POLYCONDENSATION OF 2-METHYL-6-PYRIDINEALDEHYDE*

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LINEAR polymers of phenyl- [1,2], α , β - and γ -pyridineacetylene [3] have low electrical conductivity ($\sigma_{300^{\circ}\text{K}} \sim 10^{-15}-10^{-16}$ ohm⁻¹ cm⁻¹ when $\Delta E = 1-2$ eV) owing to the fact that continuous conjugation does not cover the whole of the macrochain. Authors studying the absorption spectra [4] and the NMR spectra of polyvinylenes [5] showed that the polyene polymer chain consists of separate noncoplanar conjugated blocks, and also that the size of the conjugated block depends on the type of monomer and on the polymerization conditions. At the same time it was found that the π -electrons of the phenyl and pyridine side groups are not coplanar with the π -electrons of the polyene chain (with the exception of the terminal rings), and this not only reduces the extent of the conjugation but also lessens the π -orbital intermolecular interaction.

In view of the above we attempted to synthesize polymers in which the π -electrons of the aromatic ring form a single electron system with π -electrons of the main chain. A special point of interest was the introduction of the pyridine ring into the system; the free electron pair of the latter makes a considerable contribution to the delocalization of π -electrons.

It has already been shown [6] that $poly-\alpha$ -lutidilene is formed when 2,6-dibromomethyl pyridine is treated with sodamine, though in this case also the separate conjugated segments in the macromolecule are broken by saturated . . . $CH_2-CHX...$ groups.

We studied the possibility of preparing polymers with conjugated chains by the polycondensation of 2-methyl-6-pyridinealdehyde.

We know [7] that the polycondensation of 2-methyl-6-pyridinealdehyde takes place readily in the presence of acetic anhydride and leads to the formation of dark coloured polymers with $\overline{M}_n = 2000-2600$ which dissolve in pyridine, aniline, dimethylformamide, dimethylsulphoxide, tetrahydrofuryl alcohol, and acids, and are insoluble in the usual organic solvents.

The reaction scheme is:



The resulting polymers have considerable dark conductivity ($\sigma_{300^{\circ}\text{K}}=10^{-11}-10^{-12}$ ohm⁻¹ cm⁻¹) and also photoconductivity, and give an EPR signal with a concentration of 9.6×10^{18} spins/g.

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The structural analysis of the polymers was based on the electron IR, NMR and luminescence spectra. The UV spectrum of the polymer (Fig. 1) has a band with λ_{max} at 267.5 m μ , and there are also marked inflexions at 315 and 360 m μ .



FIG. 1. Absorption spectra of polymer of 2-methyl-6-pyridinealdehyde (1) and its quaternary salt (2). Solvent-tetrahydrofuryl alcohol, concentration 1%, cell thickness 1 cm.

FIG. 2. Luminescence spectrum of polymer of 2-methyl-6-pyridineal dehyde in aniline (c=0.3 g/l.).

A feature of the spectrum is the very flattened longwave decay. The band with $\lambda_{\max} = 267.5 \text{ m}\mu$ is related to the absorption of pyridine rings. The inflexions at 315 and 360 m μ correspond to the absorption of the polyene system of the macromolecule. Assuming that the pyridine ring in the polyene system of the macromolecule behaves like a single double bond we may estimate the size of the conjugated blocks by comparing λ_{\max} for the polymer with the absorption of linear unsubstituted polyenes. In this case a band at 315 m μ will correspond to $n_c = 4$, and for 360 m μ $n_c = 6$.

The considerable longwave decay shows that the macromolecule contains conjugated segments with $n_c > 6$. This agrees with the findings based on the luminescence spectra (Fig. 2). The broad band in the spectrum from 460 to 700 m μ with peaks at 510 and 630 m μ corresponds to conjugated segments with n_c from 5 to 8. The introduction of a charge into the polyene system does not alter the appearance of the spectrum (Fig. 1).

