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Polymerization of diiodoacetylenes, their structure and electrical properties

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Abstract

Polydiiodoacetylenes (PDIA) were polymerized at different temperatures using $TiCl_4$–$AlEt_3$ and $Ti(OBu)_4$–$AlEt_3$ as catalysts. The crystallinity, concentration of unpaired spins, relaxation times, diffusion of spins, conjugations and energy gaps of the polymers were determined by X-ray diffraction, spectroscopic methods and electrical measurements. A crystalline polymer was obtained with $TiCl_4$–$AlEt_3$, while with $Ti(OBu)_4$–$AlEt_3$ an amorphous polymer was obtained. The concentration of unpaired spins for the crystalline sample was 6.7×10^{20} and 5.3×10^{20} spins/mol for the amorphous one. The energy gap for the former was 0.76 and for the latter 1.29 eV, while the electrical conductivities were 5.0×10^{-6} and 3.9×10^{-9} Ω^{-1} cm^{-1} respectively. The amorphous sample had no spin saturation, a lower diffusivity of spins and a lower conjugation, as compared to the crystalline PDIA. The relaxation times were measured only for the latter and were $T_1 = 1.189 \times 10^{-5}$ s and $T_2 = 0.745 \times 10^{-8}$ s. Both samples decomposed at 300 °C into iodine and charcoal. The stability of the PDIA against oxygen was much better as compared to polyacetylene.

Keywords: polydiiodoacetylene, conducting polymers, crystallinity, energy gaps, concentration of unpaired spins.

Introduction

The conductivity of polyacetylenes depends on the *cis–trans* configuration, crystallinity, concentration of unpaired spins (solitons) and on doping with different small molecules [1]. The unpaired spins are highly diffusive only in *trans* configuration, when the energies are equal on both sides of the spin [2]. The concentration of unpaired spins depends on the polymer chain configuration, the type of side groups and on doping. Doping with iodine increases the conductivity of polyacetylenes to metallic values. It was expected that the substitution of protons in polyacetylenes with halogens

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would also increase their conductivity [3, 4]. In our previous work the influence of the substitution of protons by bromine was described [5].

In this work the polymerization of new diiodoacetylenes under different polymerization conditions and with two different catalysts is described. The influence of chemically bonded iodine as a substitute in polyacetylene on the properties of the polymers was studied. The polymers were characterized by IR and NMR spectroscopy and by the thermogravimetric method. The electrical conductivity, conjugation, concentration of unpaired spins, diffusivity of unpaired spins and crystallinity were measured by UV–Vis and ESR spectroscopies and by X-ray diffraction. The energy gap was calculated from the dependence of the electrical conductivity on temperature.

Experimental

Materials

Acetylene was purified and dried before use. All chemicals used in this work were of p.a. grade. The diiodoacetylene was synthesized from acetylene and NaOI in water solution [6]. After purification, white crystals of diiodoacetylene were obtained. The yield of the reaction was about 90%.

Polymerization

The catalyst was dissolved in a Schlenk tube in dry toluene under a flow of dry argon. The monomer was added to the catalyst in a solution of dry toluene. Since the polymerization was highly exothermic the monomer solution was added in small portions. The polymerization temperature was between 20 and 90 °C. When the polymerization was nearly finished, the reaction was quenched by adding methanolic HCl. The polydiiodoacetylenes (PDIA) were then purified with methanolic HCl and methanol and dried in vacuum. The polymers were brown powders, which were insoluble in organic solvents. All polymerization parameters are given in Table 1. Only samples 1 and 7 were taken into consideration for further investigations. Sample 1 was highly crystalline, while sample 7 was amorphous. The dependence of

