Synthesis and properties of 1,5- and 1,8-dichloro-substituted poly(9,10-dihydroanthracene-9,10-diylidene)s

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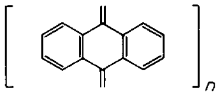
Two new dichloro-substituted poly(9,10-dihydroanthracene-9,10-diylidene)s were prepared by self-condensation of 1,5-dichloroanthrone and 1,8-dichloroanthrone. The bromination and thermal and semiconductive properties were investigated.

Keywords Polymers; thermal properties; stability; semi-conduction; dichlorosubstitution; polyconjugated polymers; poly(9,10-dihydroanthracene-9,10-diylidene)s

INTRODUCTION

Recently we have reported[1] the synthesis of poly(9,10-dihydroanthracene-9,10-diylidene)* – a polymer built up of anthracene repeating units connected with double bonds:



This polymer displays properties characteristic of poly-conjugated polymers: dark colour, limited solubility, semiconductivity and high thermal stability. On heating in solution thermochromic properties are observed, expressed in a reversible batochromic shift in the electronic spectrum (~14 nm). This thermochromism may be explained by the existence of two forms of polymer chain. In the first, low temperature form A (*Figure 1*), the double bonds between the repeating units are without strain, but the anthracene rings are not planar and are folded about the 9,10 axis. When the temperature is raised, a transition into the high temperature form B occurs, which has planar anthracene repeating units twisted at ~57° about the double bond. The existence of the two forms of polymer chains is revealed in the d.t.a. curves and in the temperature dependence of electrical conductivity.

It was of interest to investigate the properties of polymers in which the α-positions of the anthracene repeating units are occupied by bulky substituents, which hinder the conformational changes. The preparation of such polymers, and their investigation was the purpose of the present work.

EXPERIMENTAL

Materials

1,5-dichloroanthrone (m.p. 192°C) and 1,8-dichloroanthrone (m.p. 167°C) were prepared by a method described in Ref. 2. The poly(phosphoric acid) containing 84% P_2O_5 was obtained as described previously[1].

Apparatus

I.r. spectra were recorded from KBr pellets on a UR-10 spectrophotometer (Zeiss–Jena). Electronic spectra were recorded on a Specord spectrophotometer (Zeiss–Jena) in the visible region in a hexamethyl phosphoric triamide solution. The spectra at elevated temperatures were recorded in a thermostatically controlled cell. The molecular weights were determined with a vapour pressure osmometer (Knauer – Germany) in a dimethylformamide solution. The e.s.r. spectra were recorded in air with a JES-3BSX (JEOL) apparatus with diphenylpicryl hydrazyl as reference. Electrical conductivities were measured as described previously[3]. Thermogravimetric measurements were performed with a Paulik–Paulik–Erdey analyser (Derivatograph, Hungary).

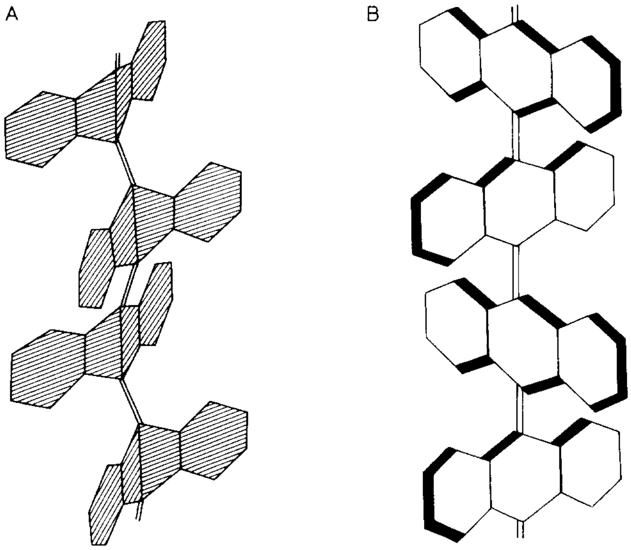


Figure 1 A and B forms of poly(9,10-dihydroanthracene-9,10-diylidene)

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* Corrected naming, earlier: poly(9,10-antracene diylidene)[1]

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Polycondensation of 1,5-dichloroanthrone

