

# Liquid/Solid Two-Phase Carbonization of Low-Molecular-Weight Chloro-/Bromo-Hydrocarbons

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**ABSTRACT:** A novel liquid/solid two-phase reaction has been discovered that enables destruction of a series of low-molecular-weight chloro-/bromo-hydrocarbons to carbon-based materials. The solid phase is anhydrous potassium hydroxide and the liquid phase is a benzene or tetrahydrofuran solution of halide and contains a certain amount of tetrabutyl ammonium bromide (TBAB) as phase transfer catalyst. The structure of the carbon-based materials have been characterized by elemental analysis, Fourier transform infrared (FT-IR), FT-Raman, and X-ray photoelectron spectroscopies, and their morphologies have been examined by wide-angle X-ray diffraction and transmission electron microscopy. The results indicate that the products are amorphous nanoparticles and contain mainly elemental carbon. They consist of  $sp$ ,  $sp^2$ , and  $sp^3$  carbon atoms simultaneously and can be regarded as carbyne analogues. This work provides a convenient method for synthesizing new carbon-based materials in relatively high yields. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1510–1515, 2000

**Key words:** carbyne analogue; two-phase carbonization; catalyzation; chloro-/bromo-hydrocarbon

## INTRODUCTION

Carbon-based materials, clusters, and molecules are unique in many ways.<sup>1</sup> This fact has spawned an increasing interest in syntheses and characterization of carbon materials.<sup>2</sup> Many forms of carbon-based materials such as diamond, graphite, and fullerenes have been studied extensively. However, the present state of knowledge in linear chain, which has  $sp$  bonding, is still fragmentary.<sup>3</sup> A polymeric form of carbon consisting of polyynes ( $-C\equiv C-C\equiv C-$ ) or polycumulene ( $=C=C=C=C=$ ) structure is referred as “carbynes.” Pure carbynes have never been obtained, thus, the presence of carbyne has been repeatedly

doubted.<sup>4</sup> On the other hand, many carbon-based materials containing short polyyne or polycumulene moieties can be obtained by various approaches, and they are defined as “carbyne analogues.” Synthetic routes to carbyne analogues mainly include: (1) Condensation of carbon vapor; phase transition of diamond or graphite and shock compression of glassy carbon<sup>5</sup>; (2) oxidative dehydropolymerization of acetylene,<sup>6</sup> electrochemical condensation of diiodoacetylene,<sup>7</sup> hexachlorobuta-1, 3-diene<sup>8</sup>; (3) completely reductive dehalogenation of perhalogenated polymers (e.g. poly(tetrafluoroethylene)).<sup>9,10</sup> [However, the redox carbonizations are often slow and complicated by side reactions.<sup>2</sup> Furthermore, recently, several works have studied the reductive carbonization of substituted carbon trichlorides with Na/K alloy. It has been found that  $(RC)_n$  with three-dimensional  $sp^3$  carbon networks are produced from these systems.<sup>11,12</sup>]; (4) dehydrohalogenation of poly(vinylidene halides)<sup>13–15</sup>; chlorinated poly-

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acetylene<sup>16</sup> in alkaline media also can produce carbyne analogues.

It is well known that low-molecular-weight carbon halides can be dehydrohalogenated into corresponding olefins or alkynes by a strong base. However, few works concern chemical syntheses of elemental carbons from low-molecular-weight halides. Recently, we have found that trichloroethane can be carbonized by dehydrochlorination under phase transfer conditions.<sup>17,18</sup> In these cases, the halides are dropped directly into the base and the yield of carbon is relatively low (~ 40%). Here, we desire to report a liquid/solid two-phase reaction for carbonization of various chloro-/bromo-hydrocarbons with one or two carbon atoms. This technique can produce carbyne-like materials in fairly high yields.

## EXPERIMENTAL

### Materials

Dichloromethane, dibromomethane, chloroform, bromoform, benzene, tetrahydrofuran (THF), and tetrabutyl ammonium bromide (TBAB) were analytical pure products of Huakang Chemical Factory (Nanjing, China). 1,1,1- and 1,1,2-trichloroethanes were also analytical grade pure and purchased from Guangdong Xilong Chemical Factory (Santou, China) and Shanghai 1<sup>st</sup> Chemical Factory (Shanghai, China), respectively. All the reagents were used as received.

