

Magnetic properties of polymerized diphenyloctatetrayne

Miriam F. Beristain^a, Maria F. Jimenez-Solomon^a, Alejandra Ortega^a, Roberto Escudero^a, Eduardo Muñoz^b, Yasunari Maekawa^c, Hiroshi Koshikawa^c, Takeshi Ogawa^{a,*}

^aInstituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Ciudad Universitaria, México DF 04510, Mexico

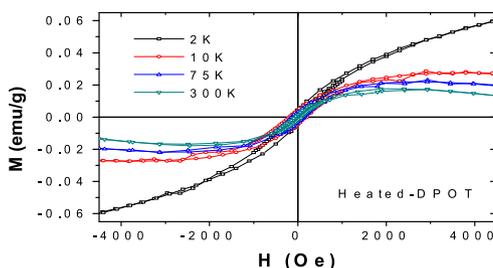
^bInstituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, Ciudad Universitaria, México DF 01000, Mexico

^cHigh Performance Polymer Group, Quantum Beam Science Directorate, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

HIGHLIGHTS

- ▶ Diphenyloctatetrayne as a precursor for carbon with high radical concentration.
- ▶ The carbon material consists of sp^2 configuration.
- ▶ A weak intrinsic metal-free ferromagnetism was observed for the carbon products.

GRAPHICAL ABSTRACT



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ABSTRACT

A new type of metal-free ferromagnetic carbon material was obtained by thermal polymerization and electron beam irradiation of diphenyloctatetrayne (DPOT). The isothermal magnetic measurements showed hysteresis loops indicating weak but intrinsic ferromagnetism with Curie temperatures of around 600 K. Electron spin resonance spectroscopy showed that the material contained stable free radicals in the range of 10^{17} – 10^{20} radicals g^{-1} depending on the polymerization process. The ferromagnetism should be due to high radical concentration although no correlation was observed between them. It was shown that an amorphous ferromagnetic carbon could be obtained from a simple crystalline solid by heating at moderate temperatures.

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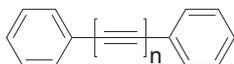
1. Introduction

Since the discovery of fullerenes and carbon nanotubes, carbonaceous materials have been considered to be of interest for applications in energy, electronics and engineering, and there have been many studies reported on novel carbon materials prepared by chemical vapor deposition, laser vaporization, arc discharge, pyrolysis, or polymerization. For example, Ding and Olesik have reported carbon nanospheres [1] and microbeads [2] from aliphatic octatetrayne monomers. The chemistry of polyynes is an attractive

theme and various unique structures have been reported [3–8], and they can be precursors for novel carbon materials. However, the synthesis of polyynes with more than 4 acetylene units is not simple and is accompanied by risk of explosion during their syntheses, this being a significant drawback for a large scale preparation. Therefore, the synthetic procedure for aromatic oligoynes with $n = 2$ –4 (Scheme 1), are thought to be more interesting from practical point of view, since their carbon contents, 95% ($n = 2$), 96% ($n = 4$), are just as high as their analogs such as hexayne, 96.6% ($n = 6$) and octayne, 97.1% ($n = 8$). The present authors have previously reported the polymerization of aromatic diacetylenes ($n = 2$), and found that they form stable sp^2 diradicals by UV irradiation [9] on heating [10] and by the action of peroxide [11]. This observation led us to investigate the radical formation of

* Corresponding author. Tel.: +52 55 5622 4728.

E-mail address: ogawa@unam.mx (T. Ogawa).



Scheme 1. Diphenyl oligoynes.

diphenyloctatetrayne (DPOT, $n = 4$) which is much more reactive than diphenylbutadiyne ($n = 2$), by thermal polymerization and electron beam irradiation. Although the present author has previously studied briefly the Gamma-ray irradiation and thermal polymerization of DPOT [12], there is no study so far on the radical formation of DPOT and magnetic properties of the reaction products as reported for other carbon materials, such as pyrolytic carbon from adamantane [13], ion beam-irradiated fullerenes [14], single-walled carbon nanotubes [15], exfoliated graphene [16], proton-irradiated graphite [17,18] and carbon nanofoams [19,20]. Therefore, in this work, it is shown that carbonaceous materials with high radical concentration and weak ferromagnetism can be readily obtained from a crystalline compound by simple processes such as heating at moderate temperatures near its melting point, or irradiating by electron beam at room temperature. The radical formation was investigated with ESR spectroscopy, and due to the high radical concentration their magnetic properties were studied using a Quantum Design MPMS magnetometer. The results are reported in this article.