NMR analysis of the polymer macromolecule was necessary in order to determine the presence of aldehyde and methyl terminal groups in the macromolecule, and to find the number of these groups. Considerable difficulties arise in using

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the NMR method of structural investigation owing to the lack of any solvent in which the whole spectrum from 0 to 10 p.p.m. could be recorded. Separate portions of the spectrum were therefore examined.

The spectrum of the initial 2-methyl-6-pyridinealdehyde (20% solution in alcohol, 25°) (Fig. 3, curve 1) consists of the signals $\delta = 2.5$ p.p.m. (--CH₃), the multiplet for protons of the pyridine ring with $\delta = 7.0-7.9$ p.p.m. and $\delta = 9.7$ p.p.m. (-CHO). The spectrum of the polymer dissolved in pyridine (Fig. 3, curve 2) has the signal $\delta = 1.5 - 2.7$ p.p.m. (CH₃ group) and one for the aldehyde protons in the region of $\delta = 9.7$ p.p.m. The signals for the remaining protons of the polymer are overlapped by the intense signal of the solvent. Measurement of the areas below the signals of the methyl and aldehyde protons shows that the $--CH_3$ -CHO groups ratio is 1:1. The spectra of the polymer were also recorded in CF₃COOH, CD₃COOD, DCOOD, etc. The spectrum of the polymer in CF₃COOH (Fig. 3, curve 4) consists of two broad polymer signals with $\delta = 1.5$ -2.7 p.p.m. (-CH₃) and 6.7-8.6 p.p.m. (protons of pyridine ring and -CH=). In the region of $\delta = 1.5 - 2.7$ p.p.m. there are also the signals of NH groups appearing through the formation of polymeric quaternary salt. The ratio of the areas. below these two signals, taking the resulting NH groups into account, shows that there is one methyl group per 2-3 units of polymer. The region of the signal



FIG. 3. NMR spectra: 1-2-methyl-6-pyridinealdehyde in ethanol; 2-4-polymer of 2-methyl-6-pyridinealdehyde in pyridine, CD_sCOOD and CF_sCOOH respectively.

for the aldehyde groups is overlapped by the signal of carboxyl groups of the solvent. The spectrum of the polymer dissolved in CD_3COOD (Fig. 3, curve 3) has the broad signal $\delta = 6.5 - 8.3$ p.p.m. of protons of the pyridine ring and =CH = groups of the polymer. The signal $\delta = 2.6$ p.p.m. for CH_3 gorups of the polymer is close to the intense signal of the methyl groups of impurities in the solvent. The ratio of the areas of the signals for CH_3 groups and for pyridine ring protons and olefin protons, taking the emerging NH groups into account as well as the fact

that the admixture of acetic acid in the CD_3COOD is not more than 6% shows that there is one methyl group for every 3-4 polymer units. As in the experiment with CF₃COOH, the signal of the aldehyde group is masked by the intense



FIG. 4. IR spectra of polymers of 2-methyl-6-pyridinealdehyde (1) and its quaternary salt (2).

signal of the carboxyl group of impurities. The low molecular weight (350-450) obtained by NMR spectroscopy seems improbable, as good films of the polymer are obtainable from solution, and it dissolves only in strong polar solvents, which one would not expect with a trimer or tetramer. The molecular weight based on reverse ebullioscopy in pyridine at $31\pm0.01^{\circ}$ is 2000-2600. The low value for \overline{M}_n obtained by the NMR method is understandable. With the highly concentrated solutions used for NMR spectroscopy (~20%) the solubility of the high molecular weight fraction is considerably reduced, and the undissolved residue is removed by filtering the solution in order to purify it. It is the dissolved low molecular weight fraction which is responsible for the observed relationship between signals of the terminal group protons, those of the pyridine rings and =CH groups.

