

EFFECTS OF CHAIN STRUCTURE OF POLYPYRROLONES ON THE ELECTRICAL PROPERTIES OF PYROLYZED POLYPYRROLONES*

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ABSTRACT

Three kinds of polypyrrolones (PMDA-DAB, PMDA-TADPE and DEDA-DAB) were pyrolyzed at high temperature in order to study the effect of the chain structure of polypyrrolones on the electrical properties of the pyrolyzed polymers. Results show that the number of fusing rings in the main chain of polymers has a little effect on the pyrolysis process, whereas, the ether bond in the main chain plays an important role during pyrolysis. Structure characterizations by elemental analysis, XPS spectra, X-ray diffraction and SEM images indicate that because the ether bond is easy to break, it is difficult to form large area planar network. This hampers the formation of the graphite-like structure in the polypyrrolones containing ether bond even after being pyrolyzed at 1200°C.

INTRODUCTION

Pyrolysis at high temperature, as a simple and cheap method to convert the insulating polymer into conductor, has attracted much attention in recent years. Various pyrolyzed polymers were studied focusing on their electrical and magnetic properties^[1-9], pyrolytic mechanism and structure^[10-12], and potential applications as carbon or graphite precursor^[11-14], L-B films^[15-16] and electromagnetic wave absorbers^[17].

Polypyrrolones are step-ladder polymers with excellent properties such as high radiation-resistance ($> 10^{10}$ Rad)^[18], heat-resistance^[19-20], ablation-resistance^[21], and high permeability and permselectivity for gases^[22-24]. They are also outstanding insulators with high thermal stability. Because of the polyconjugated aromatic heterocyclic rings in the main chain, it is expected that polypyrrolones are good

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candidates for pyrolysis at high temperature to become conductors with graphite-like structure. We have done a lot of work on the pyrolysis of this polymer^[25-27]. Moreover, Bruck^[28] and Murakami^[12] suggested that the number of polyconjugated aromatic heterocyclic rings in the main chain of polymer is favorable for graphitization at high temperature.

In this article, the effect of the number of fusing rings and ether bond in the main chain of polypyrrolones on the electrical properties of the pyrolyzed products at high temperature is reported and the pyrolyzed mechanism is discussed.

EXPERIMENTAL

1. *Synthesis and film preparation of polypyrrolones*

Polypyrrolones were prepared by condensation of various aromatic dianhydrides and aromatic tetraamines in dimethylacetamide (DMAc). A precursor solution in which the solid was about 10% by weight was obtained. The solution of the precursor was filtered and stored in a cooler until needed for film casting.

Film was prepared by casting an appropriate volume of precursor solution on a clean glass plate and heated at 85°C for 1 h to evaporate most of the solvent. Then the glass plate was put into an oven while the temperature was raised to 300°C and kept for 3 h by a slow flow of argon into the oven. After cooling, the film was removed from the glass plate by soaking in water and dried at room temperature. The monomers and the structures of three kinds of polypyrrolones used in this work are shown in Fig. 1. The major differences in structure among them are that: there are seven fusing rings in the main chain both of PMDA-DAB and PMDA-TADPE, while there are only four fusing rings in the main chain of DEDA-DAB; there is an ether bond per repeating unit in the main chain of PMDA-TADPE and DEDA-DAB, but not in the main chain of PMDA-DAB.

2. *Pyrolysis of polypyrrolones*

Pyrolysis was performed in a tube-type electrical oven. Firstly the oven was preheated to a selected temperature, then the polypyrrolones sandwiched between two quartz plates were placed in the oven and heat-treated for a required time with a slowly flowing nitrogen atmosphere. The pyrolytic temperature (T_p) varied from 700°C to 1200°C. After pyrolysis, the color of PMDA-DAB film changed to lustrous black for $T_p < 1000^\circ\text{C}$ and to bright metallic luster above 1000°C with almost no linear shrinkage but reduced thickness, whereas, a black film remained even up to 1200°C for PMDA-TADPE and DEDA-DAB with about 30% of linear shrinkage. Thus, it is certain that the different structure of the original polymers has an effect on their pyrolysis.

