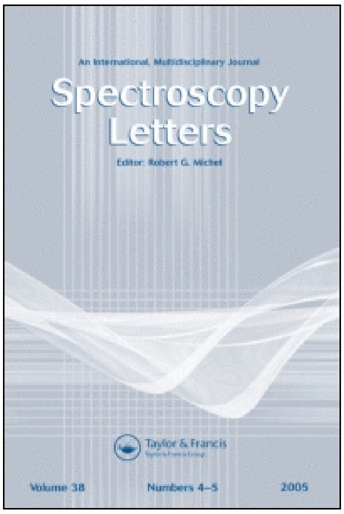

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Reflection-Absorption Infrared Spectroscopy Study of Polyacrylonitrile on Copper at Elevated Temperature

Xiaohong Gu[a]; Gi Xue[a]
[a] Department of Polymer Science and Engineering, and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, The People's Republic of China

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REFLECTION-ABSORPTION INFRARED SPECTROSCOPY STUDY OF POLYACRYLONITRILE ON COPPER AT ELEVATED TEMPERATURE

Keywords: Infrared reflection-absorption spectroscopy, PAN, Copper, Coordination, Pyrolysis

Xiaohong Gu and Gi Xue*

Department of Polymer Science and Engineering, and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, The People's Republic of China

ABSTRACT

Reflection-absorption infrared spectroscopy (RAIR) has been used to investigate the chemical structural changes in Polyacrylonitrile (PAN) film adsorbed on copper at 200 °C for different time. The formation of an almost fully conjugated C-C=C backbone occurs after heating for only 2 h due to the catalytic effect of copper. The freely dangling cyano groups in PAN molecules initially coordinate to copper surface through the triple bond in π-bonded orientation, then convert to σ-bonding

through the donation of the lone pair of electrons of nitrogen. It is suggested that this transition of the types of coordination would relate to the different geometries of PAN on copper during heating. Since the nitrile complexing and cyclization occur at the same time, the reaction process for the pyrolysis of PAN on copper surface is different from that in the bulk.

INTRODUCTION

Polyacrylonitrile (PAN) is a commercially important and widely used polymer. It has a strongly polar nitrile group attached to alternating carbons on a saturated hydrocarbon. It is well-known that PAN undergoes polymerization of the nitrile groups followed by conjugation of the hydrocarbon backbone upon pyrolysis [1-3]. The structural changes of PAN at high temperatures are generally shown as Fig.1. Recent attention is focused on surface or interfacial reactions between PAN and metals. An XPS and IR study of PAN films on aluminum and copper surfaces illustrated that a double-coupled conjugated system was formed after pyrolysis on Al at 200 °C for 2 h [4] and the C≡N groups coordinated to copper mainly through nitrogen lone-pair orbitals. However, we found that the C≡N groups of PAN coordinated to copper through the triple bond at initial stage upon heating and this interaction could influence the pyrolysis of PAN. Here, we present our reflection-absorption infrared spectroscopy (RAIR) studies of the structural changes of PAN on copper surface at elevated temperature, which focuses on the changes of the types of the coordination of PAN to copper surface during heating.

EXPERIMENTAL

PAN (Aldrich, molecular weight 9.0×10^4) was dissolved in DMF to make a 0.2% solution. Commercial copper plates were polished to a mirror finish using a series of aluminum slurries with particle size ranging from 0.3 to 0.05 μm. After polishing was completed, the mirrors were thoroughly rinsed with water, dried under nitrogen, then were immediately immersed into PAN-DMF solution at room

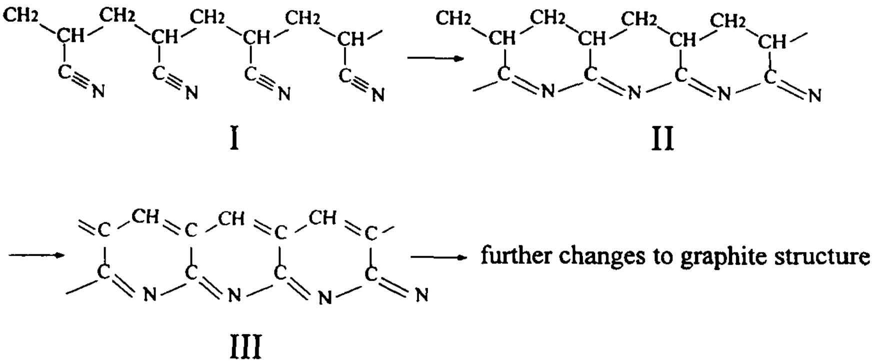

FIG. 1.Chemical structures of PAN after different stages of pyrolysis.