A solution of 1,5-dichloroanthrone (10.8 g) in poly(phosphoric acid) (140 g) was heated at 140°C in nitrogen and stirred. Samples were taken and their visible spectra recorded in dimethylformamide. After 72 h, no further batochromic shift was observed. The dark solution was poured into distilled water. The precipitated polymer was filtered, washed with water to neutral, then with ammonia water and distilled water. The product was dried and then extracted with hot ethanol, and again dried at 120°C *in vacuo.* It was a dark brown powder, soluble in hexamethyl phosphoric triamide and a 5% solution of LiCl in *N*,*N*-dimethylacetamide. Yield 7.8 g (77.5%); softening interval 250°–255°C. Calculated for $(C_{14}H_6Cl_2)_n$: C=68.60%; H=2.47%; found C=68.27%; H=3.16%; $\eta_{sp/c}=8.7\ cm^3\ g^{-1}$ (0.01 g cm^{-3} in hexamethyl phosphoric triamide at 20°C).

Polycondensation of 1,8-dichloroanthrone

The polycondensation was carried out by a method similar to the one described above. 1,8-dichloroanthrone (10.8 g) was dissolved in poly(phosphoric acid) (140 g) at 120°C, then the temperature was raised to 160°C and heating was continued for 140 h. The polymer is green and dissolves in hexamethyl phosphoric triamide and in a 5% solution of LiCl in *N*,*N*-dimethyl formamide. Yield 5.4 g (53.7%); softening interval 236°–259°C.

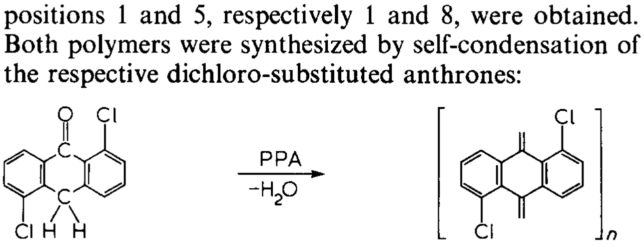
Calculated for $(C_{14}H_6Cl_2)_n$: C=68.80%; H=2.47%; found: C=68.80%; H=3.19%; $\eta_{sp/c}=9.4\ cm^3\ g^{-1}$ (0.01 g cm^{-3} in hexamethyl phosphoric triamide at 20°C).

Bromination of polymers

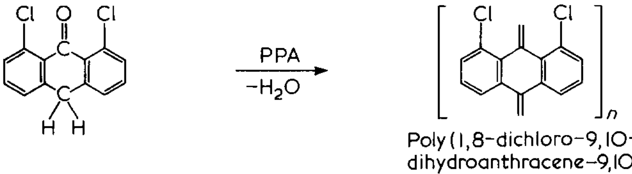
Fractions of the polymers, soluble in *N*,*N*-dimethylacetamide containing 5% LiCl were subjected to bromination. Brominating solution (5 ml, ~50% in excess) consisting of 1000 parts dry methanol, 120 parts NaBr and 5.2 cm^3 Br was added to 10 ml of the ~0.5% polymer solution. Bromination was carried out at temperature 20°C for different periods of time. It was discontinued by adding 15 ml of a 10% KI solution and 50 ml distilled water. The liberated iodine, equivalent to the excess of bromine, was titrated with 0.1 N sodium thiosulphate solution.

RESULTS AND DISCUSSION

Two new poly(9,10-dihydroanthracene-9,10-diylidene)s, containing two chlorine atoms each as substituents at positions 1 and 5, respectively 1 and 8, were obtained. Both polymers were synthesized by self-condensation of the respective dichloro-substituted anthrones:



Poly(1,5-dichloro-9,10-dihydroanthracene-9,10-diylidene) (polymer I)



Poly(1,8-dichloro-9,10-dihydroanthracene-9,10-diylidene) (polymer II)

While the synthesis of polymer I proceeded easily, the preparation of polymer II at a satisfactory yield required prolonged heating at elevated temperature. This is due to the screening of the carbonyl group by the large chlorine atoms at positions 1 and 8. The polymers have rather low molecular weights. Since they are not completely soluble in convenient solvent we determined the molecular weight only of the fractions soluble in dimethyl formamide. For both polymers it corresponds to a degree of polymerization of about 5.