2. Experimental

2.1. Synthesis of DPOT

DPOT is a known compound and was synthesized according to the methods described in literature [12,21]. 6-Phenyl-2-methylhexa-3,5-diyne-2-ol was obtained by the Cadiot–Chodkiewicz coupling reaction of 1-bromo-2-phenylacetylene with 2-methyl-3-butyne-2-ol. It was then heated in high vacuum at temperature of the distilling flask at around 180 °C in the presence of potassium hydroxide in paraffin, and phenylbutadiyne distilled out was collected. This was dimerized by the oxidative coupling in acetone with catalytic amounts of cuprous chloride and N,N,N',N' -tetramethylethylenediamine at room temperature. The yield of the Cadiot–Chodkiewicz coupling was almost quantitative being 98% and the yield of phenylbutadiyne was about 60% and the rest polymerized during distillation giving a black mass. The oxidative coupling gave quantitative yield of over 95%. DPOT was recrystallized from hexane and yellow needles with mp. 116 °C were obtained. ^{13}C NMR confirmed the structure of DPOT, (100 MHz, CDCl_3): δ (ppm): 63.64, 67.18, 74.42, 77.69, 120.48, 133.19, 128.53, 128.99.

2.2. Polymerization

2.2.1. Thermal polymerization

DPOT crystals were placed in Pyrex tubes, and they were sealed off in vacuum and heated in an oil bath, starting from 90 °C and gradually heated to the required temperature in order to avoid possible explosion. The material thus obtained is hereafter named as heated-DPOT.

2.2.2. Electron beam irradiation

DPOT was irradiated with electron beam in polyethylene bag filled with nitrogen on a water-cooled plate at room temperature (the maximum temperature of samples caused by radiation is estimated below 60 °C), using a Cockcroft–Walton type accelerator at a dose rate of 1.32 $\text{kGy s}^{-1} \text{mA}^{-1}$ to obtain total doses of 1, 3, 5, 10 and 20 MGy. The samples were irradiated at Takasaki laboratories

in Japan Atomic Energy Agency, Japan. The materials obtained under this condition are named as irradiated-DPOT.

2.3. Characterization

^{13}C NMR spectra were taken using a Bruker Avance 400 MHz spectrometer. FT-IR spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. X-ray powder diffraction was recorded on a Bruker Model D8 Advanced diffractometer with detector of PSD Vantec-1, using $\text{CuK}\alpha$ radiation of 1.540 Å. DSC and TGA analyses were performed using a Universal V3.5B calorimeter of TA Instruments at a heating rate of 10 °C min^{-1} . Particle induced X-ray emission (PIXE) analysis was done using a Van de Graaff accelerator with proton energy of 700 keV and incident angle of 45°. The detection limit is 1 ppm.

2.4. Magnetic properties

ESR spectra were taken using a JEOL RE3X ESR spectrometer. The temperature was controlled using a JEOL DVT3 variable temperature system. Accurate measurements were made for the static magnetic field and the operating microwave frequency using an NMR gaussmeter and a frequency counter, respectively Quartz tubes with an inner diameter of 3 mm supplied by Wilmad Lab-Glass were used for the ESR measurements. The spectra were taken under the following conditions: Microwave frequency: 9.17 GHz, power: 4 mW, Central Field H : 325 mT scan: ± 25 mT, Frequency Modulation: 100 kHz. Dry nitrogen gas was passed into the cavity during measurements in order to prevent condensation of water. For the temperature dependence measurements, the tube was filled with argon, and for the time-dependence measurements, the tube was sealed in vacuum. The radical concentration was calculated with the double numerical integration of the first derivative of the resonance curve from equation [22].

$$A = \int_{H_A}^{H_B} dH \int_{H_A}^H dH' S(H')$$

where H_A and H_B are the initial and final magnetic fields of the resonance curve respectively, and $S(H')$ is the absorption at magnetic field H' . NaCl:Mn^{++} crystal calibrated by atomic absorption spectroscopy, was used for determination of free radicals concentration. All spectra were taken under the same ESR spectrometry conditions.

