conversion by powdering was observed for all HDPE samples in this work including electron beam irradiated ones. This result implies that the powdering process routinely done in analytical laboratories can alter physical properties of the original samples via phase transformation so that the process should be taken with consideration. Increase of crystallinity due to high temperature and pressure was negligible, probably because the pressure during cooling period was low.

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The Generation of Stable Carbon Radicals by Pyrolysis of Poly(2,4-hexadiyne-1,6-diol)

Sang Won Park and Jeong Soo Kim*

Dept. of Polymer Sci. and Eng.,
Chungnam National Univ., Yusung-Gu,
Taejon 305-764, Korea

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Recently, organic ferromagnets have become issues in pure and applied sciences.[1] Many theoretical models and possible organic structures were proposed as possible candidates for them.[2] Most of them are based on the ferromagnetic interaction among unpaired electrons of charge-transfer-complex or alternating hydrocarbons.[3] Application of topologically symmetrical π-electron orbitals in alternating hydrocarbons is an interesting approach for polymer chemists toward organic ferromagnets, in which the degeneracy of π-nonbonding orbital is unlimited. Based on this model, several polymeric structures with polyradicals have been prepared, and some of them have showed the ferromagnetic behavior in laboratorial sense in spite of very poor reproducibilities and structural unclearness.[4]

Ovchinnikov and coworkers have reported the possibility of polymeric carbons, which have the ferromagnetic coupling of concentrated unpaired π-electrons.[5] They have obtained the carbon materials which shows a comparable magnetization with α-Fe by controlled pyrolysis of polyacrylonitrile and following magnetic separation, although detailed synthetic or pyrolytic process was not illucidated. The ferromagnetism of above polymeric carbon was assumed to be caused by the intermediate graphite-diamond structure, in which sp^2 and sp^3 hybrid orbitals are perfectly alternating.

The ferromagnetic carbon obtained from pyrolyzed PAN indicates that the highly ordered polymeric crystal can be a more useful precursor than the amorphous polymer if they can be pyrolyzed with high carbon yield. The diacetylene compound can be one of the best candidates for the purpose. We selected here 2,4-hexadiyne-1,6-diol as a diacetylene compound that has hydroxymethyl side chain, which is assumed to be pyrolyzed with high carbonyield as cellulose or PVC.

Experimental

Materials. Propargyl alcohol, acrylonitrile, and methacrylic acid were reagent grade from Aldrich Chemical Co. and used without further purification.

Suspension polymerization of polyacrylonitrile (PAN). PAN was obtained by general method of suspension polymerization. 0.1 g of poly(vinyl alcohol) was dissolved with 300 g of distilled water in 1 L four-neck-flask, and the mixture of 96 g of acrylonitrile and 4 g of methacrylic acid was added. The bath temperature was maintained at 60 ℃ and 0.25 g of potassium sulfate and 0.1 g of potassium metasulfite were then added. PAN powder was obtained through filtering and drying. The molecular weight of PAN was about 320,000 g/mol., which was calculated from the measured intrinsic viscosity.

Synthesis of poly(2,4-hexadiyne-1,6-diol)(PHDD). The reported synthetic method of 2,4-hexadiyne-1,6-diol from propargyl alcohol was modified because of its poor reproducibility.[6] 11.2 g of propargyl alcohol was added into the solution of 25 g of CuCl (0.13 mole) and 40 g of ammonium chloride (0.75 mole) in 200 mL of distilled water. The reactor was put under the oxygen atmosphere with a balloon during reaction. The addition of propargyl alcohol resulted in colour change of the reagent solution from transparent blue to brown. With the propagation of reaction, the blue dispersion was formed. The filtrate was extracted three times with diethyl ether. The product HDD was obtained as a yellow solid by evaporation of diethyl ether after drying on magnesium sulfate. The crude HDD product was recrystallized from diethyl ether, yielding needlelike crystals. The reported spectroscopic data of HDD was compared with obtained ones by us, leading to the structural confirmation of HDD.[6] The melting point of HDD was 113.8 ℃, which was higher than reported value 112 ℃.[7] HDD was topochemically polymerized by a thermal method for 90 min. The long glass tube with the diameter of 3 cm containing HDD crystals was deeply immersed into the fluidized sand bath maintained at 110 ℃. The pale yellow needles change its colour to dark brown without apparent change in crystals. Thereafter, the bath-temperature was raised to 140 ℃, that resulted in a rapid reaction, leading to the formation of black powder.

