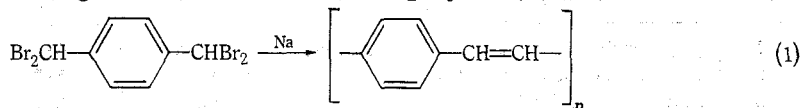


# AN ATTEMPT TO SYNTHESIZE POLY-*p*-XYLYLIDENE [AND RELATED COMPOUNDS BY A WURTZ-FITTIG TYPE REACTION\*

By K. OUCHI†

Recently McDonald and Campbell<sup>1</sup> synthesized poly-*p*-xylylidene by means of the Wittig reaction and obtained a polymer having an average polymerization degree of 9. Hoeg, Lusk, and Goldberg<sup>2</sup> treated  $\omega,\omega'$ -dichloro-*p*-xylene with sodium amide in liquid ammonia and estimated the polymerization degree of their product to be about 10. However, the absorption intensity due to olefinic CH at  $960\text{ cm}^{-1}$  in the infrared spectrum of Hoeg's product was quite small and consequently the existence of a highly conjugated structure is doubtful.

In the present work, attempts were made to synthesize conjugated polymeric materials having semi-conducting and thermoresistant properties by a Wurtz-Fittig type reaction starting from  $\omega,\omega,\omega',\omega'$ -tetrabromo-*p*-xylene (TBPX)



and from  $\omega,\omega,\omega',\omega'$ -tetrabromo-2,6-dimethylnaphthalene (TBDN).

In order to estimate the double-bond content the products were allowed to stand for 24 hr in a solution of bromine in chloroform. Analytical data are presented in Table 1.

The average molecular formulae, calculated on the assumption that four bromine atoms are attached at the end of each molecule, are given in Table 2. With samples 1 and 5 the hydrogen content is greater than the theoretical value. The double-bond content calculated from excess hydrogen is not as reliable as the bromination value because of the lower analytical precision. Generally speaking, about half the double bonds may be saturated.

The infrared spectra of these products (KBr pellets) included a strong peak near  $950\text{--}960\text{ cm}^{-1}$  which may be ascribed to absorption by a CH out-of-plane deformation vibration of *trans*-C=C-. After bromination this peak disappeared completely. For samples 1 and 3 this peak was much stronger than the one noted in the paper of Hoeg, Lusk, and Goldberg,<sup>2</sup> in which it has almost the same intensity as the peak at  $1017\text{ cm}^{-1}$ . This suggests that the product described here (samples 1 and 3) has a much higher double-bond content. In samples 1 and 3 a strong peak near  $810\text{--}820\text{ cm}^{-1}$  may be ascribed to the CH out-of-plane deformation of *para*-substituted benzene rings, and peaks at 810 and  $880\text{ cm}^{-1}$  in sample 5 are those of 2,6-disubstituted naphthalene groups. The peaks in the region of  $1400\text{--}1500$  and  $2800\text{--}3000\text{ cm}^{-1}$

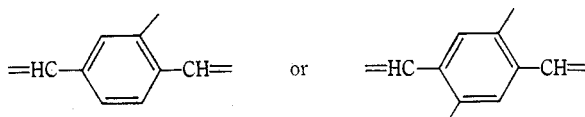
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<sup>1</sup> McDonald, R. N., and Campbell, T. W., *J. Am. Chem. Soc.*, 1960, **82**, 4669.

<sup>2</sup> Hoeg, D. F., Lusk, D. I., and Goldberg, E. P., *J. Polym. Sci. B*, 1964, **2**, 697.

may be ascribed to aliphatic CH deformation and stretching vibrations, and indicate that some saturation of olefinic bonds had taken place, perhaps when the excess sodium metal in the reaction mixture was decomposed by methanol. In sample 3 another out-of-plane deformation vibration is seen at  $870\text{ cm}^{-1}$ , which suggests the presence of the structures



Samples 1 and 5 are yellow like that of Hoeg, Lusk, and Goldberg, while sample 3 is brown. They all show a brilliant greenish yellow fluorescence in ultraviolet light, and are infusible and insoluble in all the ordinary organic solvents. From preliminary measurements the electrical resistivity for the pelleted compounds

TABLE 1  
ELEMENTARY ANALYSES OF PRODUCTS

No.	Sample	Solvent	C (%)	H (%)	Br (%)
1	Polymer from TBPX	toluene	89.3	6.4	4.2
2	Bromination product of No. 1		49.6	3.3	47.1
3	Polymer from TBPX	decalin	92.3	5.7	trace
4	Bromination product of No. 3		47.3	2.6	48.5
5	Polymer from TBDN	toluene	91.3	6.0	2.25