### Carbonization of the Halides

Typical carbonization of chloro-/bromo-hydrocarbons was 3 mL halide substrate and 5% (the molar ratio to the halide) TBAB were dissolved in 20–50 mL organic solvent (Ben or THF), and then the solution was poured to 80–120 g KOH powder and mixed by vibration. Potassium hydroxide (KOH) pellets (0.5 mm in thickness) were freshly powdered (< 2 mm in diameter) and used immediately. The reaction system was sealed and the temperature was controlled by a water bath. Black carbon gradually deposited on the surface of KOH particles. After reaction of 2 days at 30°C, 250 mL ice-cooled water was added to dissolve the extra KOH and the salts formed by the reaction. Black carbon powders were separated by filtration. Then, they were washed with a large amount of water and ethanol repeatedly. Finally, the clean products were dried under vacuum and

at 60°C to constant weight. The yield (*Y*) of carbon product was calculated by using eq. (1):

$$Y = (w_p f_c / w_t) \times 100\% \quad (1)$$

where  $w_p$  was the found weight of the carbon product,  $f_c$  was its carbon content measured by elemental analysis, and  $w_t$  was the theoretical carbon weight calculated from the weight of the halide reactant.

### Doping of Carbon Product

The doping of carbon product was conducted by immersing the dried product powders in iodine-saturated carbon tetrachloride solution for 2 h, then filtered and washed with clean solvent three times. They had been dried under vacuum at 60°C for 24 h before conductivity measurement.

### Characterization

Infrared spectra were recorded on an IFS-66V Fourier transform infrared (FT-IR) spectrometer (with KBr pellets). FT-Raman spectra were taken out by using a RFS-100 FT-Raman spectrometer of Bruker company with a typical laser power of 70–90 mW and accumulated for 1000 times scans. Elemental analysis was performed by a Perkin-Elmer 240 C elemental analyzer. X-ray photoelectron spectra were recorded using a photon electron spectrometer model VGS 5000. Curve fitting of C 1s spectrum was accomplished using nonlinear least squares procedure.<sup>19</sup> Quantification of the surface concentrations of elements was accomplished by correcting the photoelectron peak areas for their cross-sections.<sup>20</sup> The photographs of transmission electron microscopy were obtained by using an EM-200CX transmission microscopy. X-ray diffraction analyses were carried out on a XD-3A X-ray diffraction analyzer. The conductivities of iodine-doped carbon samples were measured by conventional four-probe d.c. technique.

## RESULTS AND DISCUSSION

### System Selection

We first attempted the carbonization of 1,1,1-trichloroethane in an aqueous KOH (60% by weight)/halide liquid/liquid two-phase system. Tetrabutyl ammonium bromide was used as phase transfer catalyst to accelerate the reaction.

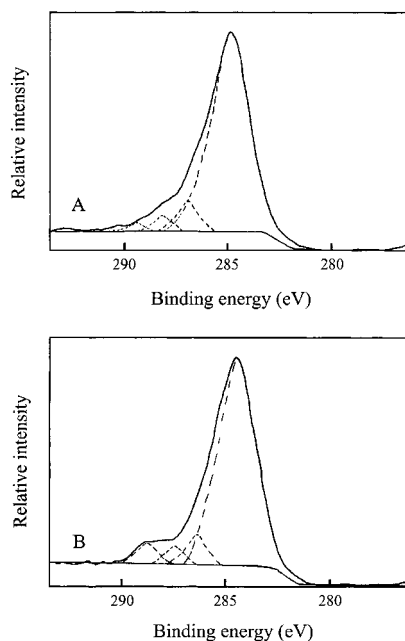
**Table I** Carbonization Products Made From Various Chloro-/Bromo-Hydrocarbons