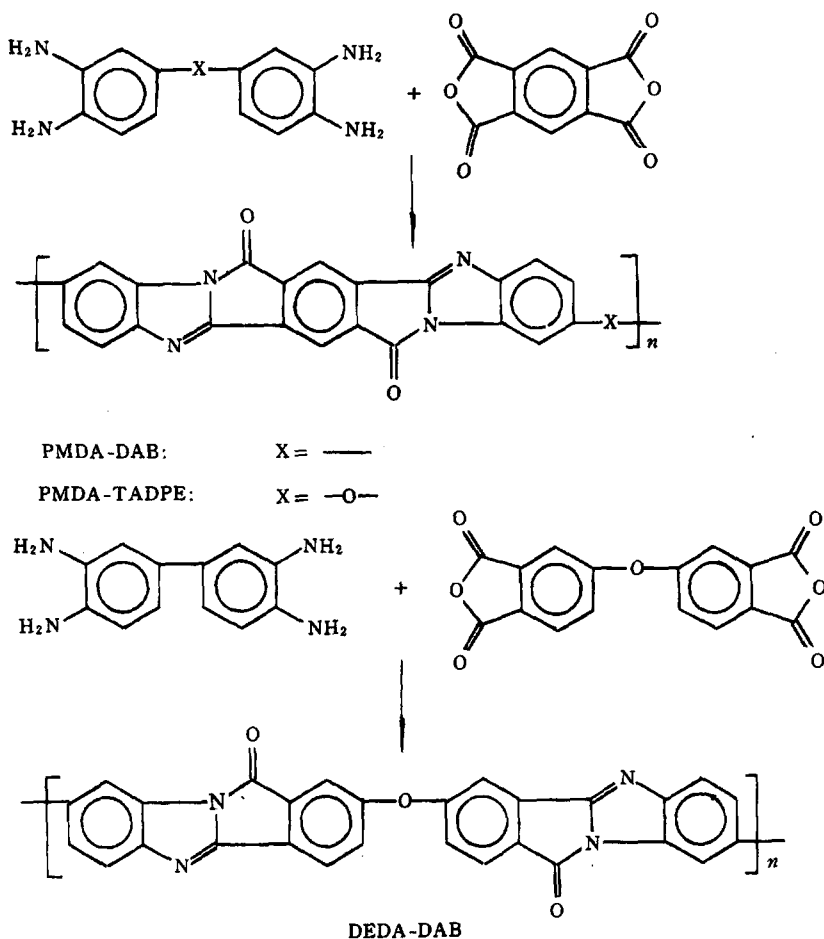


Fig.1 Synthesis and structures of polypyrrones

3. Electrical conductivity measurement and structure characterizations

The conductivity of the pyrolyzed polypyrrones was measured by a four-probe method using Keithley 196 SYSTEM DMM Digital Multimeter with ADVANTEST R6142 Programmable DC Voltage/Current Generator as current source.

X-ray photoelectron spectroscopy (XPS) spectra were measured with an ES 300 X-ray Photoelectron Spectrometer, using a Mg target X-ray source. The crystallography of the pyrolyzed film was measured using a MXP 18A-HF X-ray diffractometer with Cu target ($\lambda = 0.15405\text{nm}$). Morphology of the pyrolyzed polypyrrones was examined by a Hitachi S-530 Scanning Electron Microscope.

RESULTS AND DISCUSSION

1. Electrical properties of the pyrolyzed polypyrrones

These three kinds of polypyrrolones have similar pyrolytic time (t_p) dependence of the room-temperature conductivity (σ_{RT}): for a given pyrolytic temperature (T_p), at the early stage of pyrolysis σ_{RT} increases rapidly with increasing t_p , and then tends to a saturation value above t_p . At higher T_p , it requires shorter time to reach the saturation value. Fig. 2 shows the result pyrolyzed at 1200°C, in which it is obvious that the PMDA-DAB films have higher σ_{RT} than that of PMDA-TADPE and DEDA-DAB films obtained under the same conditions.

