## HIGHLY UNSATURATED POLYMERS COMMUNICATION 22. DIRECTED SYNTHESIS OF OLIGOMERS POSSESSING THE PROPERTIES OF SOLUBILITY, INFUSIBILITY, THERMAL STABILITY, AND HIGH ELECTRIC RESISTANCE

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In a study of polyacetylenic polymers with the general formula  $H(-C \equiv C-R-C \equiv C-)_nH$ , an important role is played by two of their properties – the ability for further polymerization upon heating and their electric conductivity, which varies within broad limits depending upon the structure of the polymer (from  $10^{-3}$  to  $10^{-20}$  ohm<sup>-1</sup> · cm<sup>-1</sup>). The first property can be used for the production of thermally stable polymers, the second for the production of semiconductors and dielectrics. The main obstacle to the use of these properties is the almost total insolubility of the compounds previously obtained in organic solvents [1-3]. The previously synthesized polymers of the polyethynylpolyarene series, in which the structure of R was selected in such a way as to interrupt the conjugation in the polymer chains, possess high electric resistance, but cannot be used on account of their insolubility [1].

It should be mentioned that in organic compounds the fusibility and solubility, as a rule, are correlated. The higher the melting point of compounds in each series, the lower their solubility in organic solvents. Therefore, to combine in one compound good solubility, which would permit the application of the substance in the form of films, with high melting point and thermal stability, necessary for their use in electronics, is impossible. We had earlier attempted to solve this problem through the use of polyphenyl hydrocarbons (from terphenyl to zexiphenyl) for this purpose, since they can be applied in the form of films by atomization and possess sufficiently high melting points and good dielectric properties. However, this method proved unsuitable in view of the fact that with all their positive qualities, films of polyphenyls do not exhibit any adhesion to glass and metal at all and are spontaneously detached from the backings, thus preventing the construction of electrical devices. The purpose of this work was to create polymers that would be capable of "cross-linking" upon heating and forming thermally stable polymers, would be sufficiently readily soluble, and thus would permit the preparation of films, and would possess high electric resistance.

We developed methods of synthesizing polymers of the diethynyldiarylenemethane series, differing in structure both of the arylene portion of the molecule and of the methylene bridge connecting the benzene rings in the molecule. It was hypothesized that the introduction of substituents into the molecule, either into the ring or into the methylene bridge, could increase the solubility of the polyacetylenic oligomers, as a result of a hindrance of close-packing of their molecules, which should show a substantial increase in volume after the introduction of substituents.

There was no sense in introducing residues of aromatic molecules as substituents for increasing the solubility, since such a change in the structure, as has been shown in certain studies of our Laboratory, does not lead to any increase in solubility. At the same time, in one of our communications [2], it was noted that the introduction of a methyl group into the methylene bridge connecting the benzene rings in the oligomer (I) imparts to it a slight but noticeable solubility



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The oligomer (I) is appreciably soluble in pyridine, but when the solvent is removed it crystallizes and does not form a film exhibiting adhesion to glass and metal. Therefore, our further efforts were directed toward the development of methods of synthesizing analogous compounds, in which the methylene bridge would carry more substituents. At the same time, we tested the influence of the introduction of substituents into the aromatic ring upon the solubility.

In accord with the aforementioned, we developed methods of synthesizing the following oligomers in an effort to solve the problem posed:



The synthesis was conducted according to a general scheme consisting of acetylation of the initial hydrocarbon, replacement of the oxygen of the carbonyl group by chlorine, and dehydrochlorination of the chloro-derivative.

The acetylation of all the initial hydrocarbons was conducted in dichloroethane with acetyl chloride in the presence of excess aluminum chloride. In the acetylation of ditolylmethane, the position in which the acetyl group is inserted remained uncertain; however, in the light of steric considerations, it is most probable that the acetyl group is inserted in the o-position to the methyl group, and not the phenylmethylene group. For the rest, the acetylation of all three hydrocarbons proceeded analogously.



The replacement of the oxygen of the carbonyl groups by chlorine was performed by the action of  $PCl_5$  in benzene solution at 50-70°. Since the products obtained in chlorination are partially dehydrochlorinated, the chlorides formed were subjected to the further reaction without preliminary isolation. Dehydrochlorination of (IX) and (X) was conducted with mixing with excess sodium amide in liquid ammonia, while in the production of (VI) it was conducted in two steps - first the mixture of chlorides was dehydro-

chlorinated by boiling with alcoholic alkali, and then the reaction was brought to completion by mixing with sodium amide in liquid ammonia. (IX) and (X) are white crystalline substances, which sublime under vacuum; (VI) is a liquid that undergoes polymerization upon vacuum distillation. Polycondensation of the diacetylenes was conducted by shaking with oxygen in pyridine solution in the presence of catalytic amounts of cuprous chloride. All three polymers are yellow powders. The least soluble was (II), which does not dissolve entirely in cyclohexanone, but only swells. (III) and (IV) are readily soluble in cyclic ketones and give syrupy solutions, which, when applied onto a glass or metallic surface, form transparent films firmly retained on the backing after the solvent is removed. When the films are heated to 300-350°, they take on a brown color; however, they remain transparent and are not spontaneously detached either from glass or from metal. These films freely withstand atomization of a second metallic layer, during which the temperature is raised to 300-350°.