TABLE 2  
AVERAGE FORMULAE AND DOUBLE-BOND CONTENT

	Sample 1	Sample 3	Sample 5
Average molecular formula	$\text{C}_{560}\text{H}_{486}\text{Br}_4$	$(\text{C}_8\text{H}_{5.9})_n$	$\text{C}_{1080}\text{H}_{852}\text{Br}_4$
Theoretical molecular formula	$\text{C}_{560}\text{H}_{420}\text{Br}_4$	$(\text{C}_8\text{H}_6)_n$	$\text{C}_{1080}\text{H}_{720}\text{Br}_4$
Polymerization degree	70	$\geq 70$	90
Theoretical double-bond content			
From excess hydrogen	53	100	27
From bromine absorption	54	43	—

subjected to a pressure of  $6000\text{ kg/cm}^2$  is of the order of  $10^{13}\ \Omega\text{ cm}$ . The X-ray diffraction patterns for all samples have one broad peak at about  $4.8\text{--}5.1\ \text{\AA}$  and a very small peak at  $2.0\text{--}2.1\ \text{\AA}$ , showing the existence of some ordered structures. Differential thermogravimetric analysis showed that all these samples had fairly good resistance to thermal decomposition and experienced little loss of weight at  $400^\circ$ . It may be concluded that although the method described is not successful for the synthesis of fully conjugated polymers it has some superiority compared with the use of sodamide in liquid ammonia,<sup>2</sup> seeing that the samples have a higher degree of conjugation and polymerization than those obtained by earlier workers.<sup>1,2</sup>

### Experimental

$\omega,\omega,\omega',\omega'$ -Tetrabromo-*p*-xylene, m.p. 167–169° (lit. 168–170°), was synthesized as described elsewhere.<sup>3</sup>  $\omega,\omega,\omega',\omega'$ -Tetrabromo-2,6-dimethylnaphthalene was synthesized as follows: 5.2 g of 2,6-dimethylnaphthalene was dissolved in 50 ml of 1,2,4-trichlorobenzene and 7.6 ml of bromine was added drop by drop with irradiation by a 500-W tungsten lamp, the mixture being stirred and maintained at about 120°. After cooling, the crystals were filtered off and recrystallized from carbon tetrachloride. Yield 47%, m.p. 167–168° (lit. 164° from bromination by *N*-bromo-succinimide<sup>4</sup>) (Found: C, 30.5; H, 1.9; Br, 67.2. Calc. for  $C_{12}H_8Br_4$ : C, 30.5; H, 1.7; Br, 67.7%). Nuclear magnetic resonance in carbon tetrachloride (using tetramethylsilane as standard) showed two peaks, one at 6.79 p.p.m. and the other at 7.82 p.p.m. The former (I) was due to the proton in  $CHBr_2$  ( $\omega,\omega'$ -dibromo-*p*-xylene, 4.45 p.p.m.;  $\omega,\omega,\omega',\omega'$ -tetrabromo-*p*-xylene, 6.60 p.p.m.) and the latter (II) to the protons attached to the naphthalene nucleus. The ratio of the peak areas II/I was 2.9 (required value is 3.0). Infrared and ultraviolet spectra show the expected features for this structure.

**Polymerization of Tetrabromo Compounds.**— $\omega,\omega,\omega',\omega'$ -Tetrabromo-*p*-xylene (4 g) was dissolved in 100 ml of solvent (toluene or decalin), about 10 g of sodium metal was added with vigorous stirring, and the reaction was continued for 21 hr at the boiling point of the solvent under a nitrogen atmosphere. The colour of the solution and the sodium changed immediately to dark brown, then black. After the reaction 200 ml of methanol was added in small portions, the reaction mixture being cooled by immersion in ice. The black colour changed to yellow (in toluene) or dark brown (in decalin). After being filtered and washed with methanol and water the product was boiled with water repeatedly until free from bromide ion, and then dried *in vacuo* at 100°. The yield was almost quantitative. The same procedure was used with  $\omega,\omega,\omega',\omega'$ -tetrabromo-2,6-dimethylnaphthalene.

### Acknowledgments

The author is indebted to Mr J. D. Brooks for valuable discussions, to Dr M. Kossenbergh for X-ray diffraction patterns, and to Mr R. J. Cosstick and Mr K. Imuta for technical assistance.

<sup>3</sup> Snell, J. M., and Weissberger, A., *Org. Synth.*, 1955, Coll. Vol. III, 788.

<sup>4</sup> Ried, W., Bodem, H., Ludwig, Ursula, and Neidhardt, H., *Chem. Ber.*, 1958, **91**, 2479.