The IR spectra of the polymer (Fig. 4) have bands at 3070, 2950, 1710, 1600, 1580, 1460, 1375, 1160, 990, 890, 790, 760 and 710 cm⁻¹. The 3070 cm⁻¹ band may be attributed to the valency vibrations of C—H bonds in the pyridine ring. Several other bands are also related to different vibrations of the pyridine ring: a band at 1600–1590 cm⁻¹ is characteristic of the valency vibrations of C=C and C=N bonds of 2,6-substituted pyridines, and a band in the region of 1460–1450 cm⁻¹ is related to a trisubstituted aromatic ring with displacement from the initial region towards lower frequencies (in the case under consideration the 2,6-substituted pyridine ring may be regarded as a trisubstituted benzene ring with substituents nearby. Two bands at 790 ad 750 cm⁻¹ correspond to out-of-plane deformation vibrations of three unsubstituted H atoms in an aromatic ring. These vibrations should also appear as medium intense absorption in

the region of 725–680 cm⁻¹. The spectra of our samples have a band in the region of 710 cm⁻¹. The terminal methyl group appears in the spectrum as weak absorption in the region of 1380–1370 cm⁻¹ characteristic of C—H bond symmetrical deformation vibrations. The terminal aldehyde group was determined from the absorption in the region of 1710 cm⁻¹ characteristic of the C=O bond, as well as from the weak absorption in the region of 1320–1260 cm⁻¹. This may



Fig. 5. Photoconductivity spectrum of polymer.

account for the band close to 2950 cm⁻¹. This band appears with *ortho*-substituted benzaldehydes (the free electron pair of pyridine acts as the *ortho*-substituent). The presence of the aldehyde groups is also shown by the increased intensity of the 1580 cm⁻¹ band observed when an aromatic ring is conjugated with an aldehyde group.



FIG. 6. Thermomechanical curve of the polymer.

The intensity of the bands characterizing the aldehyde group in the spectrum of the polymer is low, probably owing to the relatively small number of aldehyde groups.

The polycondensation of 2-methyl-6-pyridinealdehyde therefore results in a

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linear polymer in which the pyridine rings are part of the polyconjugated system, and together with the latter form a single electron system. However, as also was found with polyphenylacetylene [2, 4], there is no continuous conjugation of the macromolecule, but the latter consists of separate conjugated blocks with $n_{e}=4-8$, and moreover the size of the macromolecule considerably exceeds that of the largest conjugated block. The pyridine ring introduced into the polyene chain, and also the size of the conjugated block which is much larger compared with polyarylvinylenes increase the dark conductivity level by 3-5 orders compared with polyphenylacetylene [1] and poly- (α, β, γ) -ethynylpyridine [3]: for $\Delta E = 0.6 - 0.7$ eV values of $10^{-11} - 10^{-12}$ are obtained. At the same time the methylpyridinealdehyde polymers have considerable photoconductivity ($\sigma_{\rm ph} = 10^{-9} - 10^{-11}$ ohm⁻¹ cm⁻¹ when the degree of illumination is 10^{-14} - 10^{-15} quant/sec·cm²). Moreover the absorption spectrum largely determines the photoconductivity spectrum. As may be seen from Fig. 5, the photoconductivity spectrum of the polymer covers the whole of the visible infrared region including also some of the short-range region. The high degree of delocalization of the π -electron cloud of a polyconjugated block when the chain contains a nitrogen probably accounts for the high paramagnetism of the polymer. The EPR spectra of all the obtained products have a single symmetrical signal with a g-factor of 2.00 as is observed with polyarylvinylenes also; the paramagnetic particle concentration amounts to 9.6×10^{18} spin/g. Considering that radical processes are excluded by the method of polymer preparation the EPR signal is probably from fractions containing very long conjugated blocks in which the splitting of the π -bond is possible [8]. The stabilization of the emerging radicals is apparently due not only to electron delocalization in respect to the conjugated block but also to the formation of intermolecular complexes [9]. The larger sizes of the conjugated blocks compared with polyarylvinylenes, and also the strong intermolecular interaction probably explain the high paramagnetism and the improved thermal stability of the polymer. The products obtained are not subject to degradation when heated up to 250-300° in air for 6 hours.