Substrate	Solvent	Elemental Composition (%)				Carbon Yield (%)
		C	H	O	X <sup>a</sup>	
CH <sub>2</sub> Cl <sub>2</sub>	THF	75.85	4.49	18.82	0.84	67
CH <sub>2</sub> Cl <sub>2</sub>	Ben	73.27	4.32	21.52	0.89	37
CH <sub>2</sub> Br <sub>2</sub>	Ben	68.75	4.41	26.22	0.62	65
CHCl <sub>3</sub>	Ben	55.54	3.36	16.76	24.34	69
CHBr <sub>3</sub>	Ben	33.30	3.17	16.60	46.93	67
CH <sub>3</sub> CCl <sub>3</sub>	Ben	75.80	4.49	19.18	0.53	80
CH <sub>2</sub> ClCHCl <sub>2</sub>	Ben	75.89	5.03	18.66	0.42	81

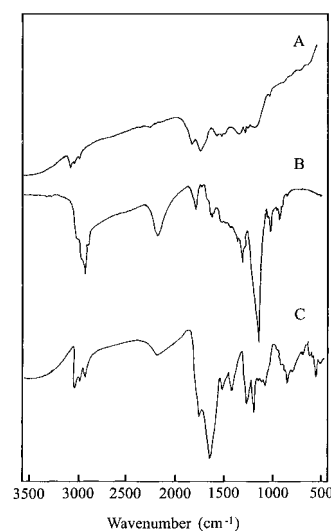
<sup>a</sup> Content of X (Cl, Br) was determined by XPS measurement.

Unfortunately, this effort was tested to be unsuccessful. A large amount of colorless gas was escaped from the organic phase and no carbon material was obtained. The gas was suggested to be 1-chloroacetylene as studied by Kimura and Regen.<sup>21</sup> Thus, for extensive dehydrochlorination of the halide, a water-free system was necessary and dry KOH therefore seemed to be a good choice. On the other hand, as pure halide solution was dropped directly into stoichiometric amount of the base, the reaction conversion was very low (< 5%), most probably due to the limitation of the base surface area and insufficient absorption of

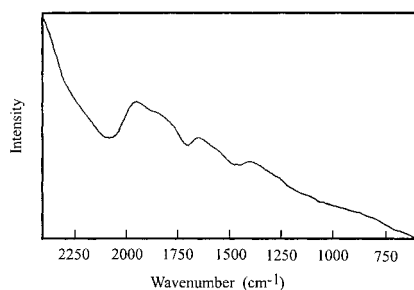
water produced in the carbonization process. KOH in excess could provide larger surface area for reaction and act as a water absorbent. The removing of water forced the reaction to form carbon. Indeed, the yield of carbon product increased by increasing the base/halide molar ratio ( $R_{b/h}$ ). As  $R_{b/h}$  increased up to about 14 : 1, the conversion of the reaction increased up to about 40%,<sup>17</sup> still much lower than the desired percentage. In the pure halide/solid KOH system, the reaction happened dramatically and was accompanied with a large amount of heat. The high reaction rate prevented the halide from mixing uniformly with the base, and caused domain reactions and regional high temperatures. This increased not only the difficulty of reaction control,



**Figure 1** X-ray photoelectron spectra of the C 1s lines of the carbons made from dichloromethane (A) and chloroform (B).



**Figure 2** FT-IR spectra of the carbons made from dichloromethane (A), 1,1,1-trichloroethane (B), and chloroform (C).



**Figure 3** FT-Raman spectrum of the carbon made from dichloromethane.

but also the chance of side reactions. Therefore, in this study, we used benzene or tetrahydrofuran as an inert solvent to dilute the halides and decrease the reaction rates. The reaction could be carried out at room temperature and its carbon yield was fairly high (Table I). It should be noted here that the ammonium salt, TBAB, was an effective solid/liquid phase transfer catalyst.<sup>22</sup> In our system without TBAB, the conversion of the reaction was found to be lower than 5%.

