

# Polymer Precursor to Diamondlike Carbon Prepared by the Polymerization of $\alpha,\alpha,\alpha$ -Trichlorotoluene and Acetonitrile

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**ABSTRACT:** A novel liquid/solid two-phase reaction of  $\alpha,\alpha,\alpha$ -trichlorotoluene ( $\text{PhCCl}_3$ ) and acetonitrile (AN) has been discovered that produces a carbon-based polymer with diamondlike structure at the atomic level. The solid phase is potassium hydroxide particles, and the liquid phase is a tetrahydrofuran solution of  $\text{PhCCl}_3$  and AN containing a certain amount of tetrabutylammonium bromide as a phase-transfer catalyst. The structure of the carbon-based polymer has been characterized by elemental analysis, Fourier transform infrared spectroscopy, and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy.

The pyrolysis of the carbon-based polymer at  $800^\circ\text{C}$  under a nitrogen atmosphere leads to the formation of a diamondlike carbonaceous material according to the results of X-ray photoelectron spectroscopy and Raman spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 16–23, 2003

**Key words:** pyrolysis; polycondensation; phase transfer catalysts

## INTRODUCTION

Diamondlike carbon (DLC) has been a focus of intense research, mainly because of its attractive mechanical, optical, electrical, chemical, and tribological properties. DLCs are usually prepared as thin films with gas precursors by different techniques, such as low-pressure chemical vapor deposition, plasma-assisted chemical vapor deposition, and plasma-source ion implantation.<sup>1</sup> In recent years, the synthesis of diamond or DLC films from polymer precursors also has been attempted.<sup>2–4</sup> In 1993, a three-dimensional, randomly connected hydrocarbon polymer, poly(phenylcarbyne) (PPC), was synthesized.<sup>2</sup> This polymer possesses a special diamondlike structure at the atomic level. This suggests that diamond or DLC may be synthesized by chemical means at relatively low temperatures and low pressures with PPC as a precursor. Indeed, crystalline diamond was obtained from PPC in 2000.<sup>3,4</sup>

However, few other polymers possessing this special diamondlike structure at the atomic level have been reported. Recently, a novel reaction of chlorofluorocarbons (CFC-22) and acetonitrile (AN) was discovered,<sup>5</sup> and the product was characterized to be a halogen-free and amorphous carbon-based polymer, which may have a linear conjugated structure. Here

we report a new condensation polymerization reaction of AN and  $\alpha,\alpha,\alpha$ -trichlorotoluene ( $\text{PhCCl}_3$ ) in the presence of solid particles of potassium hydroxide (KOH) at room temperature and under normal pressure. As phenyl is a bulky substitute group, the structure of the product is diamondlike at the atomic level. The pyrolysis of the product gives a DLC, which can be synthesized easily on a large scale.

## EXPERIMENTAL

### Materials

AN (Beijing Chemical Factory, Beijing, China) and tetrahydrofuran (THF; Beijing Chemical Factory, Beijing, China) were analytically pure and were distilled before use. Analytically pure KOH ( $\geq 85\%$ ; Beijing Chemical Factory) pellets (0.5 mm thick) were ground into particles ( $\leq 1$  mm in diameter) and then dried *in vacuo* at  $120^\circ\text{C}$  for 24 h.  $\text{PhCCl}_3$  ( $\geq 99\%$ ; Fluka Chemie GmbH, Switzerland) was used as received. Tetrabutylammonium bromide (TBAB; Beijing Daxin Fine Chemicals Institute, Beijing, China) was analytically pure and was also used without further purification.

### Polymerization

A typical polymerization of AN and  $\text{PhCCl}_3$  was carried out in a three-necked flask that consisted of one condenser, one dropper, and one glass tube for nitrogen bubbling. The flask was seated on a magnetic stirrer; 0.5 mmol of TBAB was dissolved in 15 mL of THF, and the solution was poured into 35 g of KOH

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powder in the flask. After nitrogen bubbling for 10 min, a solution of 10 mmol of AN, 10 mmol of  $\text{PhCCl}_3$ , and 5 mL of THF was dropped into the flask within 10 min under stirring. The mixture became yellow immediately and gradually turned brown and finally dark brown. The reaction was performed at 15–20°C without obvious heat emissions. After dropping, the flask was sealed and stirred for 24 h. Then, the flask was cooled in an ice bath, and 500 mL of cold distilled water was added to dissolve the excess KOH and salts formed in the reaction. The rough products were filtered and washed with a large amount of distilled water until they were neutral. After 24 h of drying *in vacuo* at 50°C, 0.45–0.50 g of a brown powder was obtained. It could be dissolved in many solvents such as methanol, THF, dimethyl sulfoxide (DMSO), and acetone but could not be dissolved in water or hexane. A solution was prepared by the dissolution of the powder in THF. With a drop of the solution on a clean glass slice, a smooth tan film was obtained after the solvent volatilized.

