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The synthesis and characterization of polydibromoacetylene

S. Leben, A. Janevski*, A. Šebenik, and U. Osredkar**

Boris Kidrič Institute of Chemistry, Hajdrihova 19, P.O. Box 30, YU-61115 Ljubljana, Yugoslavia

Dedicated to Professor Dragutin Fleš on the occasion of his 70th birthday

SUMMARY

Polydibromoacetylenes were synthesized under different polymerization conditions and with Al-Ti coordinative catalysts. For the characterization of the polymers and for the study of the correlation between polymerization conditions and properties of the polymers, ^{13}C MAS NMR, ESR and UV spectroscopies were used. The electrical conductivity of the polymers was measured in dependence on temperature. The energy gap decreased with increased crystallinity. As compared to polyacetylene the conductivity of polydibromoacetylenes was lower, but the stability against oxygen was higher. The polydibromoacetylenes were thermal stabile up to 200°C.

INTRODUCTION

The electrical behaviour of polyacetylene, especially when doped, is well known. (1). Unfortunately polyacetylene is chemically not stabile and therefore many attempts were made to improve his stability. In our previous works (2-4) we reported about the substitution of protons in polyacetylene by halogens and phenyls. The aim of the present work is the synthesis of polydibromoacetylenes (PDIBrA) and the study of the correlation between the properties of polymers and polymerization conditions.

EXPERIMENTAL

Materials: For the synthesis of the dibromoacetylene (DIBrA), acetylene and NaOBr of p.a. grade were used. The synthesis was run under the atmosphere of dry argon until decoloration of NaOBr was achieved. High explosive liquid was formed. The yield of the reaction was about 10 %. Before use dibromoacetylene was purified and dried.

Polymerization: For the polymerization of DIBrA two different catalyst systems were used. Due to the high exothermic reaction the catalyst has to be poured to the toluene solution of

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*Permanent address: OHIS Skopje

**Corresponding author

DIBrA in a Schlenk tube in small portions. The experimental conditions of polymerization are given in Table 1.

Table 1: Polymerization conditions of PDIBrA samples

Sample	Catalyst	Mol.ratio Ti:Al	Temp. (°C)	Time (h)	Yield (%)
1	$TiCl_4$-$AlEt_3$	1:1.2	0	72	21.0
2	$Ti(OBu)_4$-$AlEt_3$	1:4	0	72	6.6
3	$TiCl_4$-$AlEt_3$	1:1.2	19	3	40.8
4	$Ti(OBu)_4$-$AlEt_3$	1:4	19	3	14.9

After the polymerization was finished the polymers were washed with methanolic HCl to remove the rest of catalyst and dried in vacuum. Black insoluble polymers were obtained.

Measurements: The IR spectra were recorded on a Perkin Elmer FTIR spectrometer. The ^{13}C MAS NMR spectra were recorded on a Varian 75 MHz for carbon supraconducting magnet. The X-ray diffractograms were recorded on a Philips PV-1710 Cu-$K\alpha$ diffractometer. For reflection UV-vis measurements a Varian DMS 80 spectrometer, while for ESR measurements a Varian E-109 X-band spectrometer were used. The thermostability of the polymers was measured in a TGA apparatus under dry nitrogen. For electrical measurements pressed pellets of polymers were prepared.

RESULTS AND DISCUSSION

As can be seen from Table 1 $TiCl_4$-$AlEt_3$ is a better catalyst as compared to $Ti(OBu)_4$-$AlEt_3$ regardless to the molar ratio between Ti and Al, and regardless to temperature and to polymerization time. The yields are namely, at comparable polymerization conditions higher, when the first catalyst was used. The increasing temperature also increases the yield of polymerization. Beside this $TiCl_4$ gives at the same polymerization conditions a higher crystallinic polymer, while with $Ti(OBu)_4$ a lower crystallinity was obtained. On Figure 1 the X-ray diffractograms for sample 1 and 2 from Table 1 are given. The distances of the signals in the diffractograms are between 2.36 and 3.61 Å.