The i.r. spectra of the polymers are well defined and correspond to their structure. They are similar to one another and to the spectrum of the poly(9,10-dihydroanthracene-9,10-diylidene)^1. Exception is made only by the absorption for the carbonyl end groups. In this case it is located within the range 1685–1695 cm^{-1}, and is near to that of the initial dichloroanthrones. The lack of batochromic shift indicates that conjugation along the length of the chain in these polymers is less pronounced than in poly(9,10-dihydroanthracene-9,10-diylidene).

Both polymers are deeply coloured and absorb in the visible spectral range (*Figure 2*). Their spectra indicate the presence of conjugated chromophoric aromatic system. On heating, however, the spectra remained unchanged. The absence of thermochromism in polymers I and II is evidently determined by presence of large chlorine substituents at α-position in the anthracene rings. It is known that the 1,8′-disubstituted derivatives of dianthrone display no thermochromic properties^{4,5}. This is due to the fact that the substituents at these positions hinder the transition of one conformation form into another. The absence of thermochromism in our case indicates that such a transition in the polymer chain is

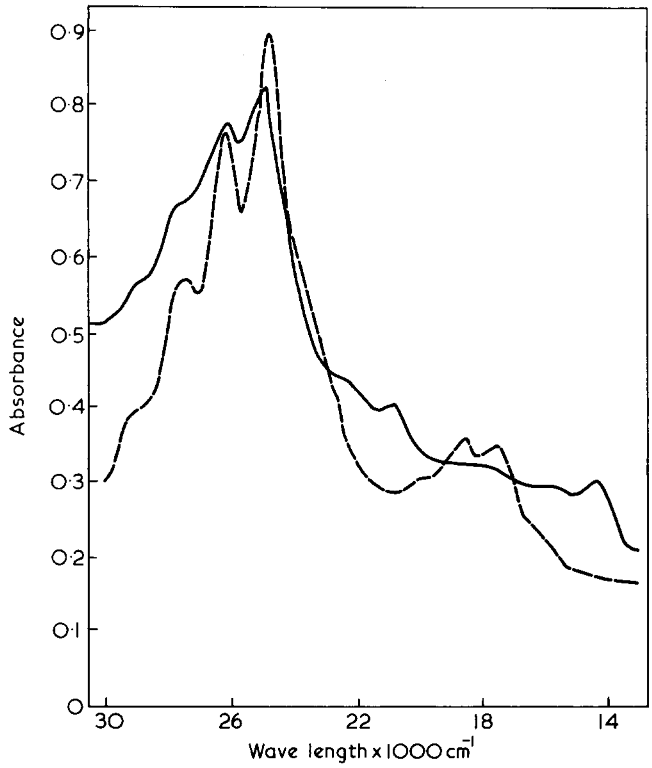


Figure 2 Visible spectra of solutions of poly(1,5-dichloro-9,10-dihydroanthracene-9,10-diylidene) (I) (———) and poly(1,8-dichloro-9,10-dihydroanthracene-9,10-diylidene) (II) (— — — —) in hexamethylphosphoric triamid

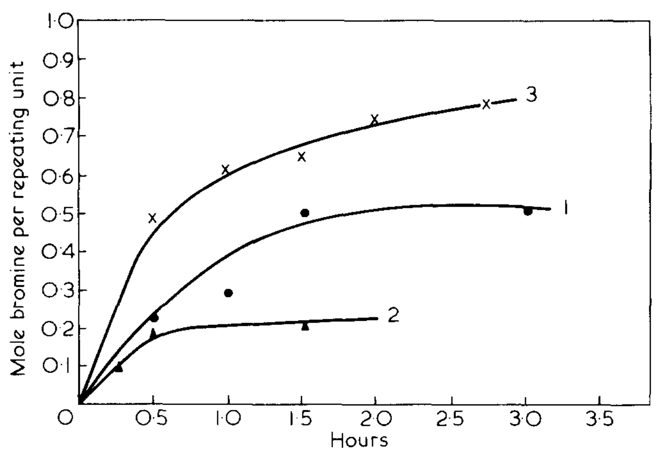


Figure 3 Kinetic bromination curves of the polymers at 20°C: 1—poly(9,10-dihydroanthracene-9,10-diylidene); 2—poly(1,5-dichloro-9,10-dihydroanthracene-9,10-diylidene); 3—poly(1,8-dichloro-9,10-dihydroanthracene-9,10-diylidene)