The conversion ratio of the reaction ( $f$ ), calculated from the weight of the product, was 30–33%:

$$f = [w_P r_P / (w_T r_T + w_A r_A)] \quad (1)$$

where  $w_P$ ,  $w_T$ , and  $w_A$  are the weights of the product,  $\text{PhCCl}_3$ , and AN, respectively, and  $r_P$ ,  $r_T$ , and  $r_A$  are their corresponding carbon contents.

### Pyrolysis

The pyrolysis of the aforementioned product was carried out in a tube furnace. Generally, the polymer was placed in a ceramic boat and introduced into the tube furnace. Air in the furnace was replaced by  $\text{N}_2$  for at least 20 min. The sample was heated at a rate of 30°C/min to 800°C under a nitrogen atmosphere, and that temperature was maintained for 2 h. The obtained carbonaceous material was cooled to room temperature under a nitrogen atmosphere.

### Structural characterization

X-ray photoelectron spectroscopy (XPS) was measured with a PerkinElmer PHI-5300 ESCA spectrograph (USA). Wide-range X-ray diffraction was carried out with a Bruker D8 Advance spectrograph with a copper target (Madison, WI). The mass spectra were recorded with a Bruker Esquire-LC mass spectrograph with the electrospray ionization mode. The electronic spectrum (in a methanol solution) was measured on an Ultra-spec 4000 ultraviolet–visible spectrophotometer (Pharmacia Bio-Tech, NJ). The NMR spectroscopy [ $(\text{CD}_3)_2\text{SO}$ , 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ ] was performed with a JEOL AL-300 FT-NMR (Japan). The Fourier transform infrared (FTIR) spectra were obtained with a Spectrum GX FT-infrared spectrometer

(KBr pellets; PerkinElmer Co.). The Raman spectra were recorded with an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, UK) employing a 632.8-nm laser beam and a CCD detector with a  $4\text{-cm}^{-1}$  resolution at 2.0 mW and 0.04 mW. The elemental analysis was carried out with a Flash EA 1112 elemental analyzer (ThermoQuest, Italy).

## RESULTS AND DISCUSSION

### Carbon-based polymer made from AN and $\text{PhCCl}_3$

The element analysis results of the carbon-based polymer show that the polymer contains 71.54% carbon, 4.62% hydrogen, 8.57% nitrogen, and 2.07% chlorine (by weight), and the remaining 13.20% should be oxygen. Accordingly, the polymer has a composition formula of  $\text{C}_{9.75}\text{H}_{7.49}\text{N}_{1.00}\text{O}_{1.35}\text{Cl}_{0.10}$ . If AN reacts with equal moles of  $\text{PhCCl}_3$ , the polymer should have a composition formula of  $\text{C}_9\text{H}_5\text{N}$ . The C/N atomic ratio of the polymer is 9.75:1, which is close to the theoretical value of 9:1. The C/H atomic ratio of the product is 9:6.92, which is a little lower than the theoretical value of 9:5. The excess content of hydrogen may result from the  $\text{CH—CN}$  or  $\text{CH}_2\text{—CN}$  groups, in which the hydrogen is not completely substituted, or because some of the nitrile groups ( $\text{—CN}$ ) in the polymer are hydrolyzed into  $\text{—CONH}_2$  or  $\text{—COOH}$ .<sup>5</sup> These reactions can increase the contents of hydrogen and oxygen. The results imply that the polymer is formed from equal moles of AN and  $\text{PhCCl}_3$ , and some side reactions are present in the polymerization process.

The X-ray diffraction pattern of the polymer (Fig. 1) only shows a broad peak at about  $2\theta = 21^\circ$ , indicating that the polymer is amorphous. The polymer powder is soluble in THF, DMSO, or methanol, but it is insoluble in benzene or water. The mass spectrum of the polymer (in THF), illustrated in Figure 2, shows many lines in the mass range of 150–1300. These lines are mainly quasimolecular ions due to the use of the electrospray ionization technique. There are a large number of N atoms in the molecules; as a result,  $\text{NH}^+$  ions can easily be formed. Some lines in the spectrum may belong to multiple-charged ions; therefore, the real molecular mass may be larger.<sup>6</sup> The mass spectroscopy results demonstrate that the polymer is an oligomer with a wide mass dispersity. The main line of the mass spectrum is 620, which may be assigned to the product formed from five  $\text{CH}_3\text{CN}$  molecules and five  $\text{PhCCl}_3$  molecules.

The  $^1\text{H-NMR}$  spectrum (Fig. 3) of the polymer exhibits a broad resonance proton peak centered at 7.3 ppm, which is characteristic of phenyl rings. The sharp peak at 2.48 has been assigned to the proton of the solvent DMSO. The three broad and weak peaks between 3 and 4.5 ppm are attributed to the protons of  $\text{CH—CN}$  or  $\text{CH}_2\text{—CN}$ , which are not completely sub-