Although the two samples differ in crystallinity, from Figure 1 it can be also concluded, that the structure of both polymers is identical. The ^{13}C MAS NMR spectra show a small signal between 15 to 30 ppm, which belong to the $-C_2H_5$ end groups in PDIBrA originated from catalyst, and the big broadband signal between 115 and 145 ppm, which belongs to the conjugated double bonds of PDIBrA chain. The identical structure for both polymers was confirmed by the UV-vis spectra (Figure 2) as well in which the maximum at 520 nm belonging to $\pi\text{->}\pi^*$ transition, indicates the conjugation of both polymers.The wavelength of the absorbed UV light increases with increasing segments of conjugated double bonds.(5)

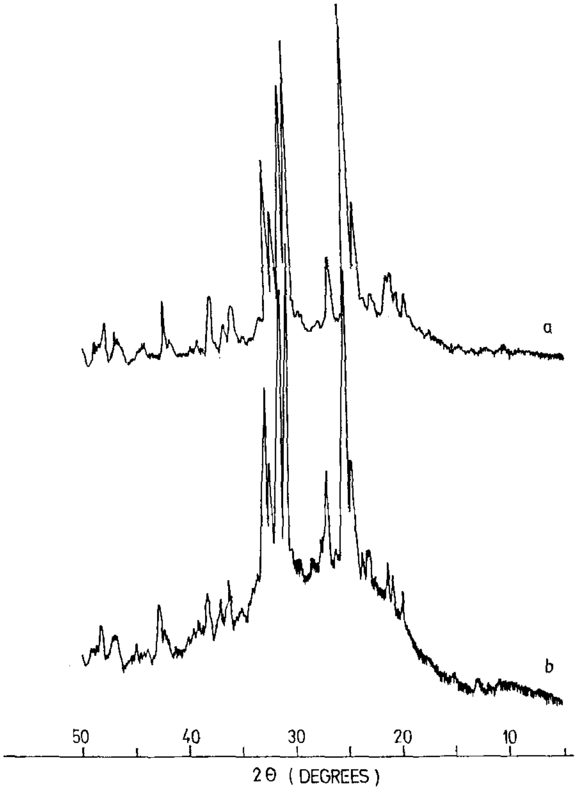

Figure 1: X-ray diffractograms for a) sample 1 and b) sample 2

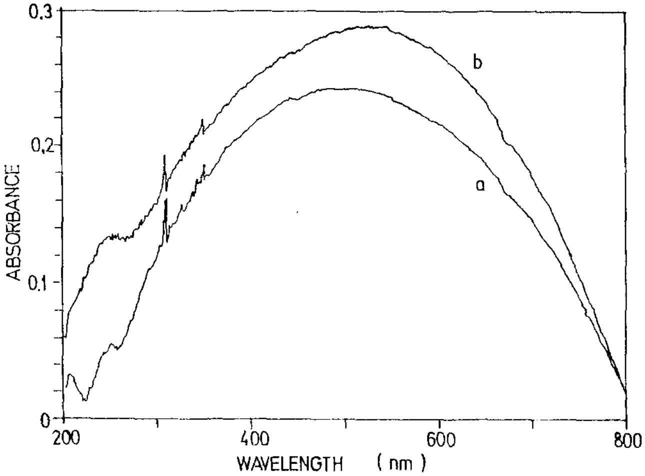

Figure 2: UV-vis spectra for a) sample 1, and b) sample 2

The ESR measurements show that the concentration of unpaired spins is $2.94 \cdot 10^{20}$ spin/mol for sample 1 and $0.93 \cdot 10^{20}$ spin/mol for sample 2. The constant g is 2.004 and the line-width 8.2 G. The saturation curves are given in Figure 3. The saturation for sample 1 was achieved at 4.47, while for sample 2 at 6.0 $(mW)^{1/2}$.