The effect of T_p on σ_{RT} for polypyrrolones pyrolyzed for 1 h at each T_p was shown in Fig. 3. These pyrolyzed polypyrrolones exhibit similar T_p dependence of σ_{RT} , which consists of two stages: at low T_p σ_{RT} increases markedly with increasing T_p , then tends to a constant at higher T_p . For all of the three kinds of polypyrrolones the same transitional temperature of two pyrolysis processes (T_c), about 800°C, was estimated from Fig. 3 and the two pyrolysis processes have been demonstrated as carbonization at $T_p < 800^\circ\text{C}$ and graphitization at $T_p > 800^\circ\text{C}$ [26]. The σ_{RT} of pyrolyzed PMDA-DAB is higher than those of the other two under the same pyrolytic conditions.

The I-V characteristic for all kinds of polypyrrolones pyrolyzed at different temperature for 1 h exhibit Ohm's law as shown in Fig. 4, which is one of the typical characteristics of metal. The temperature dependence of the conductivity ($\sigma(T)$) of polypyrrolones pyrolyzed at 1200°C for 1 h was measured respectively. The best fit of them is $\ln\sigma T^{1/2}$ vs. $T^{-1/4}$ as shown in Fig. 5, which can be explained by the

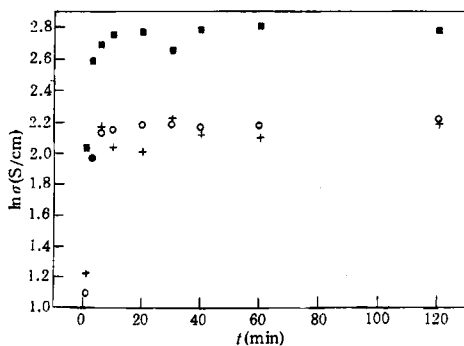


Fig. 2 Dependence of pyrolysis time on room-temperature conductivities of polypyrrolones pyrolyzed at 1200°C ■ PMDA-DAB; ○ PMDA-TADPE; + DEDA-DAB

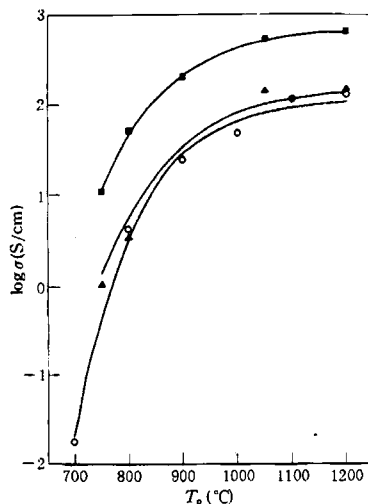


Fig. 3 Dependence of pyrolytic temperature on room-temperature conductivities of polypyrrolones pyrolyzed for 1 h ■ PMDA-DAB; ▲ PMDA-TADPE; ○ DEDA-DAB

three-dimensional Variable-Range Hopping model (3D-VRH model)^[29]:

$$\sigma(T) = (\sigma_0/\sqrt{T}) \exp\{-(T_0/T)^{1/4}\}$$

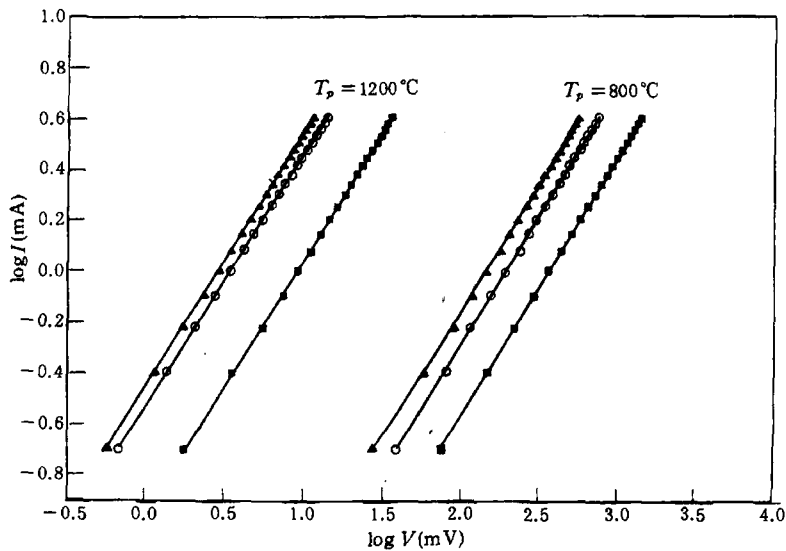


Fig. 4 I-V curve of polypyrrolones pyrolyzed at different temperature for 1h
▲ PMDA-DAB; ■ PMDA-TADPE; ○ DEDA-DAB

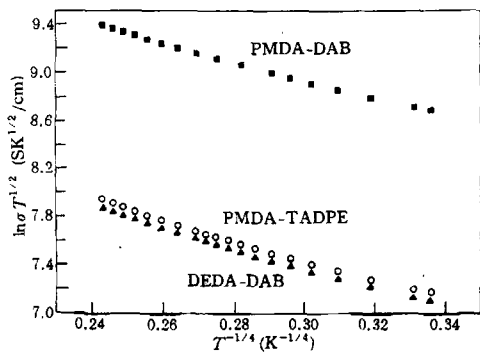


Fig. 5 Temperature-dependence of conductivities for polypyrrolones pyrolyzed at 1200°C for 1h

In addition, the anisotropy in conductivity was measured for polypyrrolones pyrolyzed at 1200°C for 1h. The conductivity in the plane of the surface of pyrolyzed film ($\sigma_{\parallel}$) was measured by the four-probe method and that perpendicular to the surface ($\sigma_{\perp}$) was measured by two-probe method. The results are listed in Table 1. The anisotropy in conductivity of pyrolyzed PMDA-TADPE is a little greater than that

of pyrolyzed DEDA-DAB but the pyrolyzed PMDA-DAB has greater anisotropy in conductivity.

From the above, we can see that the structure of the original polymer surely has the effects on the pyrolytic product. Pyrolyzed PMDA-TADPE and DEDA-DAB have similar electrical properties, but the anisotropy in conductivity of pyrolyzed PMDA-TADPE is a little greater than that of pyrolyzed DEDA-DAB. The difference

of their original structures is only the number of fusing rings in their main chain (seven in PMDA-TADPE, four in DEDA-DAB). So the number of fusing rings has a little effect on the pyrolysis process in this system. The difference of electrical properties between pyrolyzed PMDA-DAB and the other two polypyrrolones (different σ_{RT} and anisotropic conductivity at the same pyrolytic conditions) indicates that the ether bond in the main chain of the original polymers plays an important role in the pyrolysis process. In order to make clear how the ether bond affects the pyrolysis of polymers, detailed structure characterization of pyrolyzed polypyrrolones has been performed.

Table 1 Anisotropy in conductivity for polypyrrolones pyrolyzed at 1200°C for 1h

Sample	$\sigma_{\parallel}$ (S/cm)	$\sigma_{\perp}$ (S/cm)	$\sigma_{\parallel}/\sigma_{\perp}$
PMDA-DAB	760	4.8×10^{-3}	1.6×10^5
PMDA-TADPE	260	0.23	1.1×10^3
DEDA-DAB	255	0.66	4.0×10^2

2. Structure characterizations

The results of elemental analysis of pyrolyzed polypyrrolones at different T_p for 1h are listed in Table 2 together with that of the original polymers. PMDA-TADPE and DEDA-DAB have the similar results, in which most of the hydrogen and oxygen were removed from residue after pyrolyzed at 800°C and the content of nitrogen was reduced a little, however, for PMDA-DAB all of the oxygen was removed and only a little of hydrogen and nitrogen were released. After pyrolyzed at 1200°C, both hydrogen and oxygen were removed completely from the residue of PMDA-DAB but a certain percentage of nitrogen, about 3.74%, still remains in it, whereas, for PMDA-TADPE and DEDA-DAB all three elements are present to a certain content in the pyrolysates, in which the content of nitrogen is lower than that of pyrolyzed PMDA-DAB. These results suggest that there are different pyrolysis mechanisms between the PMDA-DAB and the other two polypyrrolones.