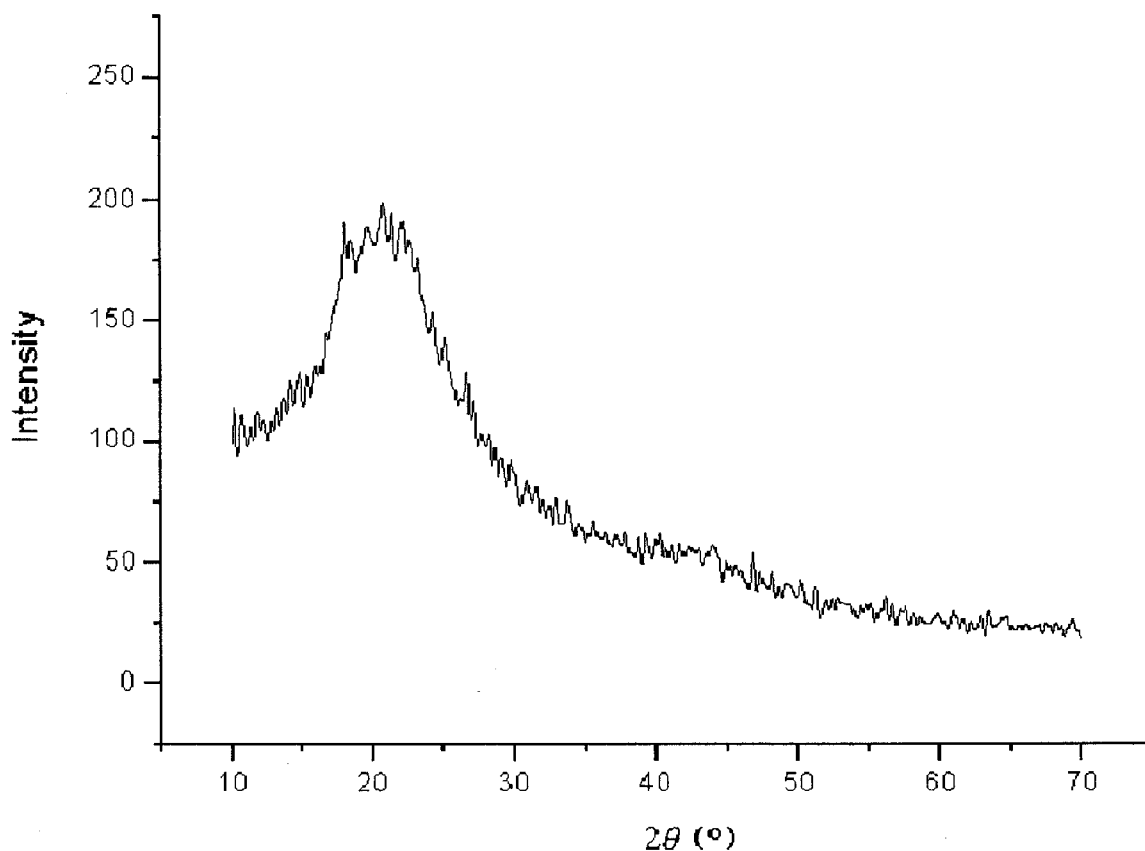


Figure 1 X-ray diffraction pattern of the polymer.

stituted. The  $^{13}\text{C}$ -NMR spectrum [Fig. 4(a)] of the polymer shows no resonance peaks other than those of phenyl rings in the  $\text{sp}^2$  carbon region (110–150 ppm). The results imply that the polymer does not have a structure with conjugated  $\text{C}=\text{C}$  double bonds on the main line.<sup>6</sup> The strong peaks centered at 39.5 ppm are attributed to the carbon of the solvent DMSO. The sharp peaks between 126 and 139 ppm are assigned to phenyl rings and the carbon atom of the nitrile groups ( $-\text{CN}$ ). The sharp peak at 89 ppm is assigned to the

quaternary carbon atom substituted by phenyl or nitrile groups ( $\text{Ph}-\text{C}$  or  $\text{C}-\text{CN}$ ). The sharp peaks at 81, 68, 66, and 60 ppm are assigned to the secondary and tertiary carbon atoms substituted by nitrile groups ( $\text{CH}-\text{CN}$  or  $\text{CH}_2-\text{CN}$ ), which are not completely substituted.<sup>6</sup> In the distortionless enhancement by polarization transfer (DEPT) spectrum of the polymer [Fig. 4(b)], the peaks at 68 and 60 ppm, which are downward, are assigned to secondary carbon atoms ( $\text{CH}_2$ ). The peaks at 81 and 66 ppm and the peaks

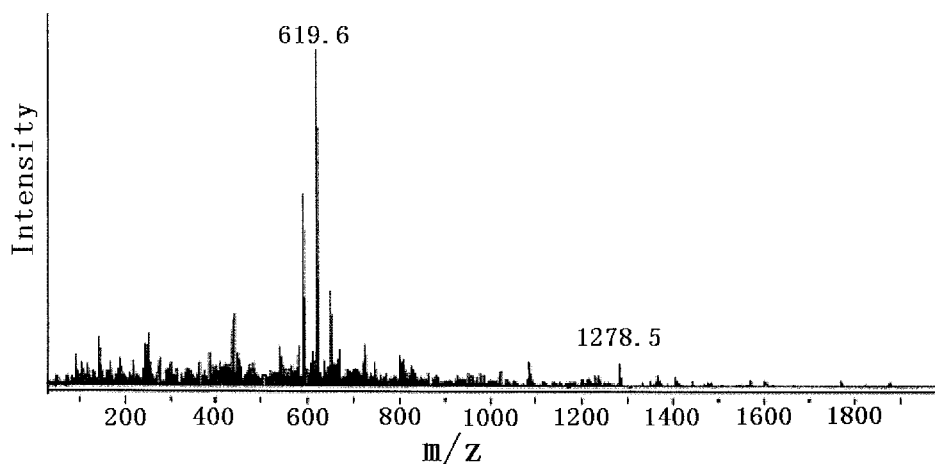


Figure 2 Mass spectrum of the polymer in THF.

