Synthesis and properties of poly(9,10-anthracene diylidene)

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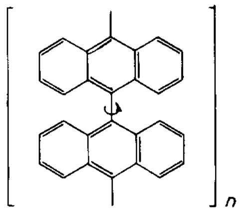
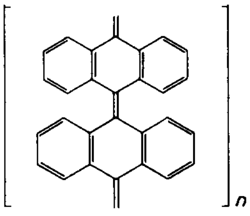
A new conjugated polymer, poly(9.10-anthracene diylidene) has been prepared by self-condensation of anthrone in poly(phosphoric acid). The polymer exhibited high thermal and oxidative stability, thermochromism, semiconductive and paramagnetic properties.

INTRODUCTION

The semiconductive properties of anthracene are well known and have been the subject of many investigations. It is of considerable interest to prepare a polymer with anthracene as a constitutional repeating unit. Such a polymer has already been synthesized[1–4]. The repeating units, however, are connected with single bonds which permits their rotation to some extent:


(I)

Such a rotation disturbs the chain coplanarity and in this way the conjugation. Hence, the number of conjugated repeating units is smaller than the total number of repeating units in the macromolecule. Consequently, it is of further interest to prepare a polymer with anthracene repeating units connected by double bonds. Free rotation around the double bond in this case is impossible, and only some torsional motions may take place. It may be assumed that the polymer repeating units lie in the same plane:


(II)

It is expected that such a polymer will exhibit better semiconductive properties and should have high thermal stability.

EXPERIMENTAL

Materials

Anthrone (Chemapol Czechoslovakia) was twice recrystallized from ethanol (m.p. 162°–165°C). Dianthrone was obtained according to the method given in ref 5 (m.p. 255°C). Poly(phosphoric acid) was prepared from AR P_2O_5 (Reanal Hungary) and distilled water and then heated for 24 h at 120°C. Its P_2O_5 content was 84% (determined refractometrically[6]).

Apparatus

I.r. spectra were recorded from KBr pellets on a UR-10 spectrophotometer (Zeiss–Jena). Electronic spectra were recorded on a Specord spectrophotomer (Zeiss–Jena) in the visible region in a hexamethyl phosphoric triamide solution at various concentrations (0.0012–0.012 g/l). Spectra at elevated temperatures were recorded in a thermostatically controlled cell. E.s.r. spectra were recorded in air using a JES-3BSX (Jeol) apparatus with diphenylpicryl hydrazyl as standard. X-ray patterns were photographed with a DPOH-1 apparatus (USSR) with a Cu cathode and with a monochromator. Electrical conductivities were measured as previously described[7]. Thermogravimetry was performed on a Paulik–Paulik–Erdey analyser (Derivatograph, Hungary)

Polycondensation of anthrone

A solution of anthrone (18 g) in poly(phosphoric acid) (240 g) was heated at 140°C with stirring in nitrogen. Samples were removed and visible spectra were taken in dimethylformamide. After 15 h no further bathochromic shift occurred. The dark solution was poured into a large volume of distilled water. The precipitated polymer was filtered, washed with water, then with a 5% solution of ammonium hydrogen carbonate and again with water until neutral. It was then dried, extracted with methanol, and again dried *in vacuo* at 130°C. The product was a black powder soluble in *N*-methyl pyrrolidone, hexamethyl phosphoric triamide and a 5% solution of LiCl in *N,N'*-dimethyl acetamide. Yield 14.9 g (83%); softening interval 259°–264°C. Calculated for $(C_{14}H_8)_n$: C = 95.42%, H = 4.57%; found, C = 93.52%, H = 4.62%. $\eta_{sp}/c = 7\ cm^3/g$ (0.001 g/cm^3 in *N*-methyl pyrrolidone at 20°C).

