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Synthesis of Conductive Polymers: Poly(arene methides) Having Naphthalene and Anthracene Rings

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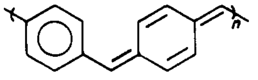
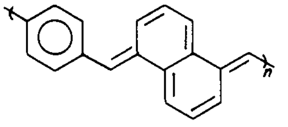
ABSTRACT: We have synthesized three new conjugated hydrocarbon polymers by DDQ dehydrogenation of the products of $SnCl_4$-catalyzed Friedel–Crafts reactions of α,α'-xylene dichloride with naphthalene (II) and anthracene (III) and of the Friedel–Crafts self-condensation product of 1-(chloromethyl)naphthalene (IV). These polymers are intractable solids that were characterized by infrared spectral analysis and by characterization of the Friedel–Crafts precursor polymers IIa, IIIa, and IVa. The conductivities of polymers III and IV increase from 10^{-12} to a maximum value of 10^{-4} S/cm on doping with AsF_5; the conductivity of polymer II increases from 10^{-12} to 10^{-6} S/cm on doping with AsF_5. Polymer II has a DP of 5.5, whereas polymers III and IV have DPs of 21 and 58, respectively.

Introduction

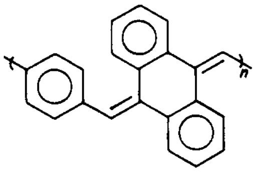
As part of our continuing program to synthesize conductive polymers having the poly(arene methide) (PAM) structure,[1] we report the synthesis of some polynuclear PAMs—II, III, and IV—derived from naphthalene and anthracene.



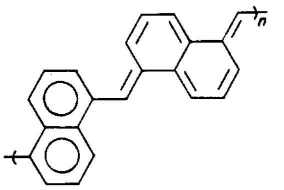
I



II



III



IV

Poly(p-phenylene)[2,3] and various polynaphthalenes[3] have been reported, but of the possible PAMs, only the phenylene derivative I[1] has been reported.

The simplest example, I, is of interest because it has a degenerate ground state and is predicted to have a low band gap and low ionization potential compared to polyacetylene.[4] The ground state of polymer IV is also degenerate, but II and III do not have degenerate ground states; however, all three possess the analogous alternating arene–quinonoid ring structures.

While none of these polymer has been reported previously, polymers of naphthalene and anthracene have been reported. Thermoset resins have been made[5] fron benzene, naphthalene, anthracene, phenanthrene, and pyrene by condensation with p-xylylene dichloride in the presence of $SnCl_4$. Molecular structures of these products were not reported. Polymerizations of aromatic hydrocarbons with sulfur have also been reported,[6] as well as the hydrocarbons poly(p-phenylene) and polynaphthalenes.[7] None of these polymers possesses a conjugated backbone. A conjugated polymer has been reported[8] by a Ziegler–Natta polymerization of 9-ethynylanthracene; however, electrical conductivity was not studied. A number of other conjugated polymers with aromatic pendant groups have been reported.[9]

Experimental Section

Materials. Materials whose commercial sources are not given were purchased from Aldrich Chemical Co. Only those materials that were purified are listed. α,α'-Dichloro-p-xylene and 1,4-cyclohexanedione were crystallized from CCl_4. Dimethylformamide (Gold Label 99+%), p-xylene (99+% reagent), p-dioxane (99+%), tetrahydrofuran (99+%), and ethanol (Florida Distillers Co., 190 proof) were dried over 4A molecular sieves. Dichlorodicyanobenzoquinone (DDQ) was dried under vacuum in a dessicator over Drierite and transferred under N_2. Naphthalene was recrystallized from methanol–water; anthracene was recrystallized from toluene. 1-(Chloromethyl)naphthalene was fractionally vacuum distilled, and a middle fraction was used. Aluminum chloride (anhydrous powder) was sublimed under reduced pressure before use and transferred under N_2. Palladium on carbon was used under nitrogen.