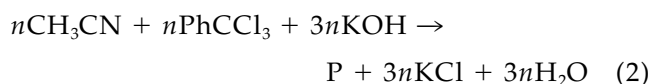
between 126 and 130 ppm, which are upward, are attributed to the tertiary carbon atom (CH). The peaks at 89 ppm and the peaks between 130 and 139 ppm, which disappear in the DEPT spectrum, are assigned to quaternary carbon atoms (C).<sup>6</sup>

The UV-vis spectrum of the polymer (in methanol; Fig. 5) also confirms that the polymer does not have a conjugated structure. Only an intense and broad absorption ( $\lambda_{\max} = 206$  nm) appears in the UV-vis spectrum, which is similar to the UV-vis spectrum of PPC.<sup>2</sup> This absorption band at about 200 nm of PPC (in methanol) has been attributed to extensive  $\sigma$  conjugation that extends across the three-dimensional network backbone. However, the electronic spectrum of cinnaminitrile (*trans*-PhCH=CHCN, in methanol) exhibits a wide and strong peak at 272 nm, indicating the conjugation among phenyl, C=C, and —CN groups.

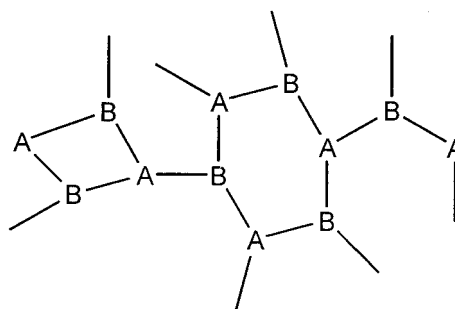
The FTIR spectrum of the polymer is illustrated in Figure 6(a). The figure shows a weak absorption of C—Cl in the region of 500–650  $\text{cm}^{-1}$ , indicating extensive dehalogenation.<sup>5,6</sup> The vibrations of the phenyl ring appear at 3058, 3026, 1955, 1885, 1808, 1598, 1493, 1446, 1074, 1029, 865, 759, 743, and 695  $\text{cm}^{-1}$ . The three weak bands at 1955, 1885, and 1808  $\text{cm}^{-1}$  and three strong bands at 759, 743, and 695  $\text{cm}^{-1}$  demonstrate that the phenyl ring is singly substituted. The vibration of the nitrile group (—CN) is at 2199  $\text{cm}^{-1}$ . The vibration

bands of CH<sub>2</sub> are found at 2930 and 2870  $\text{cm}^{-1}$ . The wide band at 3384 is assigned to the vibration of the —OH group.<sup>3</sup> The Raman spectrum of the polymer (0.04 mW) is shown in Figure 7(a). There is no peak except a delivity, which is assigned to a fluorescence band.

On the basis of the elemental analysis and spectral examinations previously described, the reaction and structure of the polymer can be postulated as follows:



P is



where A is Ph—C and B is C—CN.