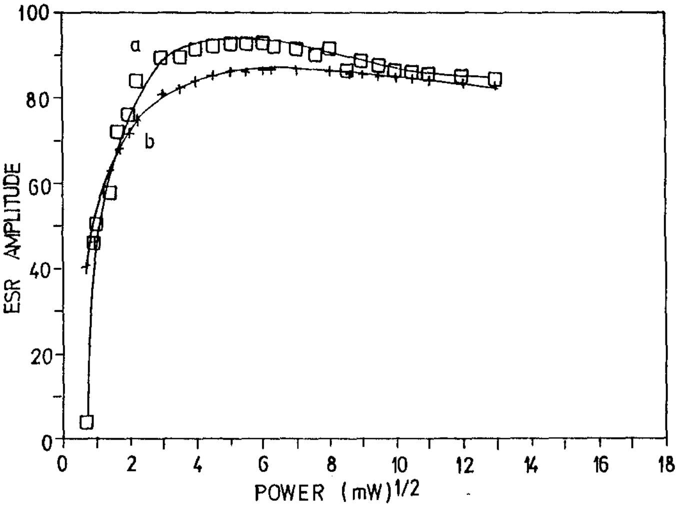

Figure 3: Saturation curves for: a) sample 1, and b) sample 2

By measuring the influence of the temperature on the linewidth (ΔH_{pp}) it was possible to conclude that the unpaired spins were diffusive. This is possible only when both sides of spins are energetically equivalent in the trans-transoid chain.(6) From this it can be concluded, that the polymers are of trans-transoid structure and therefore identical in molecular structure.

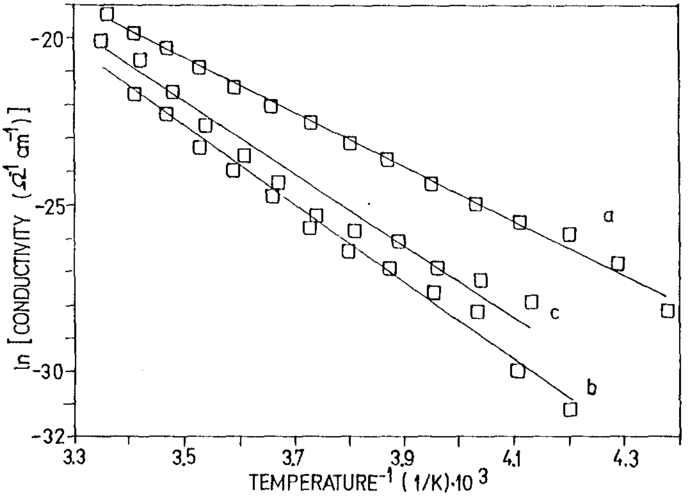

Figure 4: Dependence of the electrical conductivity on the inverse temperature for: a) sample 1, b) sample 2, and c) sample 4

In Figure 4 the dependence of the electrical conductivity on the inverse temperature for samples 1 and 2, and for sample 4 from Table 1 is given. This dependence indicates the semiconducting character of the investigated polymers. The energy gap (E_g) for the more crystalline sample 1 was 1.39 eV and 2.03 eV for the less crystalline sample 2. The calculated value E_g for PDIBrA was 0.794 eV.(7,8) The difference between the calculated and observed values indicates a lot of irregularity of the polymer chains and interrupted conjugation. The less coordinative catalyst $Ti(OBu)_4$-$AlEt_3$ increases the irregularity of the polymer and the energy gap.

In table 2 the electrical properties of PDIBrA samples are given.