The X-ray photoelectron spectroscopy (XPS) of pyrolyzed polypyrrolones supports the results obtained from elemental analysis. For the PMDA-DAB films pyrolyzed at 1200°C for 1 h obvious N_{1s} peak can be observed which consists of two kinds of nitrogen^[26]. For the residues of PMDA-TADPE and DEDA-DAB pyrolyzed at 1200°C, the signal of N_{1s} are very weak and cannot be well separated from noise, which indicates that the concentration of nitrogen is less than 1%.

X-ray diffraction patterns of pyrolyzed polypyrrolones at 1200°C for 1 h are shown in Fig. 6. For PMDA-DAB, the peak is narrow and sharp and the lattice space

obtained from the position of the peak (0.343 nm) is close to the $d_{(002)}$ of graphite (0.335 nm)^[30], which indicates that a graphite-like structure forms in the pyrolyzed PMDA-DAB film. The patterns of pyrolyzed PMDA-TADPE and DEDA-DAB show that even up to 1200°C their structures are disordered, and no graphite-like structure forms in them.

Table 2 Elemental analysis of polypyrrolones before and after pyrolysis

Sample	$T_p(^{\circ}\text{C})$	C(%)	N(%)	H(%)	O(%)
PMDA-DAB	the original	67.40	14.61	4.53	11.88
	800	84.69	11.73	2.66	0
	1200	96.25	3.74	0	0
PMDA-TADPE	the original	59.57	13.00	3.64	18.92
	800	72.34	10.60	0.92	4.62
	1200	96.18	1.2	0.54	1.4
DEDA-DAB	the original	66.20	11.02	3.72	15.10
	800	74.82	8.30	1.03	3.32
	1200	96.42	1.01	0.56	1.38

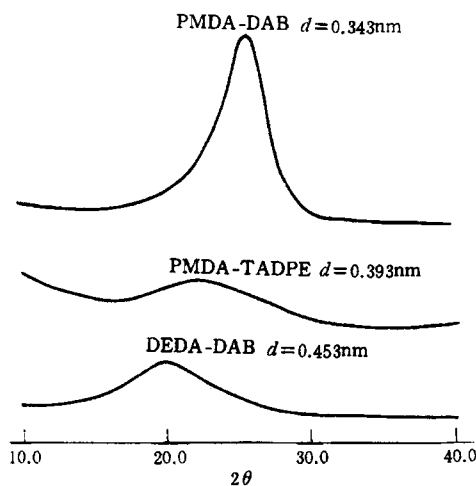


Fig. 6 X-ray diffraction patterns of polypyrrolones pyrolyzed at 1200°C for 1h

It can be observed directly from scanning electron microscopy (SEM). Fig. 7 shows the SEM images of the cross-section for polypyrrolones pyrolyzed at 1200°C for 1 h. A perfect layered structure similar to graphite forms in the pyrolyzed PMDA-DAB. For PMDA-TADPE, there is a tendency to form layered structure but not for pyrolyzed DEDA-DAB, which results in the different anisotropy in conductivity between them.