It was found by X-ray structural analysis that the polymers are amorphous products. Only separate diffuse halos are seen in the X-ray pictures.

A thermomechanical study of the polymer (Fig. 6) also showed that it is a typical linear amorphous polymer with a softening point in the region of 190° . Flow ceases before 90% deformation of the polymer is reached; this is probably due to crosslinking in the course of thermal processing.

The tertiary nitrogen atom in the polymer makes it possible to introduce a positive change into the polyene system by the formation of quaternary polymeric salt. We attempted to carry out a Menshutkin reaction but the lack of solvents for the polymers in question makes this difficult. A quaternary polymeric salt was obtained in dimethylsulphoxide and tetrahydrofuryl alcohol. Dimethylsulphoxide proved unsuitable because in this solvent a lot of reactions take place between polymer and solvent and between solvent and alkyl halide. A slow reaction took place in tetrahydrofuryl alcohol and the yield of quaternary salt was quite small. In view of the results of elementary analysis we conclude that practically every monomer unit in the resulting polymeric quaternary salt has a charged nitrogen atom. It is difficult, however, to come to a definite conclusion regarding the chemical composition of the monomer unit, since it is mainly the low molecular weight portion of the polymer that is involved in the reaction.

Moreover the hydrolysis of RI leads to the formation of HI which reacts with the pyridine rings of the polymer chain. The IR spectra of polymeric quaternary salts generally coincide with those of the initial products (Fig. 4).

The increased intensity of the band at $1380-1370 \text{ cm}^{-1}$ in the IR spectrum is caused by the appearance of N-ethyl groups in the macromolecule; the increased intensity of the bands characterizing the aldehyde group is probably due to the fact that the reaction resulting in the quaternary salt mainly involves a low molecular weight fraction in which the number of aldehyde groups is relatively rather high.

When very dilute the obtained acetone-soluble product showed an anomalous rise in viscosity characteristic of polyelectrolytes (there was a marked rise in the viscosity of the solution starting at 0.025% concentration). The paramagnetism of the polymeric quaternary salt is retained; there is no change in the dark conductivity level.

EXPERIMENTAL

2-Methyl-6-pyridinealdehyde [10] was obtained by the scheme:



Into a three-necked 100 ml flask with a thermometer, reflux condenser and stirrer were placed 4.92 g of 6-methyl-2-hydroxymethylpyridine and 40 ml of dioxane. 2.6 g of comminuted selenious acid were added to the solution obtained, and the reaction mass was heated, while stirring rapidly, to 80°; this temperature was then maintained for 3 hr. The mixture was cooled, Se was filtered off, followed by washing with three portions of dioxane. The solvent was distilled off with a dephlegmator and the residue was vacuum-distilled and a fraction was taken with b.p. $67-68^{\circ}/8$ mm which crystallized into a substance with m.p. 32°. Yield -50%of theory. The NMR spectrum of 2-methyl-6-pyridinealdehyde recorded in CCl₄ showed signals at 2.5 p.p.m. (-CH₃), 7.0-7.9 p.p.m. (multiplet for protons of pyridine ring) and 9.7 p.p.m. (-CHO).

No signals from protons of impurities appeared in the spectrum.

Polycondensation of 2-methyl-6-pyridinealdehyde [7]. A mixture of 1.6 g 2-methyl-6-pyri-

dinealdehyde and 1 g of acetic anhydride were placed in a dry glass ampoule in an inert atmosphere. The sealed ampoule was heated to 200° and kept at this temperature for 5 hr. The ampoule was then opened and the reaction product was dissolved in 10% hydrochloric acid. The solution was filtered and the polymer precipitated with a large excess of concentrated aqueous ammonia or NaOH. The precipitate was filtered and purified by repeated reprecipitation from hydrochloric acid by ammonia. The product was washed with water to pH = 7, after which it was dried at 100° to constant weight. Polymer yield: 1 g.