temperature for 5 min. After withdrawal of the sample, the solvent was first evaporated in air and then rinsed with ethanol and dried. The PAN-coated specimen were heated in oven at 200 °C for various periods of time, and then analyzed with RAIR spectroscopy. The spectra were recorded with a Bruker RFS 66V Fourier-transform infrared spectrometer fitted with an external reflection accessory at an incident angle of 88°. The IR beam is polarized with its electric field vector parallel to the plane of incidence. 500 scans were averaged at a resolution of 4 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1}.

RESULTS AND DISCUSSION

The reflection-absorption spectra of PAN on copper substrates before and after heating at 200 °C for 0.5 h are shown in Fig. 2A and 2B, respectively. The bands near 2935 cm^{-1} are attributed to CH_2 stretching vibration and 1452 cm^{-1} to CH_2 bending mode. The strong band at 2244 cm^{-1} in Fig. 2A is characteristic of freely dangling C≡N stretching mode. As can be seen, a dramatic change occurs in spectrum after the specimen were heated for 0.5 h. The band at 1452 cm^{-1} becomes rather weak, while strong and broad bands appear near 1580 cm^{-1}, indicating a partially conjugated hydrocarbon backbone have been developed. This is consistent

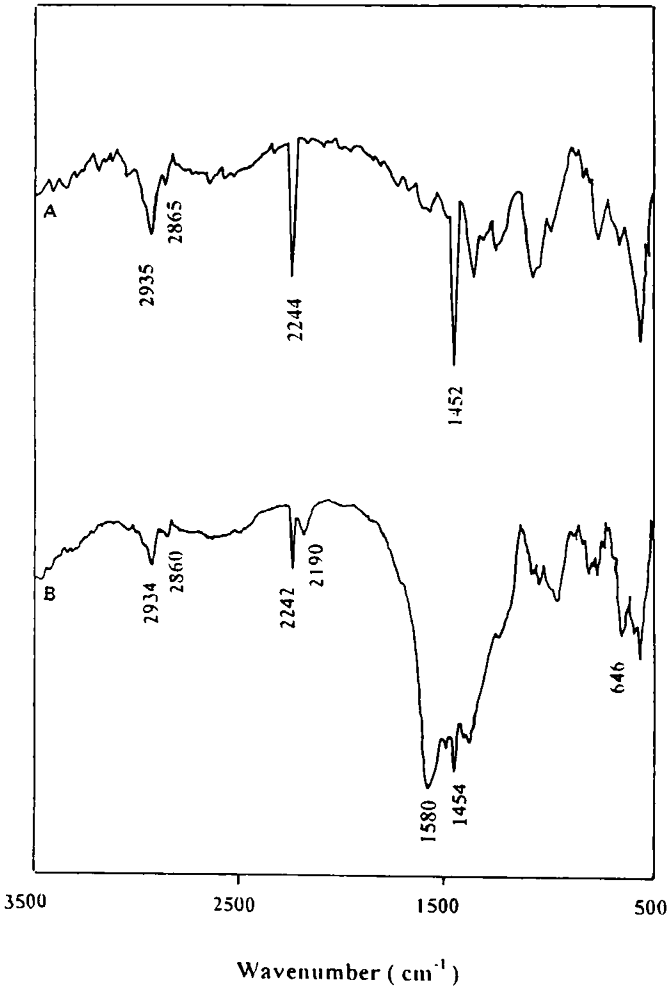

FIG. 2.RAIR spectra of PAN on copper after heating at 200 °C for: (A) 0 h (B) 0.5 h.

with the reduction of the intensity of the CH_2 stretching band near 2934 cm^{-1} and the C≡N vibration mode at 2242 cm^{-1}. It is well known that copper can in particular function as a catalyst for thermal dehydrogenation of hydrocarbon compounds [5]. Another alternative explanation is that PAN molecule can find a more favorable conformation and/or orientation on the metal surfaces which later may facilitate the cyclization as well as the conjugation reaction [4]. Similar surface geometry effects on the surface-induced reactions have been found in the case of graphilization of PAN on silver surface [6,7] and the spontaneous polymerization of vinyl molecules on Ag elucidated by SERS spectroscopy [8].