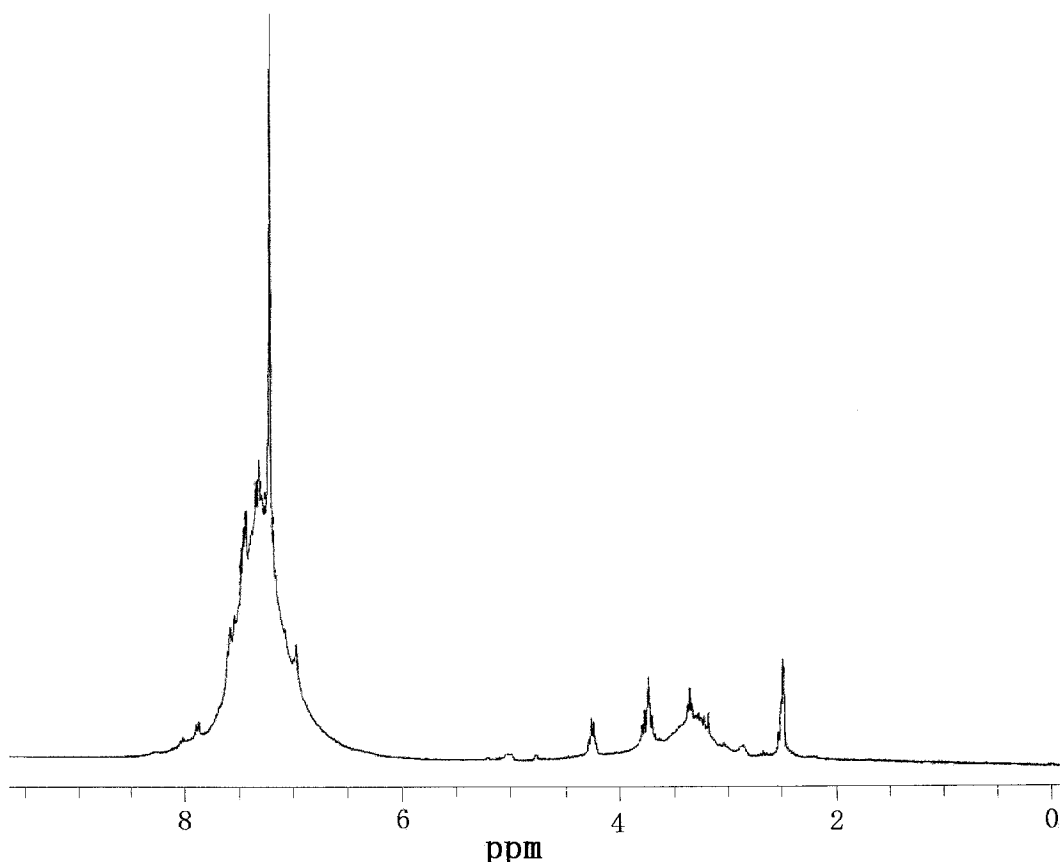


Figure 3 <sup>1</sup>H-NMR spectrum of the polymer in (CD<sub>3</sub>)<sub>2</sub>SO.

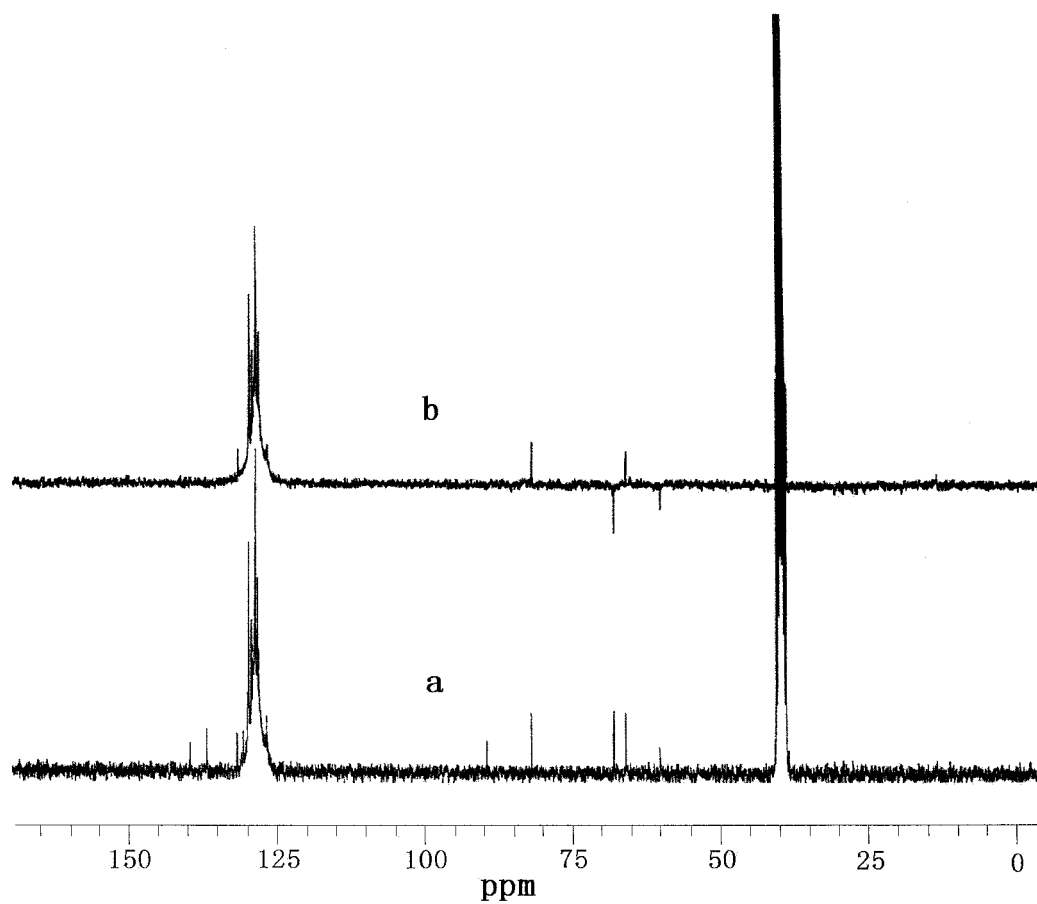


Figure 4 (a) <sup>13</sup>C-NMR spectrum and (b) DEPT spectrum of the polymer in (CD<sub>3</sub>)<sub>2</sub>SO.