Found, %: C 82.46; H 5.18; N 13.72. Calculated, %: C 81.55; H 4.85; N 13.60.

Preparation of quaternary polymeric salts. 1.6 g of C_2H_5I was added to a solution of 0.54 g of polymer in 30 ml of tetrahydrofuryl alcohol. The mixture was heated in a dry sealed ampoule (purged with argon) at 90° for 30 hr.

On opening the ampoule the solvent was removed at $52-54^{\circ}/5$ mm. The residue was treated with hot acctone to separate the reacted polymer. The quaternary salt was separated from solution in acctone by precipitation with ether. Purification was affected by repeated reprecipitation. The polymer was vacuum-dried over P_2O_5 ; yield: 0.1 g.

Found, % C 40.05; H 2.52; N 6.61; I 46.82.

The IR spectra of the polymers were recorded on a Hitachi–Perkin–Elmer apparatus in the region of 4000–600 cm⁻¹. Samples in disc form with KBr were prepared.

An ISP-51 spectrophotometer with an SEP photoelectric attachment (0.4/0.402 aperture) was used to record the fluorescence spectra of solutions of the polymers in aniline (0.3 g/l.) in the region of 400-700 m μ .

X-ray photographs of polymer powders were obtained with an URS-55 diffractometer with K_a Cr radiation and a vanadium filter to eliminate β -radiation.

The NMR spectra of the polymers were obtained on a JNM-3H-60 apparatus.

The EPR spectra were recorded on an EPR-2 radiospectrometer.

The electron spectra of the polymer and its quaternary salt were obtained by means of an SPh-4A spectrophotometer.

The electrical conductivity of polymer powders under a pressure of 300 kg/cm^2 measured in a vacuum apparatus at 10^{-2} mmHg over the range $20-150^\circ$ using an E-6-3 terachmmeter. The conductivity activation energy was found using the equation

$$\sigma = \sigma_{0^6} - \frac{E}{2kT}$$

The photoconductivity of the polymers was determined on a device which enabled us to measure changes in conductivity under the effect of a monochromatic beam of light (with an intensity of 10^{14} - 10^{15} quanta/sec·cm³. The measurements were carried out *in vacuo* (10^{-5} mmHg) using polymer films 5-10 μ thick, prepared from solution in pyridine.

The thermomechanical curve was obtained under uniaxial compression (discs $2\cdot 20-3\cdot 5$ mm thick) with a constant load on a Tsetlin device. The specific pressure amounted to $0\cdot 8$ kg/cm², and the heating rate was 100° /hr.

The number-average molecular weights of the polymers were found by "reverse" ebullioscopy at 30° in pyridine.

CONCLUSIONS

(1) Using the polycondensation of 2-methyl-6-pyridinealdehyde as an example a method of preparing polymers with heteroatoms in the conjugated chains has been developed.

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(2) The results of IR-, UV- and NMR analysis, together with the luminescence spectra prove that the polymers are linear and consist of separate conjugated blocks each containing 4-8 elementary units.

(3) It has been shown that the polymers produce EPR signals and have increased dark conductivity ($\sigma_{300^{\circ}K} = 10^{11} - 10^{12} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$) and photoconductivity ($\sigma_{ph} = 10^{-9} - 10^{-10} \text{ cm}^{-1}$).

(4) Quaternary polymeric salts have been obtained.

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INITIATION OF POLYETHYLENE OXIDATION IN THE SOLID PHASE*

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IMPORTANT results were obtained in a quantitative study of the oxidation of hydrocarbons by means of initiated oxidation [1]. This method is based on measurement of the rate of oxidation in the presence of an initiator ensuring that

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