One can also find that a new broad band appears near 2190 cm^{-1}. The substantial red shift and band broadening indicate the direct interaction between the cyano groups of PAN molecules and the copper surface. From the studies of the metal-nitrile complexes and the nitriles adsorbed on metal surfaces, it has generally been accepted that the end-on coordination (σ-bonding) through the nitrogen lone pair electrons results in an increase in the C≡N stretching frequency from that of the free molecule. On the other hand, the side-on coordination (π-bonding) through the triple bond is known to result in a decrease in the C≡N stretching frequency [6-7, 9-11]. Since adsorption of PAN on metal surface necessitates the bonding of cyano group to metal surface, it is reasonable to observe the frequency alteration for C≡N vibration mode. Therefore, we propose that the new band at 2190 cm^{-1} results from the side-on coordination of nitrile on copper surface. Additionally, the band at 640 cm^{-1}, which is assigned to Cu_2O mode, is obviously observed upon heating, implying that the cyano groups mainly coordinate to copper ions or/and the oxide layer.

With increasing time at elevated temperature, the bands characteristic of aliphatic CH_2 stretching and bending modes at 2936 and 1452 cm^{-1} almost disappear completely and those near 1580 cm^{-1} become rather strong after 2 h heating (Fig. 3A). The total absence of CH_2 modes, together with an enhanced C=C-H band near 806 cm^{-1}, implies that a conjugated hydrocarbon backbone is fully developed after