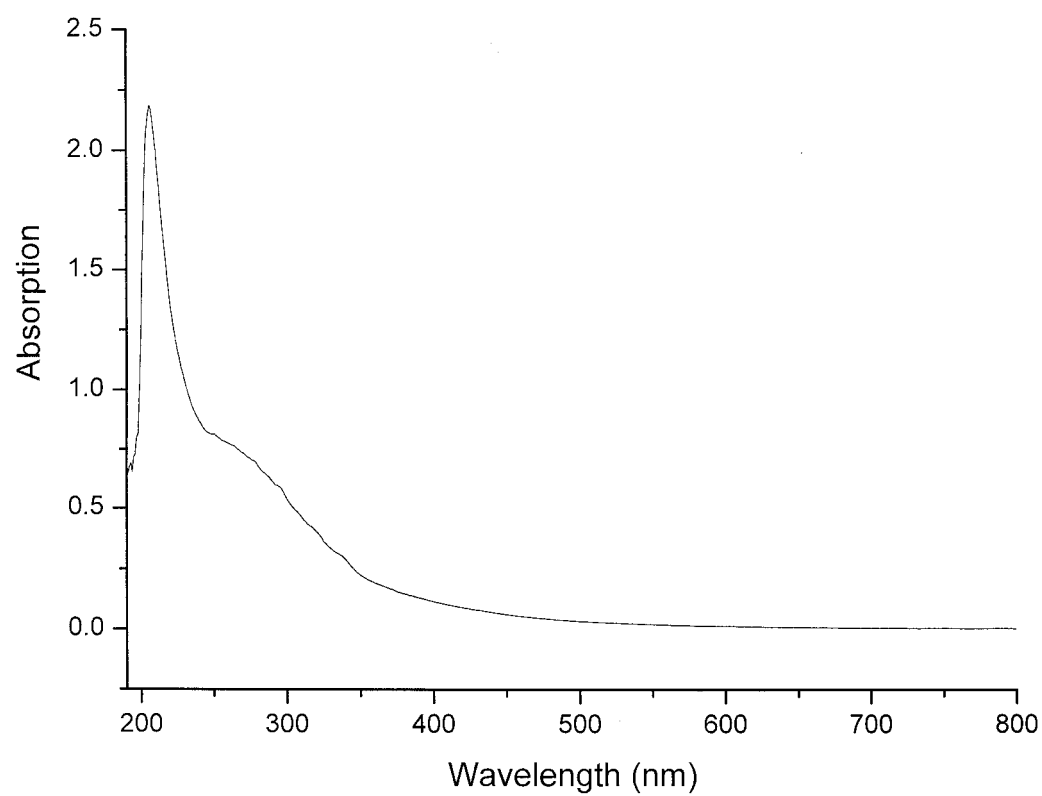


Figure 5 UV-vis spectrum of the polymer in methanol.

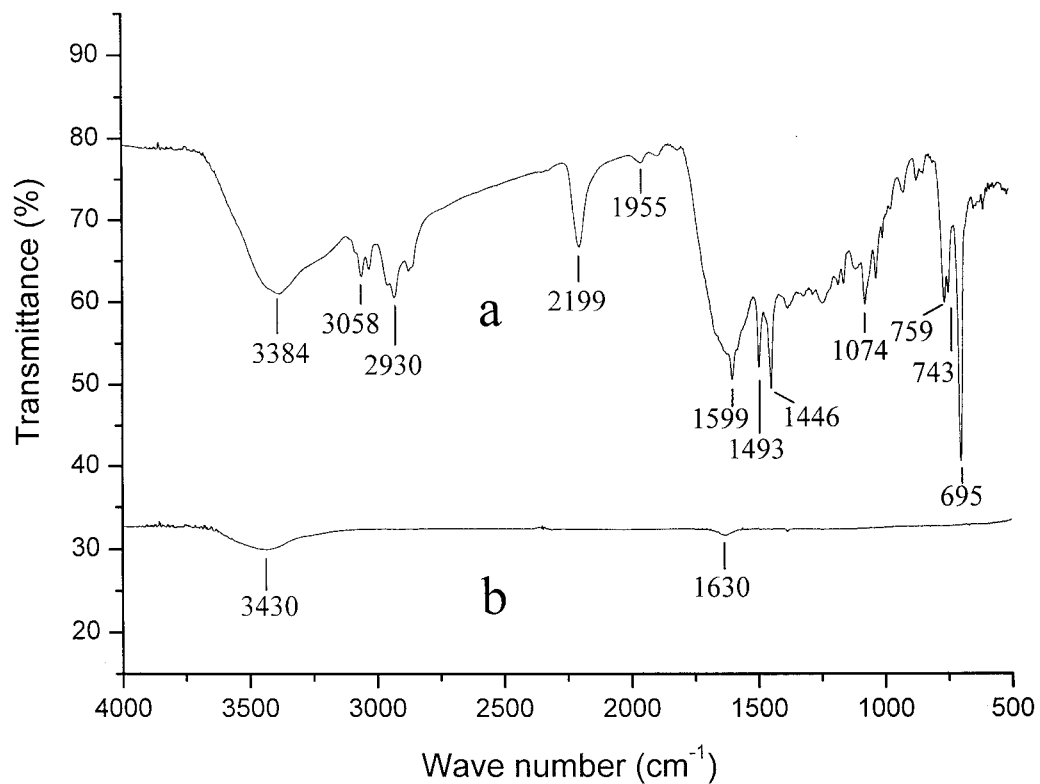


Figure 6 FTIR spectra of (a) the polymer and (b) the pyrolysis product.