In measurements of the electric conductivity of the oligomers (II)-(IV), preliminarily heated in a stream of nitrogen to 300°, the following data were obtained: for (II)  $\rho_{20} = 5.7 \cdot 10^{13}$  ohm · cm, for (III)  $\rho_{20} = 4.2 \cdot 10^{15}$ ,  $\rho_{273} = 1.6 \cdot 10^{13}$ ; for (IV)  $\rho_{20} = 1.1 \cdot 10^{14}$ ,  $\rho_{278} = 4 \cdot 10^{13}$  ohm · cm. These data give a basis for assigning (II)-(IV) to the class of insulators.

## EXPERIMENTAL

<u>Production of 2,2-Diphenylpropane</u>. To a mixture of 330 ml of benzene and 12.5 g AlCl<sub>3</sub>, 38 g of 2,2-dichloropropane was added at 5° over a period of 1 h, then another 4 g of AlCl<sub>3</sub> was introduced, and mixed for 2 h at 18°. The mixture was decomposed by pouring out onto ice, the benzene layer was washed with water, dried over CaCl<sub>2</sub>, and redistilled. Yield 28.2 g (42.6%) 2,2-diphenylpropane with b.p. 115-117° (2 mm);  $n_D^{18}$  1.5720. According to the data of [4]: b.p. 90-95° (1 mm);  $n_D^{25}$  1.5692.

A cetylation of 2,2-Diphenylpropane. To a mixture of 28.2 g 2,2-diphenylpropane, 70 g acetyl chloride, and 130 ml of freshly distilled dichloroethane we added 136 g of AlCl<sub>3</sub> over a period of 1 h at 5°, mixed with 0.5 h at 18°, for 1 h at 50°, cooled, and decomposed by pouring out onto ice. The mixture was extracted with benzene, and the organic layer washed with water and dried over CaCl<sub>2</sub>. After distillation of the solvent, we obtained 31.5 g of the product, from which 2,2-bis(4'-acetylphenyl)propane (VII) was isolated by distillation; yield 49.0%; b.p.  $215-220^{\circ}$  (1 mm) [4].

<u>Chlorination of 2,2-bis(4'-Acetylphenyl) propane(VII)</u>. A mixture of 12 g (VII) and 23 g  $PCl_5$  in 100 ml of benzene was kept for 0.5 h at 18°, 15 min at the boiling point of benzene, cooled, and poured out onto ice with ether. The ether-benzene layer was washed with water, and dried over CaCl<sub>2</sub>. The mixture of chlorides obtained was used for the dehydrochlorination reaction without isolation.

<u>Production of 2,2- bis (4'-Acetylphenyl)propane (IX)</u>. An ether-benzene solution of the mixture of chlorides from the preceding experiment was added to sodium amide in liquid ammonia (produced from 9 g Na). The mixture was mixed for 3 h, and 20 g NH<sub>4</sub>Cl and 200 ml of the crude ether were added. The organic layer was removed, washed with water, and dried over CaCl<sub>2</sub>. The ether solution was passed through a column with Al<sub>2</sub>O<sub>3</sub> and the ether distilled off. We obtained 4.57 g of the diacetylene (IX); yield 43.8% [based on the diacetyl (VII)]; m.p. 91-93° (alcohol). Found %: C 93.34; H 6.68. C<sub>19</sub>H<sub>16</sub>. Calculated %: C 93.40; H 6.60. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2119 (C=C); 3364 (=C-H).

Oxidative Polycondensation of the Diacetylene (IX). Portions of  $0.1 \text{ g Cu}_2\text{Cl}_2$ and 0.8 g of the diacetylene (IX) were dissolved in 20 ml pyridine and shaken in an atmosphere of oxygen until the absorption of gas ceased. The reaction mass was decomposed with water, the product washed with water until the absence of copper and chloride ions in the wash waters, washed with alcohol, ether, and dried. We obtained 0.71 g of the polymer (III), representing a powder readily soluble in a number of organic solvents, infusible up to 500°. Found %: C 93.25; H 6.03.  $H(C_{19}H_{14})_6H$ . Calculated %: C 94.05; H 5.95.

