

STUDY ON THE THERMOSTRUCTURALIZATION OF PAN THIN FILM

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Introduction

It is well known that one of the earliest works for the synthesis of the so-called thermally structured polymers was done about 30 years ago by Topchiev⁽¹⁾. In particular, PAN (polyacrylonitrile) has been investigated by many authors for producing conductive, optical anisotropic and high radiation resistance materials⁽²⁻⁵⁾. In our previous papers the authors have reported the results of in-situ and on-line FTIR studies on the Kinetics of the $-C\equiv N$ bond transformation into the conjugated $C=N-$ bond and the gaseous products of high temperature pyrolysis of acrylonitrile copolymer^(6,7). In the present study, the changes of chemical structure and composition of PAN thin film during different stages of processing are studied by IR, WAXD and XPS techniques. These very significant results provided the scientific bases for understanding of the conversion of PAN thin film to carbon film.

Experimental

The copolymeric sample used in this study was kindly supplied by Jilin Chemical Industrial Company. The copolymer film was smeared on a glass plate with dimethylformamide (DMF) as solvent. After thermostabilizing for 24hr. at 210 °C in oven, the film was placed in a specialized pyrolytic furnace. All experiments were performed in purified N_2 and heated according to a linear program. The samples of the thermostabilization derived from PAN thin film obtained.

The changes of the chemical structure and composition of PAN thermostabilized film were determined by IR, WAXD and XPS techniques. FTIR spectra were recorded on a perkin Elmer-1700 model FTS systems. The X-ray diffraction measurements were carried out using a Rigaku D/max-rA model X-ray

diffractometer, operating at 40KV, 80mA. The perkin-Elmer PHI 5300ESCA was used for XPS measurement.

Results and Discussions

FTIR serial spectra of PAN film measured at various temperature are shown in Fig.1. Figure 1a shows that the different peak intensities for the various absorption peaks of sample were appeared. After PAN film thermostabilized for 24h at 210 °C in air, in Fig.1b the disappearances of the acrylamide group ($1665cm^{-1}$) and the carbonyl group ($1721cm^{-1}$) absorption peaks shown that the sample through the intermolecular condensation releases carbon dioxide (CO_2) and carbon monoxide (CO) and might be the break up of the bond in the molecular chain of the unclosed ring step-ladder structure under heating. In PAN macromolecular the nitrile group ($2244cm^{-1}$) drops quickly and the presences of the nitrile group with the olefinic double bond ($2198cm^{-1}$) and the conjugated >N=C- group bond ($1576cm^{-1}$) were caused by the forming of aminonitrile or iminonitrile groups and the polymerization of the nitrile groups; the newly weak absorption of the C-H out-of-plane bending mode of the aromatic rings ($800cm^{-1}$) appeared. When the pyrolysis temperature raising to 650 °C (see Fig.1c) the absorption peak at $800cm^{-1}$ is enhanced and widened, the absorption peak at $1576cm^{-1}$ shifted to $1564cm^{-1}$ and 1145 shifted to $1144cm^{-1}$ and widened. The absorption peak at $1576cm^{-1}$ shifted to $1557cm^{-1}$ go on and the intensity of the absorption peak decreased, simultaneously the absorption peaks at $1145cm^{-1}$ and $800cm^{-1}$ were decreased when the pyrolysis temperature reaching to 850 °C (Fig.1D).

As can be seen from Fig.2, Carbon, nitrogen and oxygen are three basic elements in sample. As the pyrolytic temperature raised the relative intensity of the light-electron peak of Carbon (C1s) was raised markedly

and which of nitrogen and oxygen (N1s and O1s) were dropped. These phenomena might be the results of the C-N and C-O bonds in the structure of sample were broke and were released in forms of HCN, N₂, CO and CO₂.

As can be seen from Fig.3, WAXD intensity curves of sample various with increasing pyrolysis temperature. Two equatorial diffraction maximum at room temperature (one at $2\theta = 17^\circ$ corresponding to (100) reflections and the other at $2\theta = 29.3^\circ$ from (110) reflections of the orthorhombic structure of PAN film) almost disappear, simultaneously the pattern show a very broad and asymmetrical new (101) peak at $2\theta = 21^\circ$, corresponding the (002) planes of the hexagonal cell of graphite-like carbon (Fig.3b). This indicates that the lineal molecular chains of PAN film transformed into thermally stabilized ladder polymer structure. Further raising the temperature the diffraction peak (101) shifted to a direction of high angle degree slightly (see Fig.3c,d and e). This exhibited the increasing of a stacking structure of like-graphite layers.