### Elemental Analysis

The elemental contents of the carbon products examined by elemental analysis (C, H,) and X-ray photoelectron spectroscopy (Cl, Br) are listed in Table I. According to this table, the products made from the halides with equal numbers of hydrogen and halogen atoms almost have no halogen component, indicating extensive dehydrohalogenations. On the other hand, the carbons prepared from chloroform and bromoform contain a little amount of halogen. The atomic ratio of halogen and carbon is found to be 0.15–0.21 : 1.00. All the carbons have hydrogen and oxygen components, most probably due to complicated surface oxides (such as —OH, —COOH, —C=O) resulted

from oxidation by the air during purification and characterization processes.<sup>2</sup>

### XPS Spectra

The carbons made from the halides with equal numbers of halogen and hydrogen atoms show a typical XPS spectrum of C 1s line of Figure 1A. This spectrum has a strong electron band with C 1s line at about 284.5 eV that can be assigned to elemental carbon.<sup>23</sup> There are several weak shoulder bands of carbonyl groups (C=O) and hydrohalogenated carbon atoms (—CHX—, —CX<sub>2</sub>—CH<sub>2</sub>—) are appeared at 287.1, 288.5, and 289.3 eV, respectively.<sup>24</sup> The band at 289.3 eV is so weak that almost can be neglected. However, in the spectrum of the carbon obtained from chloroform or bromoform (Fig. 1B), the 289.3 eV is relatively stronger and can be found clearly because of relatively higher halogen contents. Figure 1 also shows the population of elemental carbon occupies about 70–80% of all the carbon atoms.

### FT-IR Spectra

FT-IR spectrum of the carbon made from dichloro- or dibromomethane is shown Figure 2A. This figure shows no absorption of C—Cl in the region of 570–700 cm<sup>-1</sup>, indicating an extensive dehydrochlorination of the halide. Strong absorption typical of cumulene carbon (=C=C=) appears at 1625 and 1705 cm<sup>-1</sup>.<sup>14</sup> In comparison, the band at 2159 cm<sup>-1</sup> attributed to the valence vibration of carbon-carbon triple bonds is much weaker.<sup>10,25</sup> The bands in the region of 2800–2900 cm<sup>-1</sup> are assigned to the valence vibration of CH<sub>2</sub> groups. The overall feature of Figure 2A is quite similar to that of the polycumulene-like materials made from poly(vinylidene dichloride) (PVDC).<sup>15</sup> On the other hand, the IR spectra of

**Table II** FT-Raman Data of the Carbon Products:  $I_{c-C}/I_{a-C}$  Indicates the Raman Intensity Ratio of the Band at Around 1900 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>

Substrate	Raman Bands			$I_{c-C}/I_{a-C}$
CH <sub>2</sub> Cl <sub>2</sub>	1950 (s&b)	1612 (m)	1421 (w)	4.65
CH <sub>2</sub> Br <sub>2</sub>	1919 (s&b)	1641 (m)	1387 (w)	3.19
CHCl <sub>3</sub>	1873 (s&b)	1624 (m)	1360 (w)	3.26
CHBr <sub>3</sub>	1927 (s&b)	1598 (m)	1369 (w)	2.46
CH <sub>2</sub> ClCHCl <sub>2</sub>	1965 (s&b)	1661 (m)	1416 (w)	3.13
CH <sub>3</sub> CCl <sub>3</sub>	1876 (s&b)	1599 (m)	1369 (w)	2.67

**Table III** X-ray Diffraction Data of the Products Made From Different Halide Substrates

Substrate	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Br <sub>2</sub>	CHCl <sub>3</sub>	CHBr <sub>3</sub>	CH <sub>2</sub> ClCHCl <sub>2</sub>	CH <sub>3</sub> CCl <sub>3</sub>
2θ (°)	21	22	21	28	22	21

the carbons made from trichloroethanes show relatively stronger bands of carbon-carbon triple bonds and carbon-carbon single bonds around 2130 and 1100 cm<sup>-1</sup>, respectively (Fig. 2B). These results demonstrate that they have relatively higher concentrations of polyene moieties. The carbons obtained from chloroform or bromoform show an IR spectrum (Fig. 2C) with relatively stronger C—X bands in the region of 500–700 cm<sup>-1</sup>, indicating that they have halogen components while they also show polycumulene structures.