Magnetic properties were determined using a Quantum Design MPMS (Magnetic Property Measurement System) magnetometer over a temperature range 2–300 K. Gelatin capsules were used as sample holders. The magnetic response of the gelatin capsules is negligible compared to the magnetic measurements of samples. The magnetization–temperature (M – T) measurements were carried out at different magnetic intensities. For the measurements of magnetic susceptibility in general was used 2000 Oe, and for the determination of coercive forces, the isothermal measurements (M – H) were carried out at different magnetic fields from –5000 to 5000 Oe. The M – T measurements were performed in two modes; zero field cooling (ZFC) and field cooling (FC) to observe reversibility in the measurements. In the case of ZFC, the sample was first cooled to 2 K, and once the thermal equilibrium was reached the magnetic field was applied, and the measurement was performed up to 300 K. In the case of FC, the measurements were performed with decreasing temperature. These measurements are a normal procedure to observe possible reversible process in magnetic

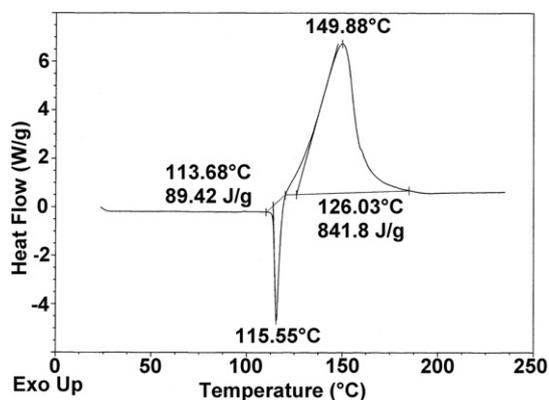


Fig. 1. DSC thermogram of DPOT at a temperature ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 .

systems. Pascal constants were taken into account for the determination of the inverse of magnetic susceptibility.

3. Results and discussion

In order to study the thermal behavior of DPOT, DSC was performed (Fig. 1). The endothermic peak at $115\text{ }^{\circ}\text{C}$ corresponded to the melting of DPOT, and immediately took place the exothermic reaction of polymerization of triple bonds. The polymerization was completed within 8 min at $190\text{ }^{\circ}\text{C}$ releasing heat of $210.45\text{ kJ mol}^{-1}$ ($50.3\text{ kcal mol}^{-1}$). This value is in accordance with those of other octatetraynes such as dithiophenyloctatetrayne ($52.6\text{ kcal mol}^{-1}$) and diquinolyloctatetrayne ($52.2\text{ kcal mol}^{-1}$) [23]. A second run for the same sample once heated to $200\text{ }^{\circ}\text{C}$ showed very little exotherm indicating that the reaction was nearly completed. Thermal gravimetric analysis in nitrogen atmosphere showed that DPOT initiates its weight loss at around $400\text{ }^{\circ}\text{C}$, and about 75% remained at $900\text{ }^{\circ}\text{C}$.

The products obtained by electron beam irradiation at different doses were brown and soluble in acetone, and only a small portion was insoluble. The shiny black powder obtained from heated-DPOT was insoluble in most of organic solvents, indicating the formation of a highly conjugated and cross-linked material.

The X-ray diffraction patterns of pristine DPOT, irradiated-DPOT and heated-DPOT are shown in Fig. 2. The crystalline structure of DPOT [24] and derivatives have been previously reported [25,26], where the compounds have structures in which the benzene rings

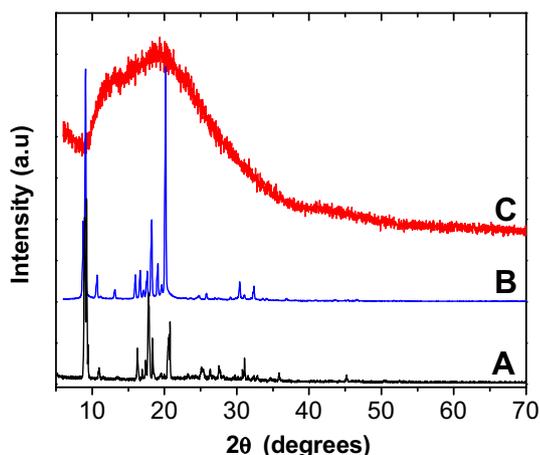


Fig. 2. X-ray diffraction patterns of (A) DPOT, (B) irradiated-DPOT (10 MGy) and (C) heated-DPOT (T5).