Instrumentation. Molecular weights were determined by vapor-phase osometry using a Wescan Molecular Weight Apparatus, Model 233-400. Differential scanning calorimeter scans were recorded on a Du Pont DSC Model 910 instrument. The remaining instrumentation has been described in the preceding paper in this issue.[10]

Poly(p-xylylene-co-1,5-naphthylene): Copolymer IIa. Naphthalene, 3.73 g (0.0171 mol), was mixed in a polymerization tube with 3.00 g (0.0171 mol) of α,α'-dichloro-p-xylene. The mixture was flushed with N_2 for 15 min and the the tube was immersed in a silicone oil bath at 120–130 °C until the solid mixture melted. At that point, 0.15 mL of $SnCl_4$ was added to start the polymerization. The tube was left in the oil bath at the same temperature until the evolution of HCl ceased. The polymer was washed with hot water several times and then dried. The dry material was dissolved in $CHCl_3$, reprecipitated from methanol, and left to dry under vacuum at 50 °C. The yield was quantitative; the solid did not melt, but there was a noticeable change to a rubbery material at 130 °C. Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.17; H, 6.03; Cl, 0.81. Molecular weight was 1277 which corresponds to a $\overline{DP}$ of 5.5. IR (KBr pellet) 3050, 2950, 1600, 1500, 1060, 780–740 (d) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3–4 (2 peaks ratio 1:4), 6–7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 38.5, 41.6 (2s), 124–138; UV ($CHCl_3$) 250.4 (3.46), 278.4 (3.45), 300 (3.31) nm (numbers in parentheses are log ϵ).

Dehydrogenation of IIa to II. DDQ, 2.01 g (0.0087 mol), was mixed in dry xylene with 2.0 g (0.0087 mol) of IIa in a glovebox. The dark mixture was heated under N_2 for 1 day. As the xylene came to a boil, a brown solid began to precipitate. After the heating period, the mixture was cooled and filtered. The dried solid weighed 3 g. This brown solid was extracted in a Soxhlet extractor with THF to remove unreacted DDQ and DDHQ by product. Of the product mixture, 1.22 g dissolved in the THF and was identified as DDHQ by its IR spectrum. The THF-insoluble residue was identified as the dehydrogenated II by its IR spectrum which shows the complete disappearance of CH_2 absorption at 2900–3000 cm^{-1} as well as the band at 1390 cm^{-1}. Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.29 Found: C, 84.71; H, 5.16. Repeated purification and analysis failed to give expected values. Burning a sample of this product over an open Bunsen burner left a residue which disappeared only after burning for 5 min.

This product shows no sign of melting up to 400 °C as confirmed by the DSC scan which shows only a shift in the base line between 200 and 300 °C that is not retraced on cooling the sample and heating it again.

Poly(p-xylylene-co-1,9-anthracenylidene): Copolymer IIIa. This polymer was prepared following the procedure for IIa

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Table I
Conductivity as a Function of Time of Doping with AsF_5

polymer II		polymer III		polymer IV	
time,[a] h	conduct., S/cm	time, h	conduct., S/cm	time, h	conduct., S/cm
0	ca. 10^{-12}	0	ca. 10^{-12}	0	ca. 10^{-12}
24	1.4×10^{-6}	2	7.4×10^{-6}	4	4.9×10^{-6}
48	2.4×10^{-6}	7	2.8×10^{-5}	30	1.8×10^{-5}
240	1.9×10^{-6}	24	5×10^{-5}	59	8.1×10^{-5}
		30	1×10^{-4}	82	1.1×10^{-4}
		51	6.6×10^{-5}	106	2.8×10^{-5}
		70	5×10^{-5}		
		90	2.8×10^{-5}		

[a] Time = 0 represents samples prior to doping.

except that the mixture was heated to 200 °C. The yield was quantitative; the solid did not melt, but there was a noticeable change to a rubbery material at 200 °C. Anal. Calcd for $C_{22}H_{16}$: C, 94.26; H, 5.74. Found: C, 94.32; H, 5.65. Molecular weight was 5861 which corresponds to a DP of 21. IR (KBr pellet) 3040, 2920, 1900, 1615, 1500, 1440, 1020, 870, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.1, 3.7, 4.2 (4 H), 6.5–8.2 (12 H); ^{13}C NMR ($CDCl_3$) δ 32, 38, 41 (3s), 122–138 (7 peaks); UV ($CHCl_3$) 264.8 (3.50, 350.4 (3.18), 368.0 (3.30), 387.2 (2.83) nm (numbers in parentheses are log ϵ).

Dehydrogenation of IIIa to III. DDQ, 1.65 g (0.0073 mol), was mixed with 2.0 g (0.0071 mol) of IIIa in a drybox and treated as was IIa. A light greenish-brown solid precipitated as the xylene started to boil. The recovered solid, 2.94 g, after extraction with THF, gave 1.23 g of DDHQ identified by its IR spectrum. The remaining 1.7 g was identified as III by its IR spectrum which shows the disappearance of the CH_2 absorption at 2900–3000 cm^{-1} as well as the appearance of a new band at 1500 cm^{-1}. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 85.49; H, 5.05. This material did not melt up to 400 °C and left a residue upon burning in an open flame for 5 min. The DSC scan was almost identical with that of II.