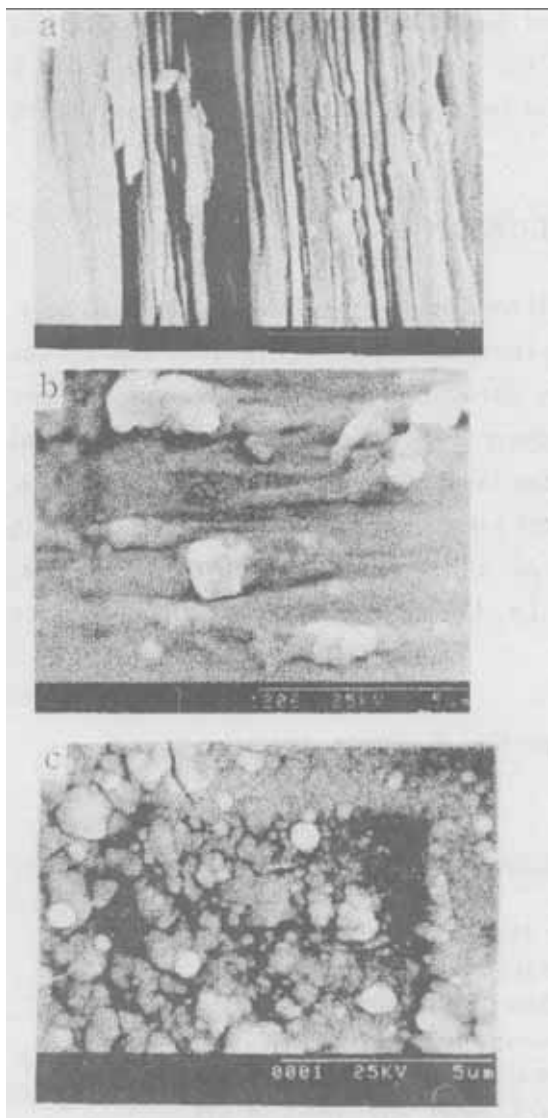


Fig. 7 SEM images of cross-section of poly-pyrrolones pyrolyzed at 1200°C for 1h, a) PMDA-DAB; b) PMDA-TADPE; c) DEDA-DAB

Thus, PMDA-TADPE and DEDA-DAB have similar change of structure during pyrolysis, which are very different from PMDA-DAB, and this difference is mainly caused by the ether bond in the main chain of the polymers. This is consistent with the results obtained from their electrical behaviors. The function of the ether bond might hamper the formation of graphite-like structure in pyrolyzed products because, as we know, it is easy to break while heat-treated.

Based on the discussion above, the different pyrolytic mechanisms of PMDA-DAB, PMDA-TADPE and DEDA-DAB may be described as follows:

1. For PMDA-DAB with no ether bond in the main chain, polycondensation among molecular chains occurs firstly during pyrolysis to form a large planar network^[26], which is easy to arrange parallel to the surface of the film, resulting the formation of layered graphite-like structure in the residue. This explains the greater anisotropy in conductivity.

2. For pyrolyzed PMDA-TADPE and DEDA-DAB, because of the existence of the ether bonds in their main chain, at first the polymers break into small fragments when pyrolyzed. Then some of these fragments are released and others recombine and rearrange during further pyrolysis. This explains the linear shrinkage of these films. However, these small fragments are disorderly dispersed in the pyrolysate, so that it is difficult to form large planar network. Thus, up to 1200°C the residue is composed of disorderly dispersed fragments and no graphite-like struc-

ture forms in it. The disorderly dispersed fragments resulted in low anisotropy in conductivity. But more fusing rings of the original PMDA-TADPE results in a little greater anisotropy in conductivity of pyrolyzed PMDA-TADPE than that of pyrolyzed DEDA-DAB.

CONCLUSION

The different electrical properties of three kinds of pyrolyzed products of polypyrrolones indicate that the ether bond in the main chain of the polymer has obvious effects on the polymer's pyrolysis process. Structure characterizations suggest that it is difficult to form the graphite-like structure in the polymer containing ether bond in main chain. The reason is that the ether bond is easy to break during pyrolysis, which hampers the formation of large area planar network. The number of fusing rings in the main chain of polymers has also a little effect on the pyrolysis process.

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Keywords:

Polypyrrolones; Pyrolysis; Electrical properties; Structure characterizations

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