

**POLYMERIZATION OF SUBSTITUTED PHENYLACETYLENES: CHARGE TRANSFER COMPLEXES OF *p*-DIMETHYLAMINOPHENYLACETYLENE\***

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An investigation was carried out of the thermal and anionic polymerization of substituted phenylacetylenes (*o*-nitro, *p*-nitro and *p*-dimethylamino). Thermal polymerization gives rise to conjugated oligomers. Under the conditions of anionic polymerization only dimer is formed from *p*-dimethylaminophenylacetylene. The radical polymerization of the charge-transfer complex of *p*-dimethylaminophenylacetylene with maleic anhydride (molar ratio 2 : 3) yielded an alternating copolymer, which binds another molecule of maleic anhydride per each dimethylamino group, by a weak charge transfer interaction.

The polymerization of phenylacetylene has been extensively studied<sup>1</sup>. It provides linear polymers with a system of conjugated double bonds in the main chain. No attempt has been made, however, to polymerize phenylacetylenes with substituents capable of donor or acceptor properties. Such substituents were expected to influence both the polymerization and the properties of the polymers, by forming CT complexes.

**EXPERIMENTAL**

UV spectra were measured on Cary model 14, some on Optica CF-4, using chloroform as solvent, in concentrations of about 1 mol/l and sample thickness 0.1 mm. IR spectra were measured on UR-10, Zeiss, in KBr pellets, NMR on JEOL-60.

**Materials**

*p*-Dimethylaminophenylacetylene (I) was prepared as follows: *p*-Dimethylaminoacetophenone obtained from *p*-bromodimethylaniline in 72.3% yield by analogy to ref.<sup>2,3</sup> was converted to *p*-dimethylamino- $\beta$ -chlorocinnamaldehyde, 84%, m.p. 120–121°C (2-propanol). For C<sub>11</sub>H<sub>12</sub>ClNO (209.7) calculated: 63.01% C, 5.77% H, 16.91% Cl; found: 63.16% C, 5.82% H, 17.21% Cl. The latter product yielded by simultaneous dehydrochlorination and deformylation 77% I, m.p. 51–52°C (ethanol, ref.<sup>4</sup> m.p. 52–53°C), and was purified by sublimation. For C<sub>10</sub>H<sub>11</sub>N (145.2) calculated: 82.72% C, 7.64% H, 9.65% N; found: 82.63% C, 7.77% H, 9.62% N.

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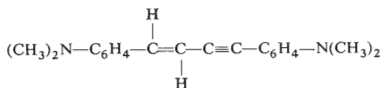
The procedure of the latter two steps was that of ref.<sup>4</sup>. In the route for *I* described in the literature<sup>5</sup>, the decarboxylation of *p*-dimethylamino- $\alpha$ -bromocinnamic acid could not be reproduced in any reasonable yield.

The following substances were prepared and/or purified according to the literature: *p*-nitrophenylacetylene (*II*), m.p. 151.5–152.5°C (ethanol, ref.<sup>4</sup> m.p. 152°C); *o*-nitrophenylacetylene (*III*), m.p. 80–81°C (ethanol-water 1 : 1, ref.<sup>6</sup> m.p. 81–82°C); maleic anhydride (*IV*), distilled, b.p. 82°C/14 Torr.

### Homopolymerization

**Thermal reaction.** Heating *I* for 24 hours at 150°C without solvent provides a dark brown polymer which was dissolved in benzene and isolated in 66.5% yield by precipitation into hexane; molecular weight 950 (VPO in benzene). From *II* after heating for 4 hours at 200°C, 97% of a brown black polymer was isolated. It was only partly soluble. Polymerization of *III* proceeds explosively at 150°C.

**Anionic reaction.** A solution in DMSO containing *I* (0.624 mol/l) and sodium salt of DMSO (0.0758 mol/l) was kept for 12 hours at 25°C, poured into water, the precipitate collected and digested with methanol for the recovery of the monomer. The rest (4.65%) after crystallization from toluene (m.p. 139–141°C) was identified to be dimer: (*E*)-1,4-bis(*p*-dimethylaminophenyl)-1-butene-3-yne



The identification is based on elemental analysis (for  $\text{C}_{20}\text{H}_{22}\text{N}_2$  (290.4) calculated: 82.72% C, 7.64% H, 9.65% N; found: 82.55% C, 7.73% H, 9.68% N), further on MS ( $m/e$  290.4), IR ( $\nu_{\text{C}=\text{C}}$  2180  $\text{cm}^{-1}$ ), and NMR ( $J$  19 c/s, after quaternizing with dimethyl sulphate and ion exchange, the chloride form was investigated in  $\text{D}_2\text{O}$  solution).