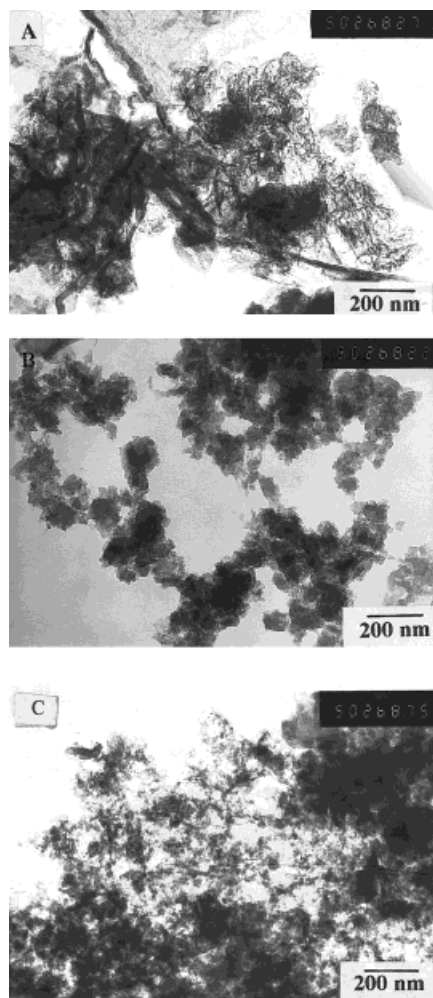
#### FT-Raman Spectra

The FT-Raman spectra of the carbon products have *sp*, *sp*<sup>2</sup>, and *sp*<sup>3</sup> hybridized carbon atoms simultaneously. Figure 3 is the spectrum of the carbon made from dichloromethane. There is a broad and strong band centered at 1950 cm<sup>-1</sup>, which is assigned to the carbon-carbon stretching mode of *sp*-bonded carbon (c—C).<sup>3</sup> Two much weaker bands at 1600 and 1400 cm<sup>-1</sup> are common for all forms of polycrystalline graphite or “amorphous carbon” with broad distribution of *sp*<sup>2</sup> and *sp*<sup>3</sup> bonded carbon atoms (a—C).<sup>3</sup> The intensity ratio of  $I_{c-C}/I_{a-C}$  is calculated to be 4.65. There are no other carbon materials that show such a strong Raman signal of *sp* hybridized carbon, indicating high concentrations of polyene or polycumulene sequences. Table II lists the Raman data of all the carbons. On the basis of elemental analysis and spectral results described above, it is reasonable to conclude that the carbon products are carbyne-like materials with high concentrations of conjugated *sp*-bonded carbon sequences and complicated with various oxide contents.

#### Morphology and Conductivity

The carbon products are amorphous and their X-ray diffraction patterns usually show only a broad peak at about 2θ = 21°, except that of the carbon made from bromoform (its peak is appeared at 2θ = 28°) as listed in Table III. Transmission electron micrographs of the carbons are shown in Figure 4. It is clear from these pictures that the carbons are nanoparticles with diame-

ters lower than 60 nm and the particles are aggregated to larger bodies. The conductivities of the carbon pellet samples prepared under a pressure of 320 kgf cm<sup>-2</sup> are measured to be in the order of 10<sup>-7</sup> S cm<sup>-1</sup>, which are close to those of the carbyne analogues synthesized chemically or electrochemically. After iodine doping, their conductivities increase up to the order of 10<sup>-3</sup> S cm<sup>-1</sup>.



**Figure 4** Transmission electron micrographs of the carbons made from dichloromethane (A), bromoform (B), and 1,1,2-trichloroethane (C).

## CONCLUSIONS

Chloro-/bromo-hydrocarbons with one or two carbon atoms can be carbonized by powdery potassium hydroxide powder under a liquid/solid phase-transfer condition. This reaction can be carried out at room temperature and normal pressure. The products are characterized to be amorphous carbon-based nanoparticles. They have a carbyne-like structure with high concentrations of polyyne or polycumulene segments and can be changed from insulators to semiconductors by iodine doping.

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