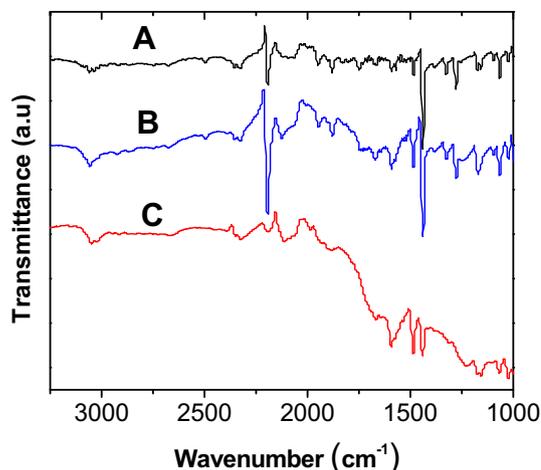


Fig. 3. FT-IR spectra of (A) DPOT, (B) irradiated-DPOT (10 MGy) and (C) heated-DPOT (T5).

are diagonally overlapped and the tetrayne chains are parallel to each other. Unlike the light-sensitive diacetylene crystals, DPOT does not undergo significant change under room light over prolonged period, although the yellow crystals become slightly darker during storage at room temperature for a few years. The irradiated-DPOT with 10 MGy kept 80% of crystallinity and very little change in its crystal structure was noted. The heated-DPOT showed a broad peak (halo) characteristic of amorphous material at $2\theta = 18.92^{\circ}$ ($\text{CuK}\alpha$), similar to the polyphenyldiacetylene obtained by Iwamura [27], but somewhat different from the carbon beads obtained from the pyrolysis of 1,8-dibutyl-1,3,5,7-octatetrayne reported by Olesik [2].

FT-IR spectra of DPOT, irradiated-DPOT and heated-DPOT are shown in Fig. 3. The irradiated-DPOT showed almost the same FT-IR spectrum of DPOT, only small broadening peaks are observed, indicating the formation of conjugated structures. The FT-IR spectrum of heated-DPOT showed that the peak at 2125 cm^{-1} corresponding to acetylenic bonds has disappeared. Cumulenic bonds ($-\text{C}=\text{C}=\text{C}=\text{C}-$) may exist but cannot be easily observed by IR spectra. The broadening of the heated-DPOT spectra in the region from 2000 toward 1000 cm^{-1} , is characteristic to amorphous polymeric materials.

The solid-state ^{13}C CPMAS NMR spectrum of the heated-DPOT shown in Fig. 4 indicates that the product mainly consists of sp^2 structures ($\text{C}=\text{C}$ bonds) at 127 ppm without triple bonds remaining, as observed in its IR spectrum (Fig. 3). The two peaks at around 60 and 200 ppm are the spinning sidebands. Nakanishi and coworkers have carried out the polymerization of di-2-thienyl and di-3-quinolyloctatetraynes, and they assumed the 1,2- and 3,4-polymerization took place, and proposed a cycloaromatized structure as a final product [23]. Ding and Olesik carried out suspension polymerization of liquid dibutyloctatetrayne and described

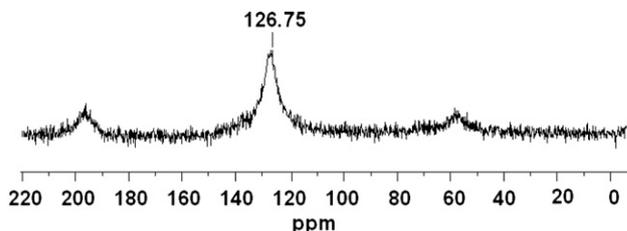


Fig. 4. Solid state ^{13}C CPMAS NMR spectrum of heated-DPOT (T5).

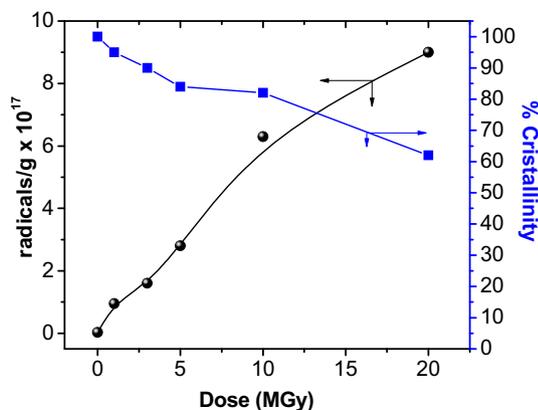


Fig. 5. Relationships between dose, and radical formation and crystallinity of irradiated-DPOT.