A solution in DMSO containing *II* (0.666 mol/l) and sodium salt of DMSO (0.0666 mol/l) was kept for 12 hours at 25°C, poured into water, acidified with hydrochloric acid. The ether extraction separated the unchanged monomer from the precipitate yielding 36.4% of the polymer of molecular weight of 660 (VPO in acetone).

### Copolymerization of *I* and *IV*

The technique used was that with twin ampoules<sup>7</sup> which were charged, deaerated, sealed under argon, and after heating to the desired temperature, the reaction was started by mixing the contents of both compartments under the following conditions: 60°C, 7 hours, 2,2'-azobis(isobutyronitrile) as initiator (0.01 mol/l), total concentration of monomers 1.5 mol/l, solvent benzene. The precipitated polymers were collected, washed with benzene and reprecipitated from pyridine into benzene.

## RESULTS AND DISCUSSION

Thermal polymerization of *p*-dimethylaminophenylacetylene(*I*), *p*-nitrophenylacetylene(*II*), and *o*-nitrophenylacetylene(*III*) provides oligomers with a system of conjugated double bonds in the main chain. Anionic polymerization starts with

transmetalation resulting in the corresponding acetylide. The next course depends on *p*-substitution in aromatic nuclei. In the nitro derivative, due to the electronegativity of the substituent, the acetylene triple bond is more reactive and the corresponding acetylide more easily dissociated and polymerized than in the case of *I*. The acetylide derived from *I* does not react in THF, in DMSO it yields only a dimer, mainly due to the low electrophility of the triple bond. The olefinic analog, *p*-dimethylaminostyrene, on the contrary, smoothly polymerizes by anionic mechanism to high molecular polymers<sup>8</sup>. To improve electrical properties of polyconjugated polymers it would be desirable to fix the polyconjugated chain in a planar configuration and form some intermolecular bonds. Both could be done by forming CT complexes of sufficient strength. *II* and *III* in the combination with *I* appeared to be weak acceptors only, their complexes in polar solvents could not be detected (in benzene or chloroform no measurement could be done due to the limited solubility). *I* gives a complex only with a monomer of greater electron affinity *i.e.* *IV*. But even in this case the value  $\lambda_{\max}$  407 nm (broad asymmetrical band) and the fact that the measurements must be done at higher concentration indicate a weak complex. By the method of continuous variation the stoichiometry of the complex was established to be three *IV* to two *I*. This is again quite different from the case of *p*-dimethylaminostyrene, where only a 1 : 1 complex was observed<sup>9</sup>. Similarly, *N*-dimethylaniline is known to produce 1 : 1 *n*- $\pi$  complexes with most  $\pi$ -acceptors<sup>10</sup>. Consequently the remaining amount of *IV* must be complexed by the phenylacetylene part of the donor molecule and the schematic structure of the complex seems to be that of two *n*- $\pi$  and two  $\pi$ - $\pi$  interactions:

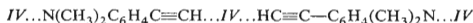


TABLE I

Copolymerization of *p*-Dimethylaminophenylacetylene(*I*) and Maleic Anhydride(*IV*)

Feed composition mol. % <i>I</i>	Yield %	Copolymer composition mol. % <i>I</i> <sup>a</sup>	
		before	after precipitation
30	34.3	29.0	50.6
40	14.9	35.6	52.9
45	28.1	38.3	50.9
50	27.9	36.7	52.6
60	23.7	32.4	50.8
70	3.3	35.2	52.6

<sup>a</sup> Based on N content (Dumas).

Radical copolymerization of *I* and *IV* provides a copolymer which, reprecipitated from pyridine into benzene, has its composition close to the molar ratio 1 : 1. This, in analogy with styrene derivatives, indicates the alternating structure. The composition of the original product, before precipitation, tends to the molar ratio two *IV* to one *I*. This is connected with the appearance of a band at 405 nm. This band disappears by reprecipitation; when measured later with an excess of additional *IV* it appears again, this change being reversible. Consequently, the original product of polymerization is a complex of the alternating *I-IV* copolymer with another *IV* complexed to each pendant dimethylaminophenyl group (Table I).

The anionic polymerization is influenced by the *p*-substitution in phenylacetylene derivatives more than the thermal polymerization. While with anionic mechanism *I* yields only a dimer the other monomers investigated provide higher oligomers. Mononitro derivatives appeared to be weak acceptors. To increase the acceptor properties it would be necessary to introduce at least two nitro groups in one nucleus.

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