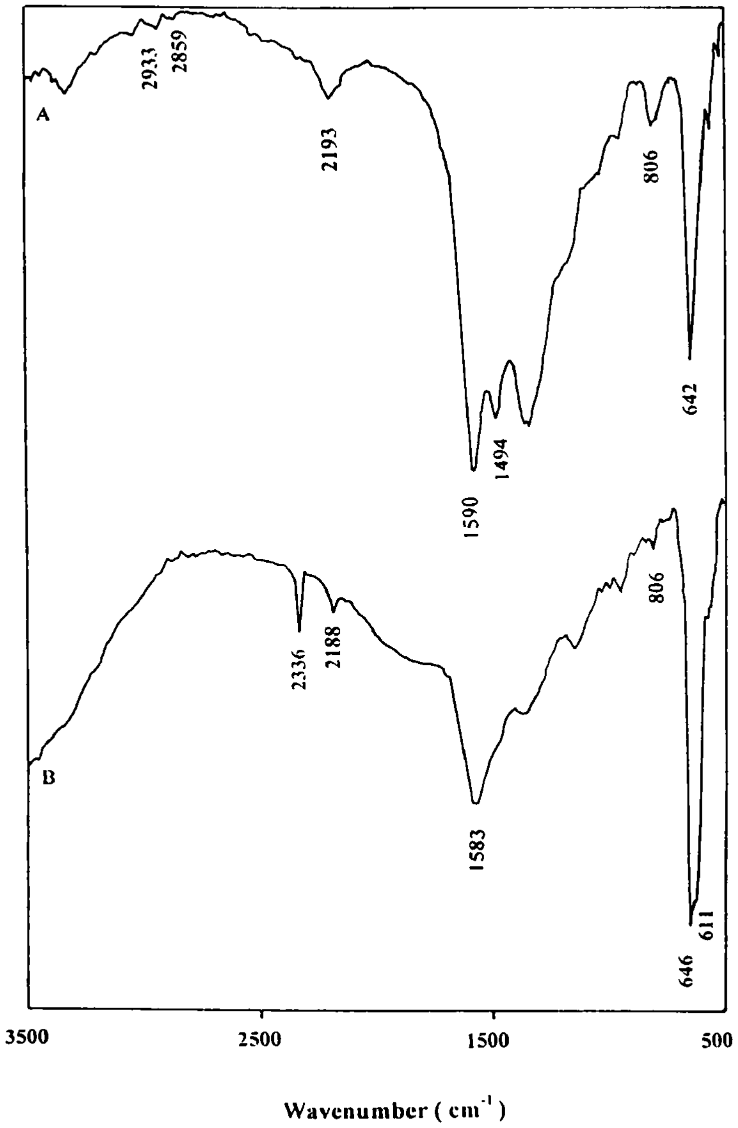

FIG. 3.RAIR spectra of PAN on copper after heating at 200 °C for: (A) 2 h (B) 5 h.

pyrolysis at 200 °C for 5 h (Fig. 3B). Meanwhile, the band of the free C≡N vibration mode is no longer present and the band near 2190 cm^{-1} become larger, indicating that all of the residual cyano groups coordinate to copper through the side-on type. However, this type of complexing seems unstable upon further heating, for the broad bands near 2190 cm^{-1} are then splitted and a new band near 2336 cm^{-1} is observed obviously. Since the end-on coordination generally results in an increase in the C≡N stretching frequency from that of the free molecule, according to the discussion above, it is reasonable to assume that some cyano groups have changed the type of coordination to copper from π-bonding to σ-bonding, and both end-on and side-on coordinated nitrile groups in PAN simultaneously.

Fig. 4 A, B and C show the RAIR spectra of the adsorbed PAN on copper after heating at 200 °C for 10, 12, and 14 h, respectively. Regarding to the types of coordination of cyano groups to copper, there is a clear tendency for the end-on form to increase in the number with time at the expense of the side-on form. On the other hand, the band near 2338 cm^{-1} tends to be rather weak comparing with those near 1580 cm^{-1}, indicating that PAN has further converted to a graphite-like structure upon heating at this temperature. It is interesting to note that, as seen in Fig. 4B, an obvious band centered at 3462 cm^{-1} characteristic of N-H stretching vibration appears. This demonstrates that the conjugation and cyclization reaction of PAN undergoes the conversion of C≡N groups into C=N and N-H groups as indicated by previous work [12,13].

One can also find that, after heating for 5 h, a shoulder at 611 cm^{-1} is observed near the band around 640 cm^{-1} in the spectrum of Fig. 3B, while after heating for 10 h, the band at 611 cm^{-1} is observed clearly and 648 cm^{-1} becomes an shoulder, as seen in Fig. 4B. These changes presumably resulted from the increase in the thickness of Cu_2O oxide with increasing the heating time and consequently the difference in optical mode at different thickness. It was reported that [14,15], the band at 611 cm^{-1} was usually observed when the thickness of Cu_2O oxide film is thicker than about