Singlet oxygen oxidations

Oxidations were performed according to the method given in ref 8. The methylene chloride solution of the substance investigated and of methylene blue (as photosensitizer) placed in a quartz vessel was irradiated for 2 h with a

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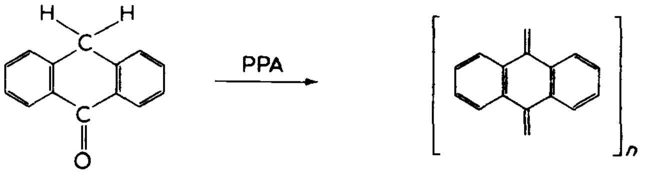
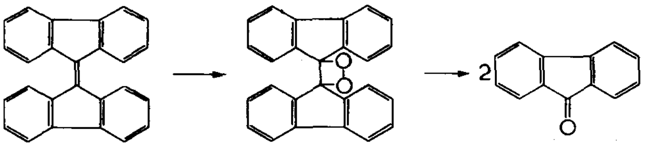
low pressure mercury lamp under a continuous oxygen stream. After solvent evaporation the residue was sublimed *in vacuo* and the product analysed.

RESULTS AND DISCUSSION

We tried several methods to prepare polymer II. Our attempts to make use of the Wittig reaction were unsuccessful. We found that 10-triphenylphosphoranyl anthrone (obtained from the method in ref 9) shows small reactivity even in boiling dimethylformamide. The Horner reaction starting with 10-bromoanthrone and triethylphosphite gave no positive results either. The Siegrist reaction[10] was also attempted. The condensation of anthrone–anil under different conditions did not lead to polymer products. The last possibility was to find out whether self-condensation of anthrone in poly(phosphoric acid) could produce this polymer. We had prepared earlier[11] a conjugated polymer by self-condensation in poly(phosphoric acid) of a similar compound: acenaphthenone. It was found indeed that the self-condensation of anthrone in poly(phosphoric acid) is a suitable method for preparing the corresponding polymer:



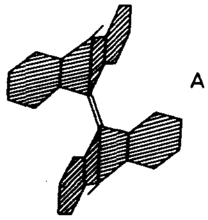
The product thus obtained shows the characteristic properties of the conjugated polymers. It is black, with limited solubility and of high thermal stability. Such properties are exhibited by all aromatic conjugated polymers: polyphenylenes, polyanthracenes, etc. Their repeating units however are connected by single bonds. Hence it was necessary to prove that in our case the repeating units were connected as expected with double bonds and not with single ones. A suitable method was polymer oxidation followed by the investigation of the reaction products. For comparison poly(9,10-anthracenylene) (I), the polymer with single bonds between the anthracene units, was also oxidized. This polymer was prepared by polycondensation of 9,10-dilithiumanthracene with 9,10-dibromoanthracene as described[1]. To elucidate the polymer structure, it was necessary to use a selective oxidation method affecting only the double bonds and not the single ones. Potassium dichromate oxidation of both polymers produced anthraquinone, thus showing that the polymers are built up of anthracene units, but without indication of the kind of connection between them. It is known that singlet oxygen affects the double (C=C) bonds and not the single ones[12]. Singlet oxygen destroys, for example, the double bonds of 9,9'-bifluorenylidene as follows[8]:



A similar reaction path could be expected in the case of polymer II but not in the case of polymer I. Both polymers were oxidized in the same manner. Poly(9,10-anthracene diylidene) (II) gave anthraquinone as oxidation product while poly(9,10-anthracenylene) (I) remained almost unaffected. These results show that the new polymer poly(9,10-anthracene diylidene) has the structure already assumed.

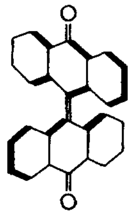
The i.r. spectrum of polymer II corresponded to its structure. There were low intensity absorption bands at 1862 and 2930 cm^{-1} (methylene group) and at 1648 cm^{-1} (carbonyl group) The carbonyl band in anthrone is situated at 1670 cm^{-1}. The lowering of the corresponding band in the polymer spectrum is due to the conjugation. The presence of these bands shows, however, that the polymer has low molecular weight. Elemental analysis data correspond to a chain consisting of 5–6 structural repeating units.

Polymer II showed absorption in both the u.v and visible regions with a maximum at about 560 nm. Upon heating a solution in hexamethyl phosphoric triamide at 100°C, a bathochromic shift (about 7 nm) was observed. No further shift occurred at higher temperatures (until 190°C). This thermochromism cannot be explained by any association–dissociation equilibrium since the absorption follows the Lambert–Beer law. Such behaviour is not unexpected since the low molecular analogue of this polymer, bianthrone, shows thermochromism as well[13,14]. This thermochromism has been the subject of many investigations[13,14]. It has been explained by the existence of two different conformations of bianthrone[13]. In the first, low temperature form, I, the double bond is without strain but the two anthrone moieties are not planar. They are folded about the 9.10 axis.