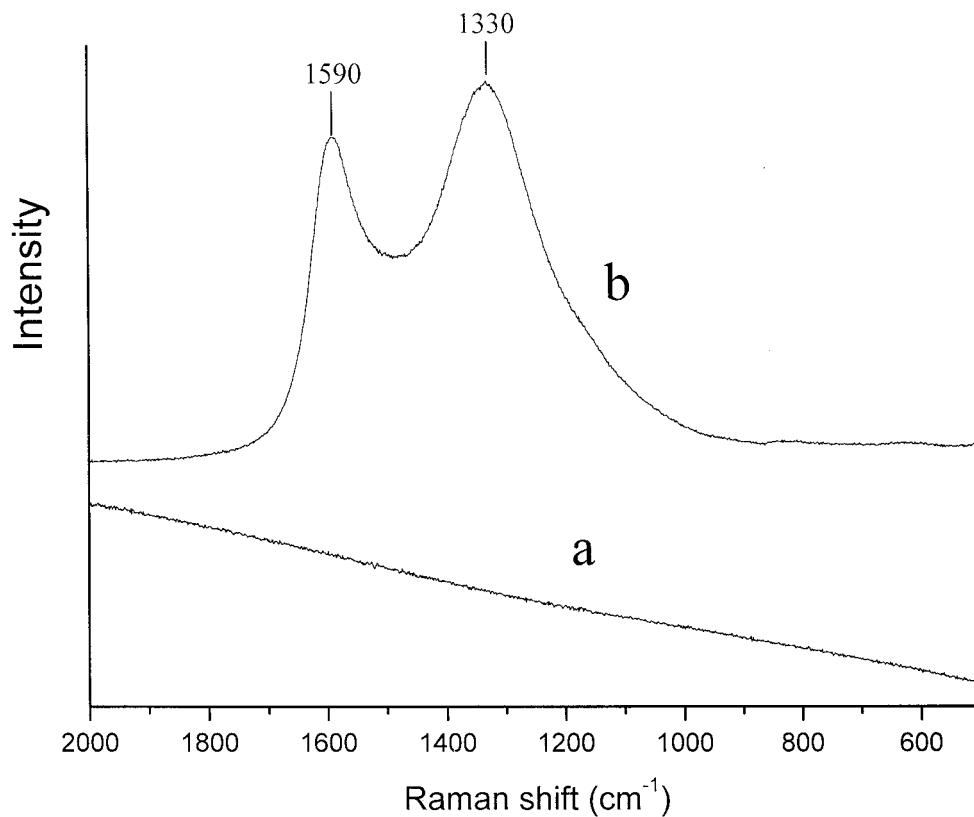


Figure 7 Raman spectra of (a) the polymer (0.04 mW) and (b) the pyrolysis product (2.0 mW).

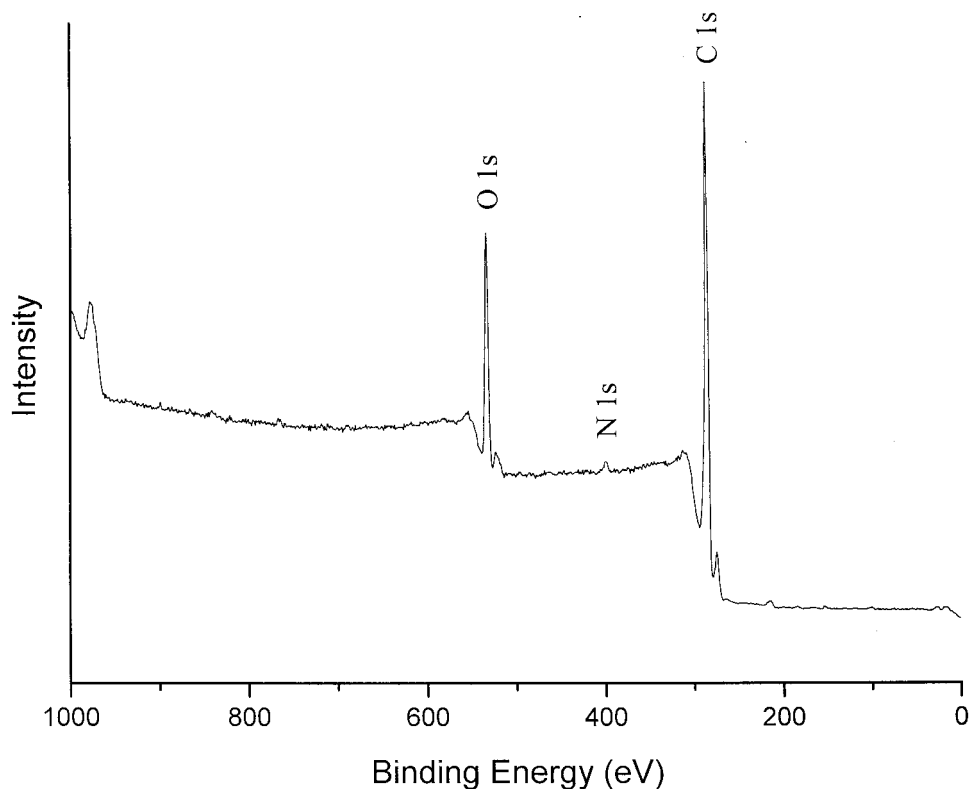


Figure 8 XPS spectrum of the pyrolysis product.