speculated structures of reaction products of 1,2-, 1,4-, 1,6-, 3,6- and cyclic polymerization [1]. Their polymerization is in liquid phase, and the structures of the products may be different from the solid-state thermal polymerization of DPOT of this work. Tykwinski reported the polymerization of a tetrayne and suggested the 1,6-addition in accordance with the intermolecular proximity of the tetrayne [4]. In any case, it is difficult to elucidate the real structure of final polymerized products and it is thought that they consist of a mixture of various sp^2 structures of condensed aromatic hydrocarbons. With respect to the mechanism of polymerization, the polymerization of DPOT can be considered to proceed similarly to that of diphenylbutadiyne [10] although DPOT is much more reactive. The polymerization proceeds by two processes; the formation of diradicals by reaction of nearby acetylenic bonds, and their coupling to form more stable conjugated diradicals. The balance of formation and consumption of radicals results in the amount of radicals remaining in the product, which are no longer attacked by oxygen when exposed to air because of their high delocalization. The formation of sp^2 structure destroys the crystal structure making the product amorphous. However, DPOT seems to undergo very slow opening of triple bonds even at room temperature in dark, since it was found by ESR to contain 7×10^{17} radicals mol^{-1} after about one year from preparation, which means that only 1 radical exists for 800,000 DPOT molecules.

The relationships between radical formation, crystallinity and electron beam irradiation are shown in Fig. 5. The radical concentration increased and the crystallinity decreased with dose. It can be seen that the reaction was not completed even with a high dose of 20 MGy, indicating that DPOT does not polymerize in the solid state by radiation as in the cases of topochemical polymerization of diacetylenes.

In order to study the change in radical concentration with heating time, the DPOT was heated at 110 °C in the cavity of the ESR spectrometer. The results are shown in Fig. 6. The radicals are rapidly formed when heated, but after about 15 h, the increase stopped reaching a maximum value of 6×10^{22} radicals mol^{-1} (2×10^{20} radicals g^{-1}). The thermal polymerization of DPOT consists of two types of reactions; (a) the formation of two radicals by the intermolecular reaction of two unsaturated bonds and (b) the recombination of the radicals formed. After 15 h, the formation and recombination seem to stop because the material becomes a hard solid, and the unsaturated bonds no longer approach each other to react. The balance between the two reactions is thought to determine the radical concentration. This product contained one radical distributed among 10 DPOT molecules (200 carbon atoms). When the sample was cooled down to room temperature the

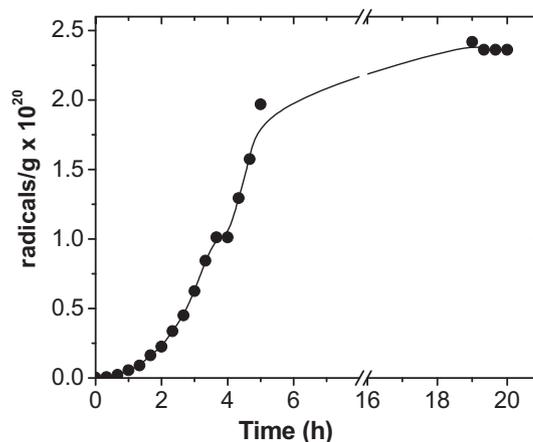


Fig. 6. Increase in the concentration of DPOT radicals with heating time at 383 K.

radical concentration increased and was found to be 7×10^{22} radicals mol^{-1} , (3×10^{20} radicals g^{-1}). The radical formation on thermal polymerization of DPOT at various heating conditions is shown in Table 1. They reached 1×10^{20} radicals g^{-1} after 20 h indicating that one radical exists for each 20 DPOT molecules. It seems that the higher the temperature the more radicals are formed, although the differences are relatively small being in the same order. There are many studies on the radical concentration of carbon materials. Snow [28] has reported an ESR study of polybutadiyne which contained 8×10^{19} radicals g^{-1} . The radical concentration of carbon nanofoam produced by high-repetition-rate laser ablation of a glassy carbon, has been reported to be 8.8×10^{20} radicals g^{-1} at 300 K [20] and the radicals are said to be sp^3 bonded carbon radicals. Shibayama et al. [29] have studied magnetism of activated carbon fiber, which contained radicals of the order of 10^{19} radicals g^{-1} , and they were attributed to the non-bonding π electrons at graphite edge. Bandow and coworkers [30] have reported magnetism of single-wall carbon nanohorns, with radical concentration of 5.7×10^{18} radicals g^{-1} , equivalent to one unpaired electron per the single-wall carbon nanohorn, and the radicals are susceptible to oxygen pressure. They assumed that the radical is located at the nanohorn tips. In the case of DPOT polymerization, the radicals are considered to be stable sp^2 radicals distributed over highly conjugated structures.