TABLE 1

Experimental data for polymerization of diiodoacetylenes

Sample	Catalyst	Molar ratio Al:Ti	Temp. (°C)	Time (h)	Yield (%)	Colour
1	$TiCl_4$–$AlEt_3$	1.2:1	25	2.5	36.0	brown
2	$TiCl_4$–$AlEt_3$	1.2:1	65	2.0	11.6	dark brown
3	$TiCl_4$–$AlEt_3$	1.2:1	70	0.2	5.3	dark brown
4	$Ti(OBu)_4$–$AlEt_3$	4:1	20	0.5	24.3	dark brown
5	$Ti(OBu)_4$–$AlEt_3$	4:1	60	1.0	42.0	black
6	$Ti(OBu)_4$–$AlEt_3$	4:1	65	0.5	41.8	dark brown
7	$Ti(OBu)_4$–$AlEt_3$	4:1	90	1.0	20.3	brown

conductivity on temperature was measured also for sample 3, which was semicrystalline.

Measurements

The thermal stability of the polymers was measured in a TGA apparatus (TA 2000 System + Thermogravimetric Analyser) under dry nitrogen. KBr pellets were prepared for recording the IR spectra (FTIR-FTIS 15/18 Biorad, Digilab and PE 1420). The MAS ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer. A Varian DMS 80 spectrometer was used for reflection UV–Vis measurements, while for ESR measurements a Varian E-109 X-band spectrometer was used. X-ray diffractograms were recorded on a Philips PV-1710 Cu Kα diffractometer. Pressed pellets of the polymers were used for electrical measurements. The dependence of electrical conductivities on temperature was measured under a dry argon atmosphere.

Results and discussion

As can be seen from Table 1 the polymerization yields were between 5.3 and 42.0% and depended on polymerization conditions and on the type of catalyst. The TGA measurements showed that the polymer powders decomposed at 300 °C to iodine and charcoal. The charcoal formed originates from the residual catalyst, from the carbon of the polymer chain and of the end groups. The polymers synthesized with $Ti(OBu)_4$–$AlEt_3$ have more charcoal than polymers synthesized with $TiCl_4$–$AlEt_3$.

The ratio C:I for the purified monomer was 1:10.6 and no traces of impurities were found. In Table 2 the elemental analysis for samples 1 and 7 is given. It can be seen that the type of catalyst has a significant influence on the course of the polymerization and on the properties of the polymers. The values for sample 7 are far from the theoretical values and far from tolerated experimental errors, contrary to sample 1, where the ratio C:I, for instance, nearly coincides with the theoretical value.

TABLE 2

Elemental analysis of polydiiodoacetylenes

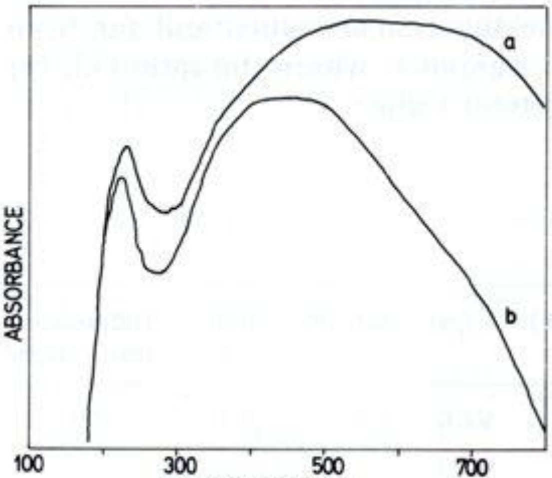
Sample	H (%)	C (%)	Ti (%)	Al (%)	I (%)	Ash (%)	Ratio C:I	Difference from 100%[a]
PDIA $TiCl_4$–$AlEt_3$ (Sample 1)	0.5	9.1	0.44	0.27	91.6	1.4	1:10	+2.6
PDIA $Ti(OBu)_4$–$AlEt_3$ (Sample 7)	1.5	12.3	0.52	1.20	56.2	3.4	1:4.5	−26.6

[a] Sum of H, C, I, and ash.