A

Upon heating or under visible light illumination, a transition of A into B occurs. In the B form the anthrone moieties are planar but they are twisted by 57° about the double bond.



B

In this form a large torsion effect occurs in the double bond. These two forms account very well for the chemical properties of bianthrone. The low temperature form, A undergoes dehydrogenation by molecular oxygen giving helianthrone and *meso*-naphthodianthrone. In B the twisted position of the anthrone moieties makes such reactions impossible and this form is very stable to oxygen. In poly(9 10-anthracene diylidene) the repeating units are connected in the same manner as the two anthrone moieties in bianthrone. The thermochromism in this case may be explained in a similar way – by the existence of two different conformations of the chain (*Figure 1*).

The change of the polymer spectrum was observed below 100°C. If this change is determined from a change in the polymer chain it could be detected by another method. It is interesting that in the d.t.a. curve (*Figure 2*) there is a peak at about 100°C. If this is determined from the transition of I into II it must be reversible. This was confirmed by repeated heating and cooling of a polymer sample.

Furthermore, an enhanced oxidative stability of the polymer at higher temperatures could be expected due to the resistivity of II (existing under these conditions) to molecular oxygen[13]. This expectation was confirmed by the thermogravimetric data (*Figure 2*) The curves in nitrogen and in air are very close to each other. This is a very rare feature in high temperature polymers.

As a conjugated polymer poly(9,10-anthracene diylidene) exhibits paramagnetic and semiconductive properties. It was found that the dark conductivity temperature dependence obeys the equation $\sigma = \sigma_0 \exp(-E/kT)$. *Figure 3* shows that breaks in the curves occur both in air and *in vacuo*. Similar breaks have been observed many times with semiconductive polymers. They have been explained more often by the polymer polydispersity than by impurities. It is interesting that in our case these breaks occur at about 80°-88°C. This temperature is close to the transition temperature of polymer in the form A to the form B. The transition changes the chain coplanarity and hence the conjugation length and probably the intermolecular interactions. Both these factors determine the semiconductive properties. Hence it could be assumed that the breaks in the temperature – conductivity curves are determined by the transition in the polymer chain. The activation energies of the conductivity (*Table 1*) are higher above the transition temperature. The bathochromic shift in the electronic spectra at higher temperatures mentioned above, is an indication of an increase of the conjugation length. In other cases such an increase leads to an activation energy decrease. The higher values observed could be a result of lower intermolecular interactions. The chain models show that polymer form B is bulkier, thus obviating intermolecular interaction.

Poly(9,10-anthracene diylidene) shows an intensive signal of electron spin resonance (*Table 1*). This signal is narrow and symmetric and has the same *g* factor as the free electron. In solution the signal is preserved, which shows that the signal is characteristic of the polymer molecules and not of the solid phase.

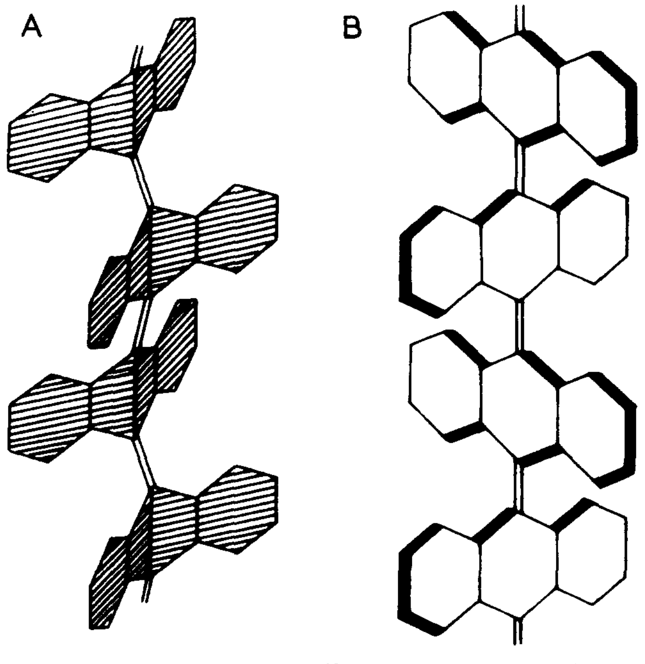


Figure 1 A and B forms of poly(9,10-anthracene diylidene)