Pyrolysis of poly(2,4-hexadiyne-1,6-diol)(PHDD). The obtained black powder was placed in a quartz tube of furnace under the nitrogen atmosphere. The temperature was raised to 500 ℃ for two hours and then to 1,000 ℃ for one hour.

Measurement of magnetic Properties. Magnetic susceptibilities were measured with a Gouy-type magnetic balance. ESR spectra were obtained with Bruker ESP-300S.

Results and Discussion

The compounds that contain diacetylene moieties can be topochemically polymerized by UV-irradiation or heat, when they have a parallel arrangement of diacetylenes and enough short distance between diacetylene moieties for reaction in crystals. HDD was prepared by a well-known oxidative coupling of propargyl alcohol as shown in Figure 1.[6] There are general prerequisites for topochemical solid state polymerization that distances among the adjacent diacetylene groups should not exceed 6 Å and shearing of side group be possible.[7] HDD has the structure that meets the both requirements. Furthermore, hydroxymethyl group of HDD is a adequate strutural part to raise carbon yield because oxidation of polymers can prevent chain breakdown into gaseous products.[8]

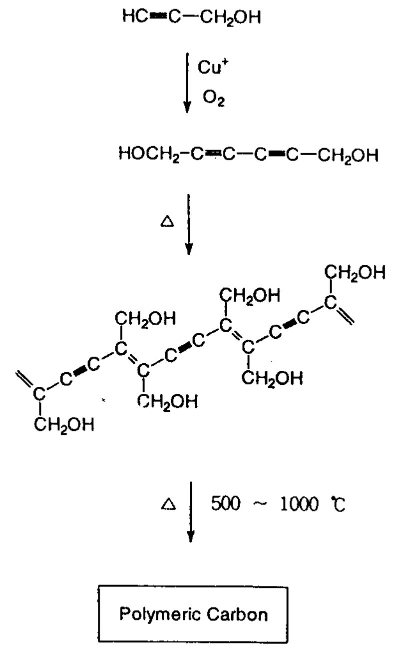

Figure 1. Synthetic pathway of PHDD.

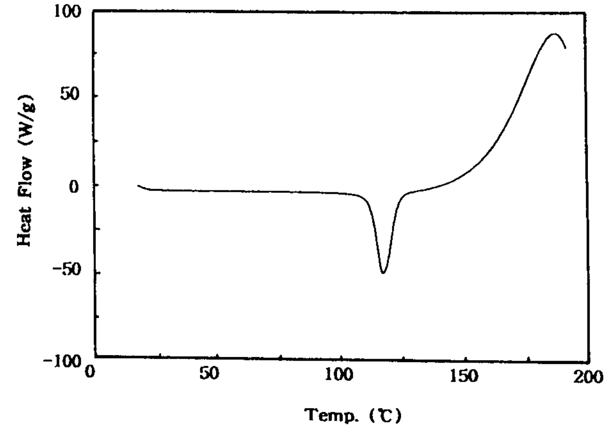

Figure 2. DSC thermogram of PHDD.

The topochemical reactivity of HDD was reported to be low.[7] The low reactivity was confirmed by the comparison of IR spectra, in which no remarkable decrease of the absorption intensity in diacetylene groups was obtained. The DSC thermogram of PHDD is shown in Figure 2. Polymerization resulted in a dark-brown crystal from pale-yellow one. Although melting endotherm of PHDD was shown at 114 ℃ in Figure 2, any melt-out of PHDD crystals was not observed, while it was done in monomer HDD. This means that partial polymerization occurs in crystals of HDD. As shown in Figure 2, rapid degradative reaction occurs above 140 ℃ with the formation of black powder. The obtained black powder was carbonized in the furnace as described in experimental part. For comparative analysis, the synthesized PAN powder was pyrolyzed under same conditions *via* air-oxidation at 254 ℃ for 60 minutes (PAN-A) or 265 ℃ for 80 minutes (PAN-B).