Table 2: Electrical properties of PDIBrA samples from Table 1

Sample	Crystallinity	E_g (eV)	Concentration of unpaired spins (spin/mol)	Conductivity ($ohm^{-1}cm^{-1}$)
1	High	1.39	$2.94 \cdot 10^{20}$	$2.94 \cdot 10^{-9}$
2	Low	2.03	$0.93 \cdot 10^{20}$	$9.35 \cdot 10^{-10}$
4	-	1.85	-	$1.65 \cdot 10^{-9}$

Although the monomer was unstable and explosive on air, the polymers were stabile against oxygen at room temperature. Their stability decreased with the increasing temperature. In Figure 5 and 6 the TGA curves for samples 1 and 2 are given. It can be seen that the maximum lost of weight is at about 280°C and that the less crystalline sample 2, has two peaks of losing weight and has more residual charcoal when heated to

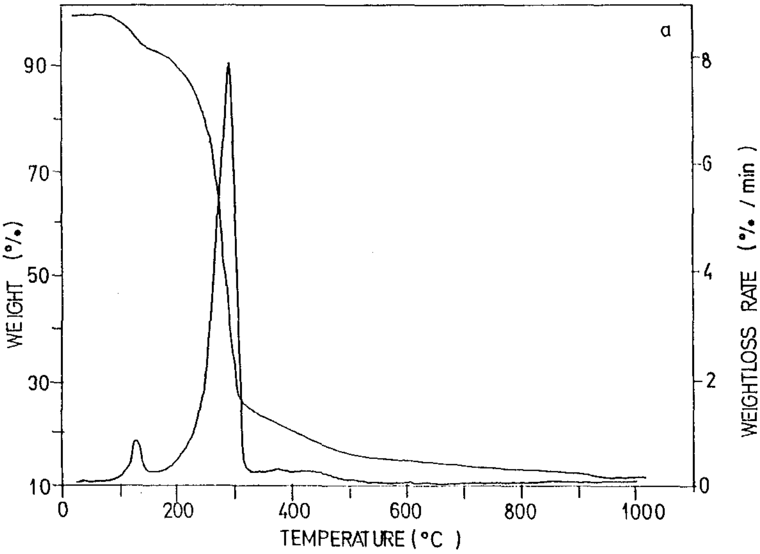

Figure 5: TGA curve for sample 1

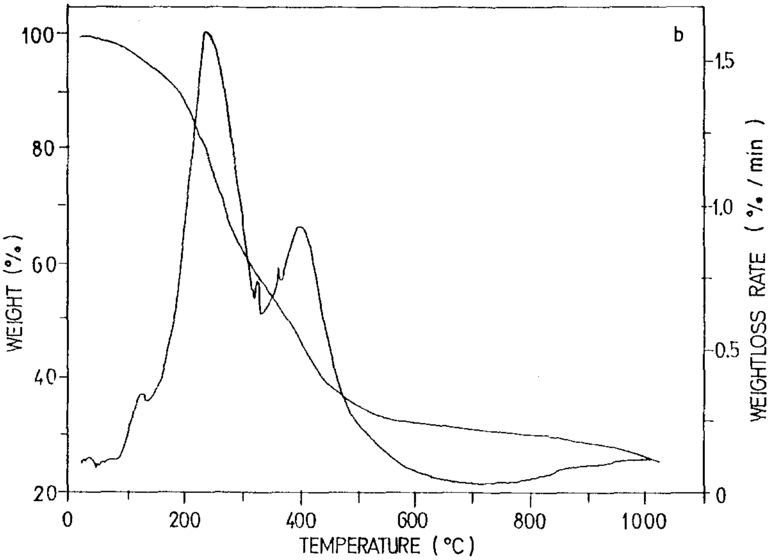

Figure 6: TGA curve for sample 2

1000°C in nitrogen atmosphere.

CONCLUSIONS

By the choice of catalyst in the substitution of protons in polyacetylene, polymers of different properties can be synthesized. Using $TiCl_4$-$AlEt_3$ as catalyst instead of $Ti(OBu)_4$-$AlEt_3$ a more crystalline polymer is obtained, while the molecular structure is identical for the polydibromoacetylene samples regardless to the type of catalyst. Comparing to polyacetylene, the polydibromoacetylenes are less conducting, but much more stabile against oxygen.

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