The structure of PDIA samples was studied by IR and MAS ^{13}C NMR measurements. In the IR spectra of all samples a strong signal of a C−I bending vibration at 640 cm^{-1} can be seen. No C−H stretching vibration at 3000 cm^{-1} was observed [7]. In the MAS ^{13}C NMR spectra, regardless of the catalyst system used, two small broad signals at 13 and 23 ppm belonging to the residual catalyst were observed. A strong broad signal at 111.7 ppm and a small one at 130 ppm belonging to −CI=CI− carbons were found.

The conjugation of the double bonds in the polymer chain depends on the planarity of the macromolecule. Because of sterical hindrances the iodine atoms can twist the polymeric chain and decrease the conjugation between the double bonds. The length of the conjugated segments was measured by the UV–Vis method. It is known [8] that the wavelength of the $\pi \rightarrow \pi^*$ transition only increases to higher wavelength with increasing length of conjugation for smaller energies. For polymers of the type $H-(HC=CH)_n-H$ the wavelength increases from 212 nm for two conjugated bonds to 703 nm for an infinite number of conjugated bonds. It was expected that a similar behaviour would be found in PDIA.

We measured the reflective UV–Vis spectra for the PDIA sample catalysed with $TiCl_4$–$AlEt_3$ and for the sample catalysed with $Ti(OBu)_4$–$AlEt_3$ (samples 1 and 7 from Table 1). The spectra are given in Fig. 1. The absorption maximum for the first sample is at 600 nm, while for the second it is at 480 nm. The absorption maximum for *trans*-polyacetylene is at 700 nm [9]. On the basis of UV–Vis spectra we were not able to make final conclusions about the conjugation between iodine atoms and double bonds but it is evident that, due to twisting of the PDIA chain, the conjugation in PDIA is smaller as compared to polyacetylene. Between the two PDIA samples, the



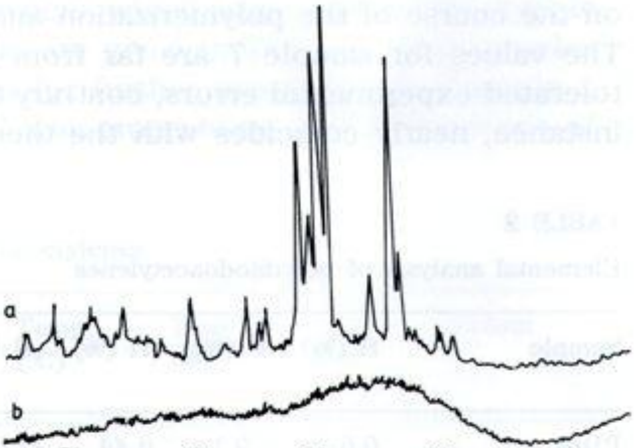


Fig. 1. Reflection UV–Vis spectra of polydiiodoacetylenes catalysed with (a) $TiCl_4$–$AlEt_3$ and (b) $Ti(OBu)_4$–$AlEt_3$.

Fig. 2. X-ray diffractograms of polydiiodoacetylenes catalysed with (a) $TiCl_4$–$AlEt_3$ and (b) $Ti(OBu)_4$–$AlEt_3$.

conjugation is smaller for the sample of PDIA synthesized with $Ti(OBu)_4$–$AlEt_3$ as catalyst.

In Fig. 2 the X-ray diffractograms for the same two PDIA samples are given. The sample catalysed with $TiCl_4$–$AlEt_3$ is highly crystalline, while the sample catalysed with $Ti(OBu)_4$–$AlEt_3$ is completely amorphous. The diffractogram of the crystalline sample has many sharp signals. This is due to high scattering of the iodine atom and to the symmetry of the crystal systems. The interplanar distances for signals of higher intensities are between 2.51 and 3.86 Å. The crystallinity of the polymer depends on the chain configuration, end groups and traces of catalyst [10]. We think that the residual catalyst and end groups (CH_3-CH_2-) prevent crystallization.

For the same two samples (1 and 7 from Table 1) the ESR spectra were recorded. The constant $g=2.004$. The concentration of unpaired spins for sample 1 is 6.7×10^{20} spin/mol, while for sample 7 is is 5.3×10^{20} spin/mol. The values are of the same order as in the case of polyacetylene [11].