The effect of temperature on the radical concentration was determined over the temperature range of 120–380 K. The line-width of ESR signals did not change significantly with temperature being a constant of 0.44 mT throughout the measurements, indicating that there is no environmental variation around the radicals. Fig. 7 shows the increase and decrease in the radical concentration of heated-DPOT (T3) with temperature. First, when it was cooled from 300 K to 130 K (square) the radical concentration increased. The sample was left in the ESR cavity for overnight, during which the temperature returned to room temperature, and it was cooled again to 130 K, and heated up to 380 K (triangle), decreasing the radical concentration reversibly. The same sample

Table 1
Radical concentration of DPOT by heating in vacuum.

| Sample | Maximum temperature (°C) | Heating time (days) | Radical concentration (10^{20} radicals g^{-1}) | DPOT molecules /radical | <i>g</i> |
|--------|--------------------------|---------------------|--|-------------------------|----------|
| T1 | 85 | 10 | 0.84 | 29 | 2.0022 |
| T3 | 105 | 8 | 1.01 | 24 | 2.0023 |
| T4 | 114 | 3 | 1.23 | 19 | 2.0021 |
| T5 | 116 | 5 | 1.03 | 23 | 2.0023 |

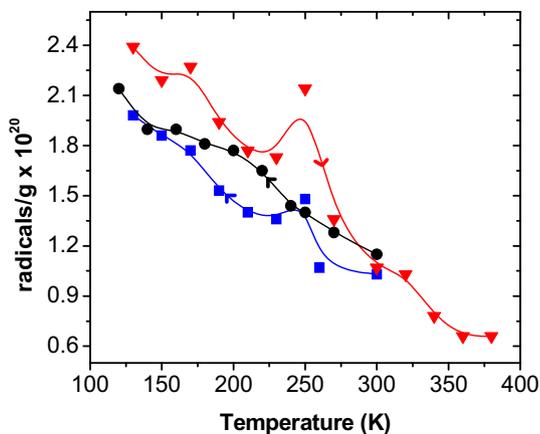


Fig. 7. Reversible changes in radical concentration of heated-DPOT (T3) with temperature. (square): First cooling from room temperature to 130 K, (triangle): Heating from 130 K to 380 K, (circle): Second cooling from room temperature to 120 K.

was left to stand at room temperature for four months, and the radical concentration increased similarly to the first cooling. This indicates that the radicals are very stable, since the radical concentration did not change during storage. The pronounced jump in radical concentration observed at 250 K during the first cooling and heating is interesting, and this was observed for all the heated-DPOT. However, this disappeared when the sample was once heated to 380 K, suggesting that a certain structural relaxation have taken place. The consistent and reversible increase and decrease in the radical concentration with temperature, is due to the thermal motion of molecules, which causes decoupling and coupling of nearby radicals. At low temperatures, the radicals are frozen, and with increase in temperature the molecular motion increases and the nearby radicals start to couple forming weak bonds thus decreasing the radical concentration. Since these radicals are extremely stable they are readily regenerated by the volume contraction when cooled. The radical concentration observed at 120 K is about 2 times greater than that at 300 K. There are observations on the temperature dependence of radical concentration. Snow has reported that the ESR intensity increased with decrease in temperature for polybutadiyne [28]. The decreases in spin density or ESR intensity with increase in temperature have been also observed by Brustolon [31] for nanographites and by Brabec [32] for a carbazolyl substituted polydiacetylene. Chuvyrov [33] also reported reversible changes of spin density with temperature change. The concentration of radicals decreased linearly with increase in temperature, and they attributed this to changes in crystal morphology. Rode also mentioned a notable change in radical concentration at a temperature range of 50–150 K for the carbon nanofoam [20]. Thus, the ESR intensity generally decreases with increase in temperature, unless the radicals are newly formed on heating.