<u>A cetylation of 2,2-Diphenylbutane</u>. To a mixture of 9.7 g 2,2-diphenylbutane, 100 ml freshly redistilled dichloroethane, and 25 ml acetyl chloride, 50 g AlCl<sub>3</sub> was added over a period of 1.5 h at 0-5°, the mixture was mixed for 1 h at 18°, for 1.5 h at 50-60°, then decomposed, gradually pouring out into a flask with ice, extracted with benzene, and dried over CaCl<sub>2</sub>. After redistillation under vacuum, we obtained 8.1 g 2,2-bis(4'-acetylphenyl)butane (VIII), yield 75.7%, b.p. 232-233° (1 mm); m.p. 162-164° (alcohol). Found %: C 81.63; H 7.65. C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>. Calculated %: C 81.60; H 7.53.

<u>Chlorination of 2,2-bis (4'-Acetylphenyl)butane (VIII)</u>. A mixture of 7.75 g (VIII), 15 g  $PCl_5$ , and 100 ml abs. benzene was kept for 0.5 h at 18° and 1 h at 75°. Subsequent treatment was as described above. The mixture of chlorides was used for the dehydrochlorination reaction, after preliminarily distilling off part of the solvent.

<u>Production of 2,2-bis(4'-Ethynylphenyl)butane (X)</u>. A solution of the mixture of chlorides from the preceding experiment was added to sodium amide in liquid ammonia (produced from 9 g Na) and mixed for 3 h. Subsequent treatment was as described above. We obtained 3.3 g of the diacetylene (X); yield 65.5%; m.p. 124-126° (alcohol). Found %: C 93.11; H 6.88. C<sub>20</sub>H<sub>18</sub>. Calculated %: C 92.93; H 7.02. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2119 (C=C); 3364 (=C-H).

<u>Oxidative Polycondensation of the Diacetylene (X)</u>. Conducted as described above with 1.2 g of the diacetylene (X) in the presence of 0.12 g  $Cu_2Cl_2$  and 40 ml pyridine. We obtained 1.1 g of the oligomer (IV), light yellow in color. Found %: C 92.68; H 6.86.  $H(C_{20}H_{16})_{6}H$ . Calculated %: C 93.59; H 6.41.

<u>Acetylation of Ditolylmethane</u>. Conducted according to the procedures described above for (VII) and (VIII). After treatment of the complex obtained from 40 g of ditolylmethane, 100 g acetyl chloride, and 204 g AlCl<sub>3</sub> in dichloroethane solution and redistillation of the product obtained, we obtained 22 g of bis(3'-acetyl-4'-methylphenyl)methane (V); yield 57.5%; b.p. 205-207° (1 mm);  $n_D^{18}$  1.5920. Found %: C 81.39; H 7.19.  $C_{19}H_{18}O_2$ . Calculated %: C 81.60; H 7.22.

<u>Chlorination of bis(3'-Acetyl-4'-methylphenyl)methane (V)</u>. A mixture of 12.2 g of the diacetyl (V), 23 g PCl<sub>5</sub>, and 100 ml of benzene was heated for 1 h at 70°. Subsequent treatment as described above. The mixture of chlorides obtained was used for the dehydrochlorination reaction without isolation.

Production of bis(3'-Ethynyl-4'-methylphenyl)methane (VI).

<u>Dehydrochlorination with KOH</u>. The solution of chlorides was heated on a water bath to boiling, and a solution of 50 g KOH in 160 ml abs. alcohol was added with mixing over a period of 1 h. The mixture was boiled for 7 h, cooled, decomposed with water, dried over  $CaCl_2$ , and used for the dehydrochlorination reaction with sodium amide.

<u>Dehydrochlorination with Sodium Amide</u>. The crude diacetylene (VI) was added to sodium amide (produced from 6 g Na), mixed for 3.5 h, then treated analogously. After distillation of the solvent and purification of the substance by passage through a column with  $Al_2O_3$ , we obtained 3.5 g (VI); yield 38.4%;  $n_D^{20}$  1.6085. Found %: C 93.56; H 6.62.  $C_{19}H_{16}$ . Calculated %: C 93.40; H 6.60. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2119 (C=C); 3335 (=C-H).

<u>Oxidative Polycondensation of the Diacetylene (VI)</u>. Conducted analogously to that described previously with 2.5 g of the initial diacetylene (VI) and 0.5 g  $Cu_2Cl_2$  in 60 ml of pyridine. Yield of the polymer (II) quantitative. Found %: C 93.25; H 5.86.  $H(C_{19}H_{14})_4H$ . Calculated %: C 93.40; H 6.60.

## CONCLUSIONS

A means of synthesizing soluble polyacetylenic polymers of the diphenylmethane series was discovered.

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