The diffusivity of the unpaired spins can be estimated from the influence of the temperature on linewidth, ΔH_{pp}, while the diffusion is possible only when both sides of the spin are energetically equivalent. This is in the case of the *trans–transoid* structure of the polymers [2, 12]. The temperature dependence of ESR linewidth is displayed in Fig. 3. The linewidth decreases with increasing temperature for both polymers. In the same temperature interval the linewidth narrowing of the polymer synthesized with $TiCl_4$–$AlEt_3$ is somewhat higher than for the polymer synthesized with $Ti(OBu)_4$–$AlEt_3$. This is a consequence of higher conjugation for the sample polymerized with the first catalyst. Due to the sterical hindrance caused by the iodine atom, the polymers are of *trans–transoid* structure and have diffusive spins regardless of the type of catalyst. It was found that the type of catalyst used for the polymerization of PDIA samples does influence the linewidth of the ESR signals. For sample 1, ΔH_{pp} is broader than for sample 7 (Fig. 3). According to Chien *et al.* [13], this broadening can be ascribed to differences in quantities of residual titanum catalyst in the polymer. The values of linewidth for polyacetylenes are between 8.9 and 18.6 G [11].

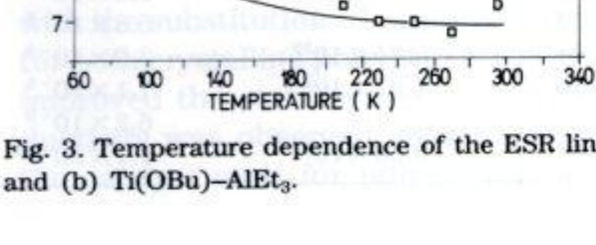


Fig. 3. Temperature dependence of the ESR linewidth for PDIA catalysed with (a) $TiCl_4$–$AlEt_3$ and (b) Ti(OBu)–$AlEt_3$.

The saturation behaviour of spins for the crystalline sample of PDIA is entirely different from that of the amorphous sample, as shown in Fig. 4.

The relaxation times T_1 and T_2 were calculated from [1, 12–14]

$$T_1 = 1.97 \times 10^{-7} \Delta H_{pp} [g(H_{1m})^2]^{-1} \tag{1}$$

$$T_2 = 1.31 \times 10^{-7} [g \Delta H_{pp}]^{-1} \tag{2}$$

where ΔH_{pp} is the value of the linewidth below saturation and H_{1m} is the microwave field strength in the ESR cavity at the maximum signal amplitude derived from the measurements performed by the pulsed modulation technique [15]. The corresponding relaxation times for PDIA catalysed with $TiCl_4$–$AlEt_3$ are $T_1 = 1.189 \times 10^{-5}$ s and $T_2 = 0.745 \times 10^{-8}$ s.

In Table 3 the concentrations of unpaired spins and the conductivities for some PDIA samples are given. The electrical conductivities are in the range 10^{-6}–10^{-9} Ω^{-1} cm^{-1}. As expected, the conductivity is better for a polymer with a higher concentration of unpaired spins. For comparison some values from the literature for polyacetylene samples are also presented in Table 3.

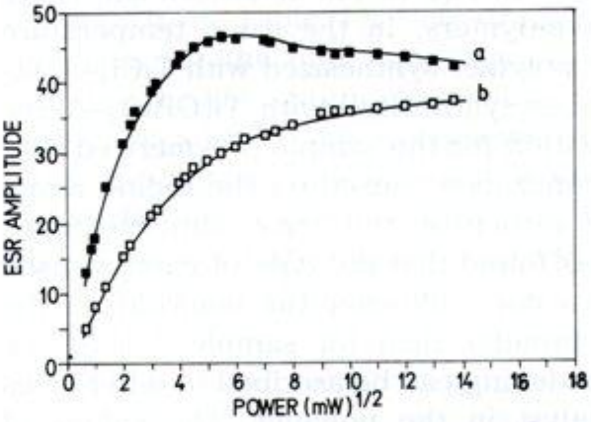


Fig. 4. ESR saturation curves of PDIA catalysed with (a) $TiCl_4$–$AlEt_3$ and (b) $Ti(OBu)_4$–$AlEt_3$.