Conclusions

PAN-based Carbon thin film was prepared successfully. IR, WAXD and XPS results show that as pyrolytic temperature raised PAN linear type structure is converted to a ladder polymer with large conjugated structure of naphthyridine rings, and crosslinked to form

a network structure with aromatic six-membered rings of a like graphite.

References

1. Topchiev, A. V., J. Polym. Sci., Part A, 1963, 1, 591.
2. Ritsko, J. J., et al., Phys. Rev. B, 1983, 27, 2612
3. Kazama, S., et al., Synth. Met., 1986, 14, 153
4. Tse-hao KO, et al., in Carbon'93 PP.193 (EXT. Abstr. 21st Biennial Conf. Carbon)
5. Kyotani, T. et al., in Carbon'94 P.578 (Ext. Abstr.)
6. Zhao, G. X., et al., J. Analytical and Applied Pyrolysis, 1992, 23, 87
7. Zhao, G. X., et al., Chinese J. Polym. Sci., 1987, 5(2), 1.

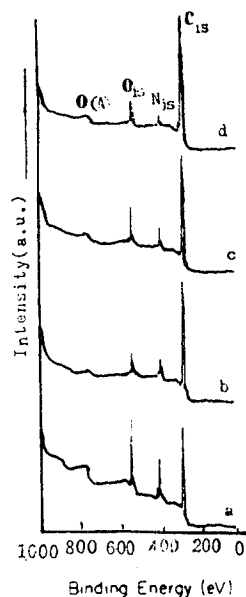


Fig.2 Serials XPS wide scan spectra of PAN film at different temperature
a-room temperature;
b-210°C; C-650°C;
d-850°C

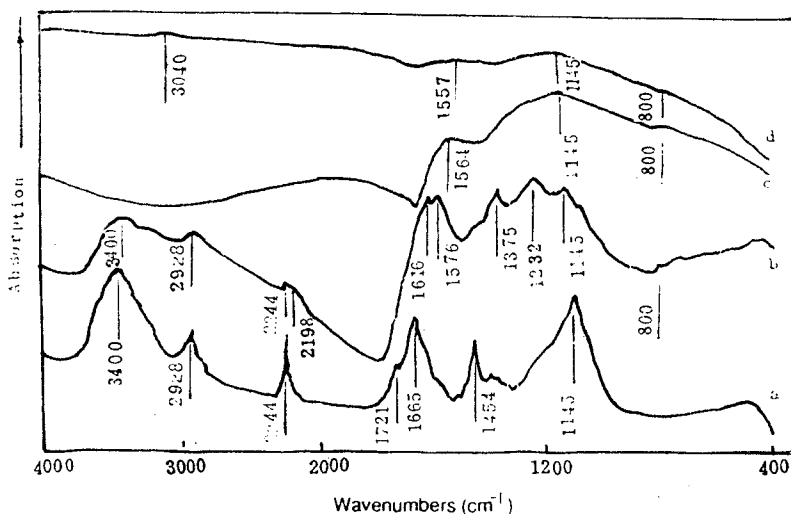


Fig.1 Serials FTIR spectra of PAN film at different temperature
a-room temperature; b-210°C; C-650°C; d-850°C;

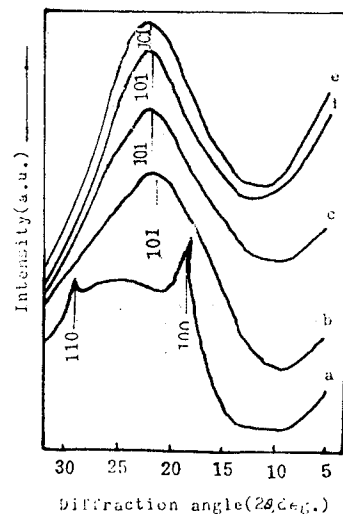


Fig.3 Serials WAXD patterns of PAN film at different temperature
a-room temperature; b-210°C;
C-650°C; d-750°C; e-850