Polymerization of 1-(Chloromethyl)naphthalene (IV). 1-(Chloromethyl)naphthalene, 50.0 g (0.283 mol), was polymerized under N_2 with $SnCl_4$ (0.2 mL) at 55 °C. The tube was left in the oil bath at the same temperature until the evolution of HCl ceased. The white fiber was washed with hot water several times and then dried. It was dissolved in $CHCl_3$, reprecipitated from methanol, and dried under vacuum at 50 °C. The yield was quantitative; the solid did not melt, but there was a noticeable change to a rubbery material at 140 °C. Anal. Calcd for $C_{11}H_8$: C, 94.24; H, 5.75. Found: C, 94.44; H, 5.99. IR (KBr pellet) 3050, 2900–2800, 1595, 1500, 1440, 1420, 1390, 1375, 1250, 1160, 830, 780, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.8 (s, 2 H), 5.8–6.8 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 34–41 (s), 124–139 (m); UV ($CHCl_3$) 248.8 (3.48), 272.8 (3.51), 292.0 (3.46) nm (numbers in parentheses are log ϵ). Molecular weight was 8072 which corresponds to a $\overline{DP}$ of 58. The DSC scan from 50 to 600 °C shows an inflection at ca. 430 °C that was not retraced upon cooling.

Dehydrogenation of IVa to IV. The procedure of previous dehydrogenations was followed. The reddish-brown solid, 2.59 g, gave 1.45 g of DDHQ. The remainder was identified as IV by its IR spectrum which shows the disappearance of CH_2 absorption at 2900–3000 cm^{-1} and of two bands at 1250 and 1150 cm^{-1}. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 85.05; H, 5.00. This product shows no sign of melting up to 400 °C and leaves a residue upon burning in an open flame for 5 min. The DSC scan was almost identical with that of II.

Heat Treatment of II, III, and IV. We heated each polymer in a tube furnace under Ar for 5 min at 350 °C. This temperature is above the DSC transitions observed for these polymers.

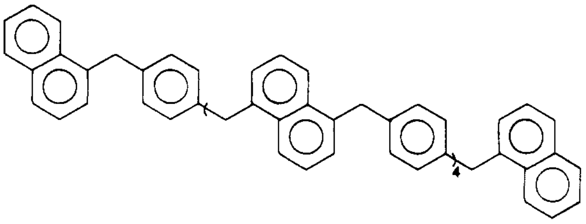
Conductivity Measurements. We performed AsF_5 doping of pressed pellets and monitored the conductivity by using the standard two- and four-probe techniques as appropriate in the manner discussed previously.[10] Table I shows the data from these measurments on II–IV.

Polymer Structures

We inferred the substitution patterns of polymers II, III, and IV from those of their respective precursors, IIa, IIIa, and IVa.

Polymer Ia. The reactivity of naphthalene toward electrophiles is known to be greater at the 1-position than at the 2-position. 1-Substituted naphthalenes in which the substituent is electron-releasing undergo substitution at the 2-, 4-, 5-, and 7-positions. The expected substitution patterns are therefore 1,2-, 1,4-, 1,5-, and 1,7-. We infer that the unequal singlets in the ^1H NMR CH_2 region are due to two different substitution patterns, each of which has two equivalent CH_2 groups. A pattern of nonequivalent CH_2 groups would give rise to singlets of equal areas. Of the above possible substitution patterns, only the 1,4- and 1,5- have equivalent CH_2 groups. The IR spectrum of IA has a single, strong band at 785 cm^{-1}. 1,4-Dimethylnaphthalene has two strong bands in that region (750 and 820 cm^{-1}),[11a] whereas 1,5-dimethylnaphthalene has a single, strong bond at 780 cm^{-1}.[11b] We therefore propose that bonding on the naphthalene ring is 1,5- rather than 1,4-.

We explain the two CH_2 ^1H NMR peaks of ratio 1:4 as arising from main-chain and end-group CH_2 units. In this case, the number of repeating units is four, as shown below. This structure has a calculated molecular weight of 1266. Our observed molecular weight of 1277 agrees quite well with this structure.