The paramagnetic susceptibilities were measured and their results are summarized in Table 1. The corrected values were obtained by the Pascal's diamagnetic constant of -6.0×10^{-6} emu/mole for carbon.[9] The difference between PAN-A and PAN-B means that thermal history plays an important role for a magnetic behavior. Before carbonization of PHDD, the sample showed the diamagnetic property irrespective of theoretical correction. But all the samples after carbonization showed very weak paramagnetism. The theoretical paramagnetic susceptibility is 1.25×10^{-3} emu/mole, which leads *ca.* 0.2-1% carbon radical content of the sample. ESR spectra

Table 1. Magnetic susceptibility of pyrolyzed PAN and PHDD

Sample	Carbon yield (%)	$\chi_g \times 10^6$ (emu/g) (measured)	$\chi_g \times 10^6$ (emu/g) (corrected)
PAN-A	54	0.48	0.96
PAN-B	54	−0.23	0.27
HDD	–	−0.97	−0.47
PHDD	22	−0.29	0.21

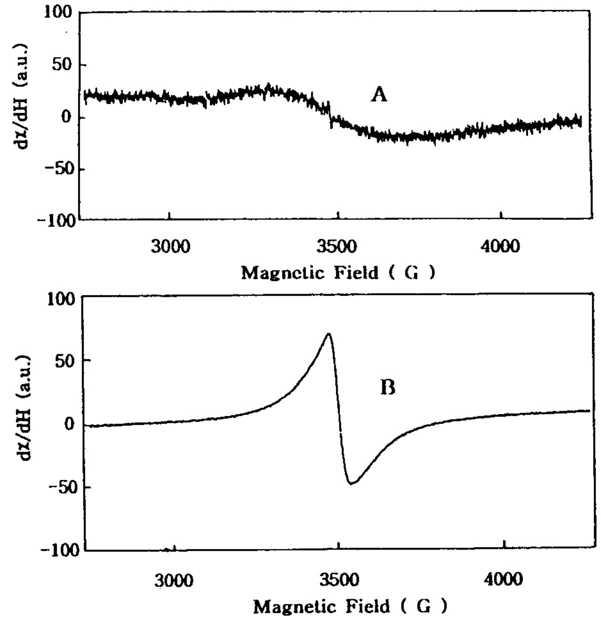

Figure 3. ESR spectra of PHDD (A) and PAN-A (B).

obtained from 9.745 GHz X-band was shown in Figure 3. Although the signal has a large fluctuation because of the conductivity of carbon powder, the calculated g-value was to confirm the presence of carbon radicals. Ovchinnikov reported that ferromagnetic carbon was obtained by pyrolysis of PAN and magnetic separation with poor reproducibility.[5] The comparative data in Table 1 suggest the possibility of forming ferromagnetic carbon by pyrolysis of PHDD. More detailed and controlled pyrolysis remained unsolved.

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1,2,4-Triazine(VI): Synthesis of 6-Ethynyl-1,2,4-triazines from 6-Bromo-1,2,4-triazines through Pd-Catalyzed Coupling Reaction

Jae-Keun Lee, In Rak Jung, Kyung-Ae Kim*,
and Sha-Joung Chang[†]

Department of Chemistry,
College of Natural Sciences,
Kyungpook National University,
Taegu 702-701, Korea
**Specialty Chemical Research Institute,*
LG Chemical Ltd/Research Park
Division of Applied Science, Korea Institute of
Science and Technology,
Seoul 130-650, Korea

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Palladium-catalyzed cross-coupling reaction of heteroaryl halides with monosubstituted olefines and acetylenes are useful for the alkenylation and alkynylation of heteroaromatic rings. Heck[1] and Sonogashira[2] reported that iodobenzene was readily coupled with monosubstituted acetylenes in the presence of catalytic amount of bis(triphenylphosphine)palladium dichloride-cuprous iodide to afford 1-substituted 2-phenylacetylenes. It is conveniently applied to the synthesis of pyridine,[3] pyrimidine,[4] pyrazine,[5] pyridazine,[6] quinazoline[7] and pterin[8] derivatives from corresponding heteroaryl halides.