH27MV and NM-GSH27T spectrometers using tetramethylsilane (TMS) as an internal standard. Gas chromatographic analyses were carried out by Shimadzu Model GC-8A using chlorobenzene as an internal standard. Thermogravimetric analyses (TGA) were conducted in air on a Seiko Instruments SSC/5200 system at a heating rate of 10°C/min. Cyclic voltammetric measurements were carried out using an arbitrary function generator HB-111 and a potentiostat HA-151 (Hokuto Denko).

Synthesis of monomers. Preparation of DEAPA is described as a typical procedure. Into the suspension of *N*,*N*-dimethylaniline (32.9 g, 220 mmol) in 50% aqueous $NaHCO_3$ (120 mL) was slowly added I_2 (27.9 g, 110 mmol) at such a rate as to maintain the reaction mixture below 15°C. After the addition of I_2, the mixture was kept for stirring and warmed to rt over 30 min. The mixture was extracted with ether, and the ether layer was washed with brine, dried over $NaSO_4$, and concentrated. The residue was subjected to SiO_2-column chromatography to give *p*-iodo-*N,N*-diethylaniline (12.1 g, 44 mmol, 20%) [7]. Into a mixture of $PdCl_2(PPh_3)_2$ (123 mg, 0.18 mmol), PPh_3 (185 mg, 0.71 mmol), CuI (150 mg, 1.0 mmol) in triethylamine (80 mL) was added 2-methyl-3-butyn-2-ol (3.73 g, 44 mmol) with stirring at rt. After 1 h, a solution of *p*-iodo-*N,N*-diethylaniline (12.1 g, 44 mmol) in triethylamine (50 mL) was added, and the reaction mixture was stirred for 24 h. Triethylamine was removed with a rotary evaporator, and the residue was extracted with CH_2Cl_2. The organic phase was washed with water, dried over $NaSO_4$ and concentrated. The residue was purified by SiO_2-column chromatography (eluent, toluene/methanol = 1/9) to yield the corresponding acetylene alcohol which was treated with KOH (5.0 g, 89 mmol) in toluene at 60-80°C for 3 h to remove acetone. The residue was filtered, and the filtrate was extracted with CH_2Cl_2. The organic layer was washed with water and dried over $NaSO_4$ and concentrated. The purification was carried out by SiO_2-column chromatography (toluene as an eluent) and sequential distillation with a Kugelrohr apparatus (1 mmHg, 120°C) to yield DEAPA (6.5 g, 44.7 mmol, 85% based on *p*-iodo-*N,N*-diethylaniline). Spectral data were as follows. DEAPA; ^1H NMR ($CDCl_3$) δ 1.14 (t, 6H, J = 11 Hz), 2.97 (s, 1H), 3.34 (q, 4H, J = 11 Hz), 6.52 (d, 2H, J = 6.7 Hz), 7.30 (d, 2H, J = 6.7 Hz); IR (KBr) 3300, 2990, 2105, 815 cm^{-1}. DBAPA; ^1H NMR ($CDCl_3$) δ 0.92 (t, 6H, J = 11 Hz), 1.32 (m, 4H), 1.53 (m, 4H), 2.95 (s, 1H), 3.24 (t, 4H, J = 11 Hz), 6.51 (d, 2H, J = 5.4 Hz), 7.30 (d, 2H, J = 5.4 Hz); IR (KBr) 3300, 2950, 2855, 2095, 805 cm^{-1}.

Polymerization. Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. Into a solution of $[Rh(nbd)Cl]_2$ (12 mg, 0.026 mmol) in dry toluene (1 mL) was added a toluene-solution (1.5 mL) containing the monomer (2.5-3.5 mmol), distilled triethylamine (1.8 mL) and chlorobenzene (internal standard, 0.1 mL) at 35°C. The solution was allowed for stirring over night, and then ca. 0.5 mL of toluene/methanol (4/1) was added. Polymers were isolated by reprecipitation into methanol, collected by filtration and dried under reduced pressure.

References and Notes

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3) Study on the electrochromism of substituted polyacetylenes is quite limited. Only one example has been reported by Yoshino et al. for poly[*o*-

(trimethylsilyl)phenylacetylene]. See, K. Yoshino, H. Takahashi, S. Morita, T. Kawai, R. Sugimoto, *J. Appl. Phys.*, **33**, L254 (1994).

4) M. Lindgren, H.-S. Lee, W. Yang, M. Tabata, K. Yokota, *Polymer*, **32**, 1531 (1991).

5) We also polymerized DMAPA with [Rh(nbd)Cl]$_2$ in the absence of triethylamine to give in 66% yield oligomers with low molecular weight below 2300 (GPC, polystyrene standards).

6) Examples for electrochromic materials based on π-conjugated polymers, see: a) T. Yamamoto, H. Etori, *Macromolecules*, **28**, 3371 (1995). b) N. Saito, T. Kanbara, Y. Nakamura, T. Yamamoto, K. Kubota, *Macromolecules*, **27**, 756 (1994). c) T. Kanbara, T. Yamamoto, *Macromolecules*, **26**, 3464 (1993). d) T. Kanbara, T. Kushida, N. Saito, I. Kuwajima, K. Kubota, T. Yamamoto, *Chem. Lett.*, **1992**, 583. e) T. Kambara, N, Saito, T. Yamamoto, K. Kubota, *Macromolecules*, **24**, 5883 (1991). f) E. J. Pern, A. I. Frank, *J. Electrochem. Soc.*, **137**, 2769 (1990). g) T. Mitsuhara, K. Kaeriyama, S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 764, (1987). h) H. Yashima, M. Kobayashi, K.-B. Lee, D. Chung, A. J. Heeger, F. Wudl, *J. Electrochem. Soc.*, **134**, 46 (1987). i) T. Yamamoto, T. Ito, K. Sanechika, M. Hishinuma, *Synth. Met.*, **25**,103 (1988).

7) Separation of unreacted *N,N*-diethylaniline from the product was impossible by column chromatography. The following coupling was conducted by using a mixture containing *N,N*-diethylaniline.