Because the polymerized DPOT contained substantial amount of radicals their magnetic properties were determined. Although no ferromagnetic metals are used in the synthesis of DPOT or in its polymerization, in order to assure the magnetism is not affected by the metallic impurities, ESR and PIXE analyses were performed. The ESR is known to be very sensitive technique to detect traces of metal impurities [34]. ESR spectrum was taken over a wide range of 0–600 mT with gain of 100, and no sign of metallic impurities was observed in the sample. Special attention was taken in the region where the signals of ferromagnetic impurities such as Fe, Ni and Co appear. In Fig. 8 is shown a sharp ESR signal of heated-DPOT with ΔH_p-p 2.1 G and g value of 2.0025, which is similar to that of metal-

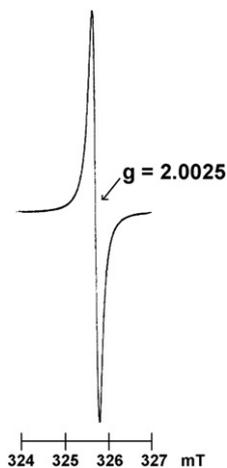


Fig. 8. ESR spectrum of heated-DPOT. Magnetic field: 330 ± 10 mT, microwave frequency: 9.1264 GHz, modulation amplitude: 0.01 mT, power: 0.01 mW, gain: 1.0, time constant 0.03 s. Sweep time 4 min.

free carbon nanotubes (CNT) studied by Kolodiazhnyi [34], who also mentioned that a broad asymmetric ESR feature with ΔH_p-p of 1042 G and g values of 2.23, for CNT, is attributed to the ferromagnetic resonance caused by metallic impurities.

PIXE analysis of an irradiated- and heated-DPOT was carried out and the results are shown in Fig. 9. The X-ray emission energies of ferromagnetic metals are shown in the same figure. There was no ferromagnetic impurity found in the samples.

The relationships between the temperature and magnetic susceptibility (χ), for pristine DPOT in a magnetic field intensity of 2000 Oe are shown in Fig. 10. It showed diamagnetic behavior as expected for an organic compound in the temperature range from 2 to 300 K, even though it contained a small amount of radicals, i.e. 2.8×10^{15} radicals g^{-1} . The magnitude of susceptibility is in the same range of other carbon diamagnetic materials such as single wall nanohorns [30] and fullerenes [35].

Fig. 11 shows the magnetic susceptibility dependence on temperature for the irradiated-DPOT (1 and 20 MGy), measured in two modes: zero field cooling and field cooling (ZFC and FC), and a reversible (according to the two modes) non-Curie behavior was observed. The irradiation significantly increased the radical concentration by two orders of magnitude than pristine DPOT

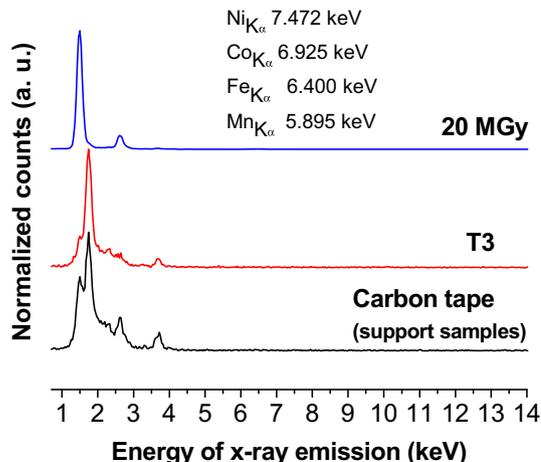


Fig. 9. Particle-induced X-ray emission of irradiated-DPOT (20 MGy) and heated-DPOT (T3).

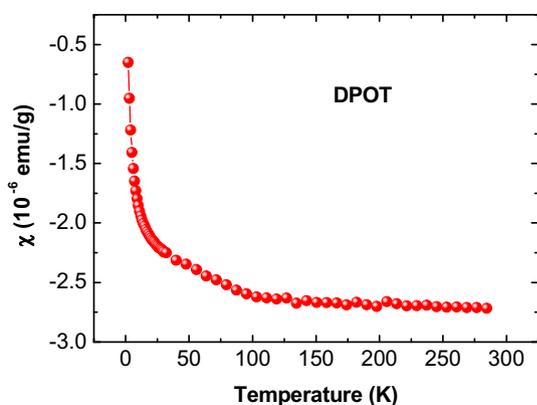


Fig. 10. Temperature dependence of the magnetic susceptibility of pristine DPOT.