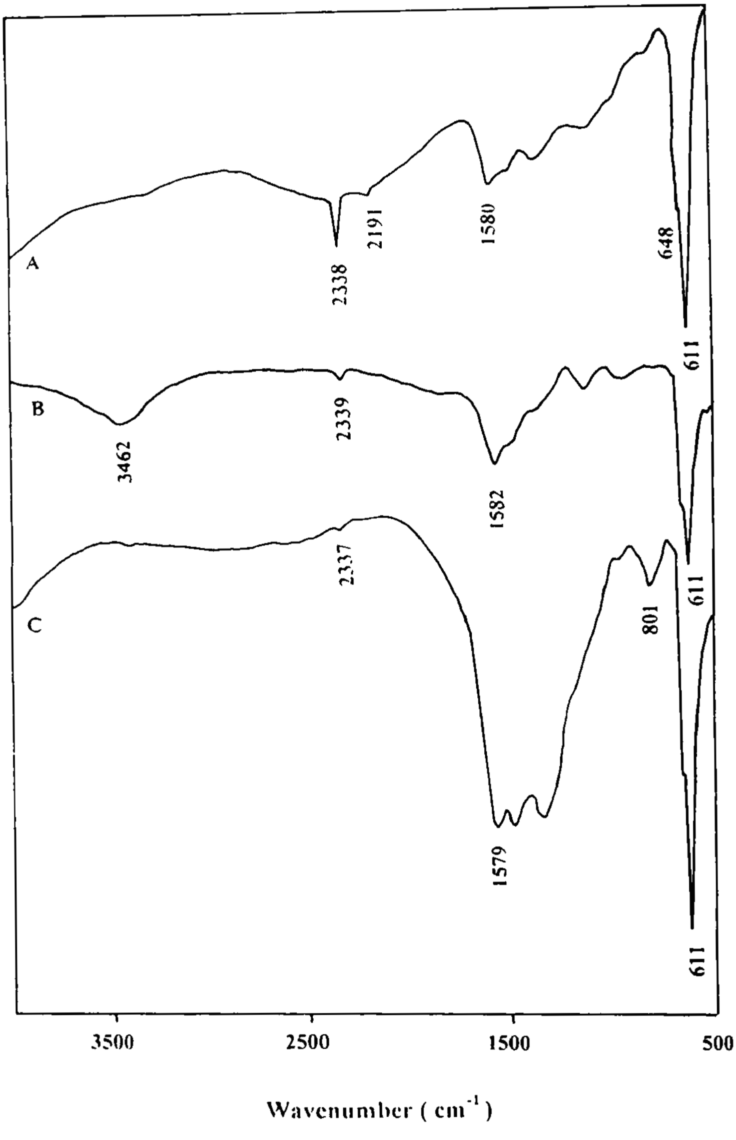

FIG. 4.RAIR spectra of PAN on copper after heating at 200 °C for: (A) 10 h (B) 12 h (C) 14 h.

2000 angstrom and in the frequency of the transverse optical mode; on the other hand, the band characteristic of Cu_2O was observed near 640 cm^{-1} when the thickness of the film was less than 2000 angstrom and in the frequency of the longitudinal optical mode.

As indicate above, during heating at 200 °C for 14 h, the freely dangling cyano groups in PAN molecules coordinated completely to copper surface through the triple bond at initial stage, then convert to coordinate copper through the lone pair electrons on the nitrogen atom. SERS studies of polybenzimidazole on silver once showed two orientations of its main chain on the surface of silver and the heteroaromtic rings stood up from the flat orientation to form an N-bonded geometry upon heating [16]. It is consistent with the result of our case, therefore, we may relate the transition to the different geometries of PAN on copper, resulting from the different rate of formation of nitrile-copper complexing and the stability under heating. It is reasonable to suggest that σ-bonding seems more stable than π-bonding for the coordination of PAN to cuprous ions or/and Cu_2O oxide layer; while, the rate of formation of the latter may be higher.

In addition, the reaction scheme given in Fig. 1 for bulk PAN is assumed to be invalid on copper surface. Since the presence of copper appears to have a catalytic effect on the rate of backbone conjugation, as discussed above, the aliphatic CH_2 groups almost disappear completely and the conjugated hydrocarbon is nearly fully developed after heating for only 2 h. Meanwhile, the reduction in intensity of the cyano groups is relatively slow and PAN molecules tend to form nitrile-copper coordination through π-bonding and σ-bonding. Thus, the chemical structure shown in stage II of Fig. 1 may be improper for this case. Moreover, since nitrile complexing and cyclization are suggested to be regarded as competitive process [4], the cyclization through the nitrile groups as well as the formation of a double-coupled conjugated system are proposed to be retarded by complexing. However, the substantial decrease in the intensity of the cyano groups indicate that the adsorbed PAN still tend to be turned into a fused ring structure as shown in the stage III of Fig. 1.

CONCLUSION

We have demonstrated that the changes of the chemical structure of PAN on copper surface is different from that in bulk during pyrolysis under heating by using RAIR. The formation of an almost fully conjugated C-C=C backbone occurs after heating for only 2 h, indicating that copper surface has a catalytic effect on backbone conjugation of PAN. The conversion of the types of coordination of cyano groups to copper during heating reveals that nitrogen-bonded orientation through the donation of the lone pair of electrons of nitrogen is more stable than π-bonded geometry through the triple bond. Additionally, nitrile complexing through σ-bonding and cyclization of PAN are competitive processes, and the pyrolysis reaction of PAN is proposed to be retarded, therefore the reaction scheme given in Fig. 1 should be involved the complexing effect.

ACKNOWLEDGMENTS

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