TABLE 3

Properties of polydiiodoacetylenes as compared to polyacetylene from the literature data [11]

Sample from Table 1	Crystallinity	E_g (eV)	Conc. of unp. spins (spin/mol)	Conductivity (Ω^{-1} cm^{-1})
PDIA 1	highly crystalline	0.76	6.67×10^{20}	8.0×10^{-6}
PDIA 3	semicrystalline	1.29		5.8×10^{-8}
PDIA 7	amorphous	1.34	5.31×10^{20}	3.9×10^{-9}
PA	highly crystalline	0.46	1.22×10^{21}	7.1×10^{-5}
PA	semicrystalline			6.2×10^{-9}
PA	amorphous	0.83	5.66×10^{19}	7.1×10^{-13}

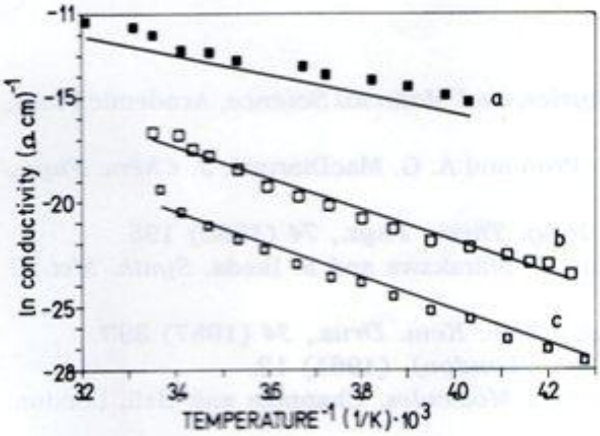


Fig. 5. Dependence of the electrical conductivity on inverse temperature for PDIA catalysed with (a) $TiCl_4$–$AlEt_3$ at 25 °C, (b) $TiCl_4$–$AlEt_3$ at 70 °C and (c) $Ti(OBu)_4$–$AlEt_3$ at 90 °C.

The dependence of the conductivity of PDIA on temperature is given in Fig. 5. This dependence is given by [16]

$$\sigma = \sigma_o \exp(-E_g/2kT) \qquad (3)$$

where σ is the conductivity, σ_o is the constant and E_g the energy gap. Since the conductivity increases with increasing temperature it can be concluded that the PDIA samples are semiconductors. The energy gaps were calculated from the slope of the straight lines in Fig. 5. These values are given in table 3. The energy gap for the highly crystalline PDIA is about two times lower as compared to the amorphous sample. The theoretically calculated E_g value for PDIA is 0.81 eV [3]. The energy gap of the crystalline PDIA is higher as compared to the value for the crystalline polyacetylene. This could be a consequence of lower conjugation in PDIA due to sterical hindrances of the side-chain iodine atoms.

Conclusions

It was found that when $TiCl_4$–$AlEt_3$ was used as a catalyst in the polymerization of diiodoacetylene a crystalline polymer was obtained. The polymer had a higher concentration of unpaired spins, longer conjugated segments, higher conductivity and a lower energy gap, as compared to polydiiodoacetylene synthesized with $Ti(OBu)_4$–$AlEt_3$ as catalyst. The experimental value of the energy gap for the crystalline sample of polydiiodoacetylene was in good agreement with the calculated value.

Higher conductivity, as compared to polyacetylene, was not achieved with the substitution of protons in polyacetylene by iodine. The conductivities for both crystalline polymers are very close. Substitution by iodine remarkably improved the stability of the polymer. No degradation or decrease of conductivity was observed after ten months in the PDIA samples regardless to the catalyst used for polymerization.

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