#### DLC made by pyrolysis of the carbon-based polymer

Only about one-third of the original weight of the polymer product is left after pyrolysis at 800°C for 2 h. The powder is converted into a black and highly reflective solid. The element analysis of a typical sample indicates that the carbonaceous material contains 88.71% carbon, 0.65% hydrogen, and 6.58% nitrogen (by weight), and the remaining 4.06% should be oxygen. There is no detectable Cl content in the pyrolysis product. That means that the product has a composition formula of  $C_{15.73}H_{1.37}N_{1.00}O_{0.54}$ . There are only weak bands at 3430 and 1630  $\text{cm}^{-1}$  in the FTIR spectrum [Fig. 6(b)], which are assigned to the vibrations of moisture absorbed in the pyrolysis product.<sup>6</sup> The vibrations of phenyl groups and nitride groups disappear extensively. The Raman spectrum [Fig. 7(b); 2.0 mW] shows only two strong peaks, one peak at 1590  $\text{cm}^{-1}$ , which corresponds to nondiamond carbon, and a peak at 1330  $\text{cm}^{-1}$ , which is indicative of diamond or predominantly  $\text{sp}^3$ -bonded DLC.<sup>2,3</sup> However, the D-band of polycrystalline graphite is usually above 1340  $\text{cm}^{-1}$  and often appears around 1355  $\text{cm}^{-1}$ .<sup>7,8</sup> The chemical composition and bonding states of the pyrolysis product were investigated with XPS (Fig. 8). The atom number C/O/N ratio on the product surface is approximately 61:11:1. The XPS spectrum (Fig. 9) shows that the C1s peak of the C—C bonding consists

of three peaks at 283.9, 285.3, and 288.8 eV, which are assigned to  $\text{sp}^2$  C—C bonds,  $\text{sp}^3$  C—C bonds, and C—O bonds, respectively. The  $\text{sp}^3$  fraction is 57.6%;

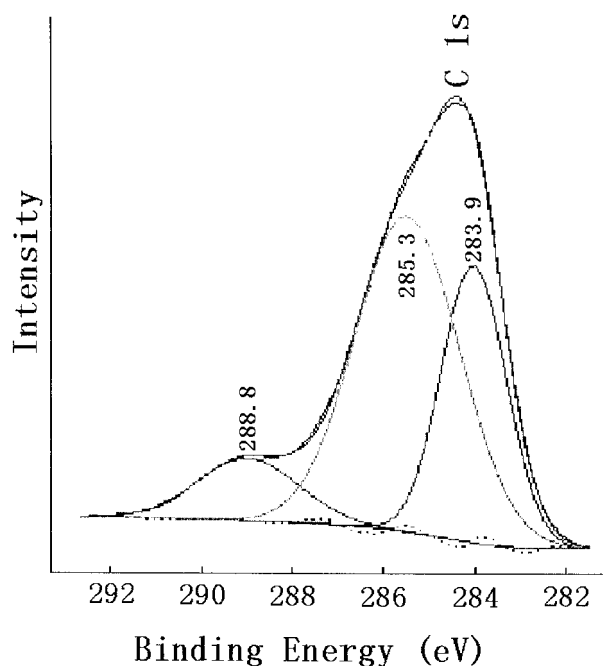


Figure 9 C1s peak in the XPS spectrum of the pyrolysis product consisting of three peaks at 283.9, 285.3, and 288.8 eV.

the  $sp^2$  fraction is 31.4% and the remaining 11.0% is attributed to C—O bonds. This means that the structure of the pyrolysis product is diamondlike. The oxygen content on the surface is higher than that of the pyrolysis product bulk, and this may be attributed to partial oxidation of the surface. The higher fraction of C—O bonds can also be attributed to the partial oxidation of the surface.

On the basis of the elemental analysis and spectral examinations, we know that the conversion of this  $sp^3$ -bonded carbon network to a predominantly  $sp^3$ -bonded carbon phase is favored even at low temperatures and atmosphere pressure.

### CONCLUSIONS

A new condensation polymerization reaction of AN and  $PhCCl_3$  can be performed in the presence of solid particles of KOH at room temperature and normal

pressure. The product is an oligomer possessing a diamondlike structure at the atomic level. The pyrolysis of the polymer gives a diamondlike carbonaceous material containing small amounts of N, H, and O as impurities.

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