Polymer IIIa. Reactivity of anthracene toward electrophilic reagents is greatest at the 9,10-positions and is known to be greater than that of naphthalene. Although the IR spectrum does not allow the assignment of a substitution pattern for this polymer, we may infer it from the number of ^{13}C NMR resonances in the aromatic region. Polymer IIIa exhibits seven intense peaks. The 9,10-anthracenediyl structure should give rise to six resonances in the aromatic region and one in the CH_2 region. Other anthracenediyl substitutions, e.g., 1,10- and 2,9-, would give rise to 16 aromatic peaks. With nonuniform substitution, the aromatic region would show many more resonances with 2,9- or 1,10-disubstitution than with a product that is mainly 9,10-disubstituted. We therefore propose that IIIa and III have the 9,10-anthracenediyl structure.

Polymer IVa. The most distinctive feature of this polymer is the singlet at 3.8 ppm (2 H) in the ^1H NMR spectrum. Such a singlet rules out all substitution patterns except 1,4- and 1,5-. Sato et al.[12] report the following infrared spectral data for 1,4- and 1,5-polynaphthalenes: for 1,4-, 730, 820, 950, and 1360 cm^{-1}; for 1,5-, 750, 1380 cm^{-1}. Our polymer IVa has bands at 750 and 1385 cm^{-1} and no bands near 950 cm^{-1}. On the basis of these data, we propose that polymers IVa and IV have the 1,5-naphthylene structure.

Heat Treatment of Polymers II–IV. The DSC scans of these polymers all show the same pattern on heating, cooling, and reheating; the base line smoothly rises to a new level which is retraced on the cooling and reheat cycle. In an attempt to determine the source of this irreversible, exothermic change, we heated each of these polymers in a tube furnace at 350 °C, a temperature clearly higher than the observed exothermic transition. These transitions could be due to a change in crystal structure, decomposition, or cis–trans conversion. Infrared spectra showed small differences from the spectra of unheated samples.

Polymer II. No new bands appeared, but the band at 780 cm^{-1} disappeared. This band is characteristic of 1,5-disubstituted naphthalenes, and its disappearance may be due to decomposition. The DSC scans cannot be attributed to cis–trans conversion but rather to decomposition and/or a glass transition. The conductivity of heated polymer II was not different from the unheated sample.

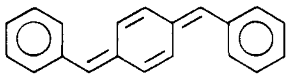
Polymer III. No new bands appeared, but the weak band at 890 cm^{-1} diminished. In this case also, we attribute the change either to decomposition or to a glass transition.

Polymer IV. New bands appeared at 1730, 1300, and 1100 cm^{-1}. The band at 1730 cm^{-1} may be attributed to a cis C=C stretch resulting from a trans-to-cis conversion or possibly to a carbonyl group produced during heating. Attempts to measure the conductivity of heated polymer IV were not successful because the powdery product does not cohere sufficiently to form a pellet.

Structure of Polymers II–IV. We have inferred the structures of the dehydrogenation products II, III, and IV from their infrared spectra and comparisons of these spectra with those of the respective precursors, IIa, IIIa, IVa. Elemental analyses were unacceptable because these compounds do not burn smoothly, and combustion during analysis was incomplete. These compounds are intractable solids, and the usual methods of characterization were not possible. The increase in conductivity of II, III, and IV on doping with AsF$_5$ (vide infra) is further evidence that extensive dehydrogenation occurred.

Electrical Conductivity

Both polymers III and IV exhibited an increase of 8 orders of magnitude in conductivity on doping with AsF$_5$ (Table I). Polymer II showed an increase of 6 orders of magnitude in conductivity on exposure to AsF$_5$. The low $\overline{DP}$ of II compared with III and IV suggests that conductivity does not depend strongly on high chain length. We have found that the three-ring oligomer[10]



also exhibits a relatively large enhancement of conductivity on doping with AsF$_5$, as do terphenyl,[13] quaterphenyl,[13] and oligomers of poly(p-phenylenevinylene)[14] ($\overline{DP}$ 7–9). In these latter cases, the high conductivities were taken to indicate that further polymerization occurred as a result of exposure to AsF$_5$.

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Registry No. II, 107890-84-6; IIa, 29352-82-7; III, 107890-82-4; IIIa, 29352-83-8; IV, 107890-83-5; IVa, 55909-60-9; DDQ, 84-58-2; AsF$_5$, 7784-36-3; α,α'-dichloro-p-xylene, 623-25-6; naphthalene, 91-20-3; anthracene, 120-12-7; 1-(chloromethyl)naphthalene, 86-52-2.

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