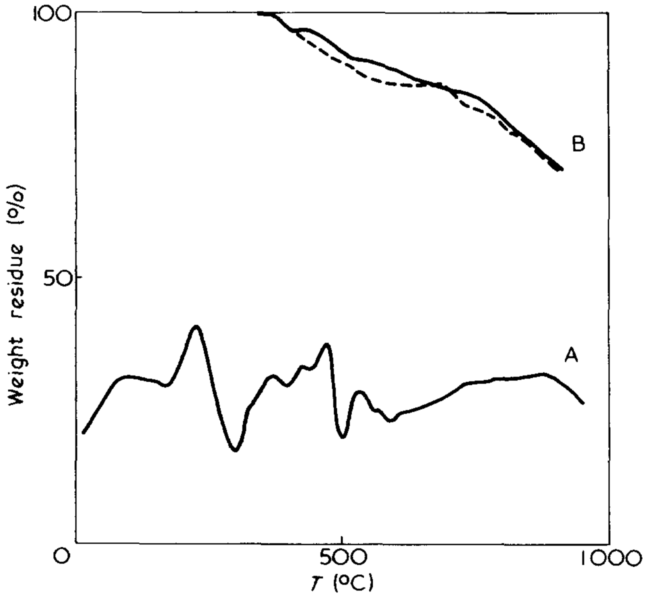


Figure 2 A, D.t.a. and B, t.g.a. curves of poly(9,10-anthracene diylidene), T = 10° C/min; (——), in nitrogen; (— — —), in air

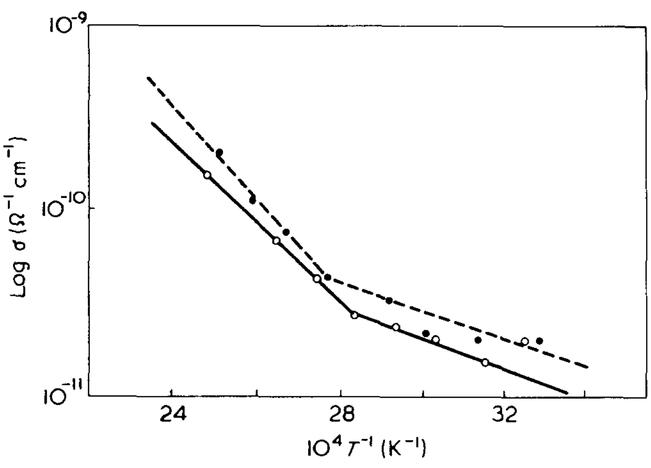


Figure 3 Temperature dependence of the electrical conductivity measured *in vacuo* (——) and in air (— — —)

Table 1 Electrical and magnetic properties of poly(9,10-anthracene diylidene)

	Electrical properties				
	Vacuum		Air		
	E_{act}(eV)^a	σ_{298K} (Ω^{-1}cm^{-1})	E_{act}(eV)^a	σ_{298K} (Ω^{-1}cm^{-1})	Unpaired spins/g
Below the break	0.16	1.35×10^{-11}	0.14	1.90×10^{-11}	1.88×10^{19}
Above the break	0.40	–	0.50	–	–

[a] 1 eV ≈ 1.6021×10^{-19} J

The X-ray patterns of the polymer indicate an amorphous structure. Annealing at 100°, 120° and 180°C for 3 h did not change the structure and the electrical conductivity.

Some of the following conclusions might be drawn from our results. Poly(9,10-anthracene diylidene), as a polymer with double bonds between the anthracene rings, exhibits good thermal stability. Its electrical conductivity is about 6 orders of magnitude higher than that of anthracene[15], but is not higher than the conductivities of most conjugated polymers. This is probably due to the fact that, contrary to our previous expectations, the repeating units in both polymer forms (A and B) do not lie in the same plane.

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