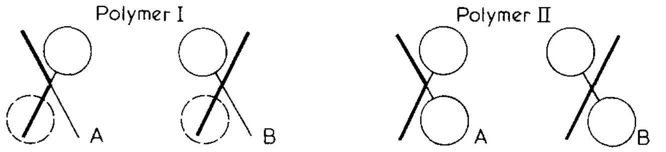


Figure 4 Polymers I and II — A and B forms, view along the chain axis. Only two repeating units are represented, the nearer one with a thicker line. The chlorine atoms are represented as rings, with a full line being above the anthracene rings (1,8-positions) and with a dashed line — under the anthracene rings (5-position). Only the chlorine atoms in the vicinity of the double bond are represented

impossible as well. A question arises: in which of these two forms do the polymer chains exist? To answer this question we subjected the polymers to bromination. One could expect that the different spatial hindrance of the double bond should determine the different bromination rate. The kinetic bromination curves (*Figure 3*) show that polymer II displayed the highest rate and degree of bromination, while the lowest was that of polymer I. The unsubstituted polymer displayed intermediate reactivity. It is known[7] that the primary act of the bromination reaction is the attack of the double bond by the bromine cation. After it has been added, there follows an attack of the obtained intermediate compound by a bromine anion, but on the reverse side of the double bond. Taking this mechanism into consideration we suppose that polymer I is in B form and polymer II in A form (*Figure 4*). The other forms of these polymers (A of I and B of II) are difficult to brominate because their double bonds are hindered by the bulky chlorine atoms on both sides. In the A form of polymer II and the B form of polymer I the initial attack occurs at the unhindered side of the double bond. It proceeds in a similar manner in the unsubstituted poly(9,10-dihydroanthracene-9,10-diylidene). The second stage of the reaction in the A form of polymer II however is facilitated, since due to the induction and mesomeric effect of the chlorine substituents the positive charge of the intermediate compound is greater, and the addition of the bromine anion is faster. The highest bromination rate of this polymer is the result. In the B form of polymer I the induction and mesomeric effect of the chlorine atoms are compensated due to the fact that these atoms are on both sides of the double bond and in two different anthracene rings. The result is the lowest bromination rate of this polymer.

The proposed chain structures for the two polymers were confirmed by a mass spectrometric investigation of the degradation products as well[8]. Taking into consideration the steric hindrance determined by the bulky chlorine substituents the chain forms A and B are probably not 'pure', i.e. some torsion of the double bonds exists in form A and some folding of the anthracene rings in form B.

The thermal stability of the dichloro-substituted poly(9,10-dihydroanthracene-9,10-diylidene)s is substantially lower than that of their unsubstituted analogue (*Figures 5* and *6*). The presence of chlorine as

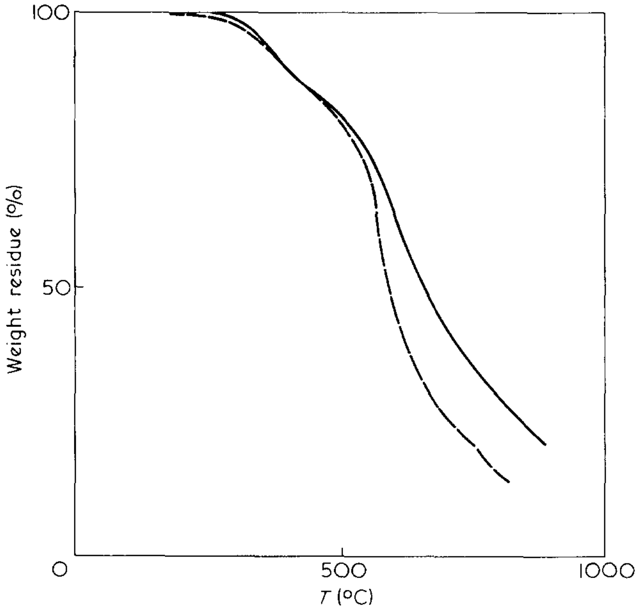


Figure 5 T.g.a. curves of poly(1,5-dichloro-9,10-dihydroanthracene-9,10-diylidene), T = 10°C min^{-1}; (— — — —), in air; (———), in nitrogen

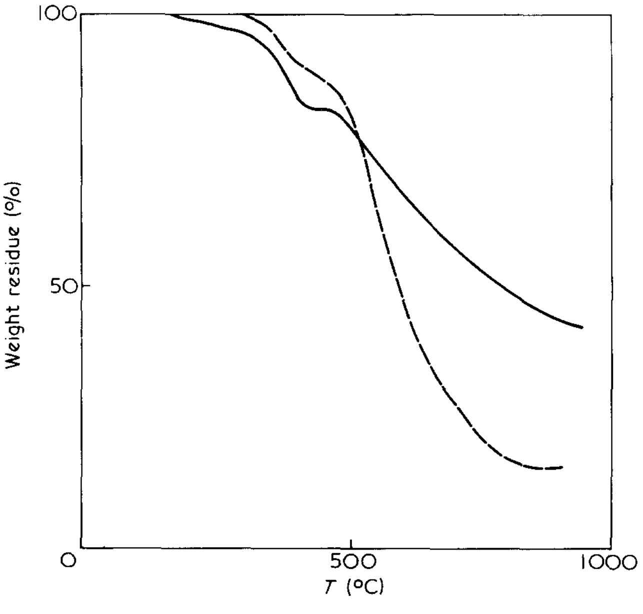


Figure 6 T.g.a. curves of poly(1,8-dichloro-9,10-dihydroanthracene-9,10-diylidene), T = 10°C min^{-1}; (— — — —), in air; (———), in nitrogen

Table 1 Electrical and magnetic properties of poly(1,5-dichloro-9,10-dihydroanthracene-9,10-diylidene) (I) and poly(1,8-dichloro-9,10-dihydroanthracene-9,10-diylidene) (II)

	Vacuum		Air		
	E_{act}(eV)*	σ_{298K} (Ω^{-1} cm^{-1})	E_{act}(eV)*	σ_{298K} (Ω^{-1} cm^{-1})	Unpaired spins g^{-1}
Polymer I	0.40	8.20×10^{-13}	0.48	1.60×10^{-12}	2.85×10^{19}
Polymer II	0.32	7.70×10^{-13}	0.50	7.25×10^{-13}	5.46×10^{18}

* 1 eV ~ 1.602×10^{-19} J

substituent has a negative influence on the thermal stability. Upon heating there is a hydrogen chloride evolution from the polymers. Both polymers, similar to other polymers with aromatic rings[9], burn with difficulty. For this reason the results of the analysis are not quite satisfactory.

The polymers I and II display semiconductive and paramagnetic properties (*Table 1*). The temperature dependence of the electrical conductivity follows the equation $\sigma = \sigma_0 \exp(-E/kT)$. It should be noted that neither polymer displays kinks in the temperature dependence of the electrical conductivity curves. A kink has been observed in poly(9,10-dihydroanthracene-9,10-diylidene), explained by the conformation changes in its chain, since it is located in the temperature range in which thermochromism is also observed. In our case the absence of thermochromism and kinks in the temperature–electrical conductivity curves indicates that no conformation changes occur in the chains of polymers I and II. Both these polymers display a conductivity lower than that of poly(9,10-dihydroanthracene-9,10-diylidene). This is due to the diminished conjugation in their molecules, and to the chlorine atoms lowering the intermolecular interactions.

The paramagnetism of polymers I and II is quite similar to that of poly(9,10-dihydroanthracene-9,10-diylidene).

CONCLUSION

The presence of chlorine substituents in the polymers I and II has a decisive influence on their properties. In comparison with the unsubstituted analogue poly(9,10-dihydroanthracene-9,10-diylidene) these properties are changed, dependent on the chain structure. This could be considered as proof for the structure attributed to these three polymers.

ACKNOWLEDGEMENTS

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