(from 10^{15} to 10^{17} radicals g^{-1}), and the results are clearly noted as the difference in the magnetic susceptibility shown in Figs. 10 and 11. The inverse of the magnetic susceptibility gave a Curie Constant (C), of $0.69 \text{ emu K mol}^{-1}$ and a Curie–Weiss temperature ($\Theta_{C-\omega}$) of about -1200 K . The high negative value of the Curie–Weiss temperature is indicative of a highly frustrated system [36]. The other irradiated-DPOT samples showed similar magnetic behavior with only small changes in the magnetic susceptibility as shown in Fig. 11 for the 20 MGy, which is in accordance with the radical formation shown in Fig. 5.

The temperature dependence of magnetic susceptibility of the heated-DPOT is shown in Fig. 12. The magnetic susceptibility was greater than irradiated-DPOT (Fig. 11), which is in accordance with the radical concentration. Thus, heating near the melting point and prolonged heating time formed more radicals. The sudden drop observed in the susceptibility at 250 K for all the samples is intriguing, and this was reversible. Iwamura and coworkers have reported a similar drop of magnetic susceptibility at 250 K for the polymers prepared from nitroxy radical-containing aromatic diacetylenes [27] and they attributed this to a magnetic phase transition. In the case of heated-DPOT of this work, the drop of magnetic susceptibility coincides to the sudden change (jump) observed in the first run and second run of the radical concentration at 250 K shown in Fig. 7, but it disappeared in the third run when the sample was once heated at 380 K, indicating that heated-DPOT has a temperature dependent structural phase transition induced by magnetic field. This type of transition appears to depend on the polymerization conditions, and further studies will be reported in future.

The temperature dependence of effective magnetic moments (μ_{eff}), of the irradiated-DPOT is shown in Fig. 13(A). The magnetic

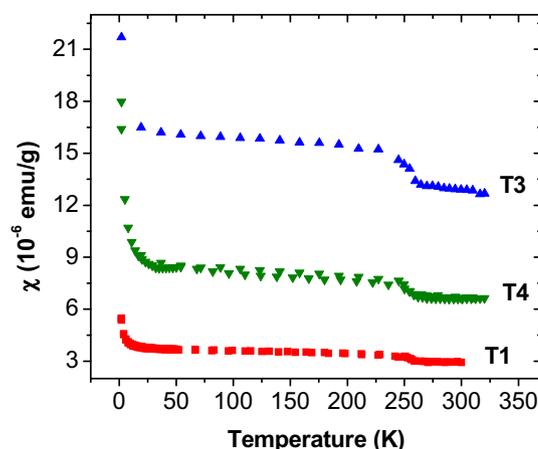


Fig. 12. Reversible behaviors of the magnetic susceptibility of heated-DPOT with temperature. Measured in ZFC and FC modes at 0.5 T.

moment increased with dose, which corresponds to the radical concentration (Fig. 5). In the case of the heated-DPOT (Fig. 13B), the effective magnetic moments were found to be higher than those of the irradiated-DPOT, in accordance with the radical concentration as mentioned in Table 1. However in the case of the heated-DPOT, the magnetic moment did not coincide with the radical concentration, since T3 showed higher magnetic moment than T4. This can be attributed to the heating conditions (Table 1) which determine the morphology (holes and paramagnetic species) of the products.

In order to confirm the weak ferromagnetic-like behavior, isothermal measurements were carried out for the irradiated- and heated-DPOT. All samples showed magnetic hysteresis loops, except the pristine DPOT, which confirms an intrinsic ferromagnetic-like behavior of polymerized DPOT. From isothermal magnetic hysteresis measurements was observed no saturation of magnetization in all samples at 2 K, indicating a weak ferromagnetic behavior, due to canted spins. At higher temperatures the ferromagnetism decreases due to the spin disorder. The large negative Curie–Weiss temperature shows the presence of high degree of geometrical frustration (spin disorder) [36].

Isothermal magnetic measurements at different temperatures showed the presence of coercive fields, indicating ferromagnetism. Fig. 14 shows the coercivity dependence on temperature for 1 MGy and T1, in which it can be seen that the ferromagnetic order remained at room temperature. Its behavior can be fit to a medium field model, $H_c(T) = H_c(0)\{1 - [T/T_c]^{0.5}\}$, where T_c is the Curie temperature, and $H_c(0)$ is the coercive field at zero temperature. For 1 MGy the $H_c(0) = 400 \text{ Oe}$ with a $T_c = 670 \text{ K}$, while T1 gave $H_c(0) = 210 \text{ Oe}$ and $T_c = 675 \text{ K}$. In both cases the T_c is similar

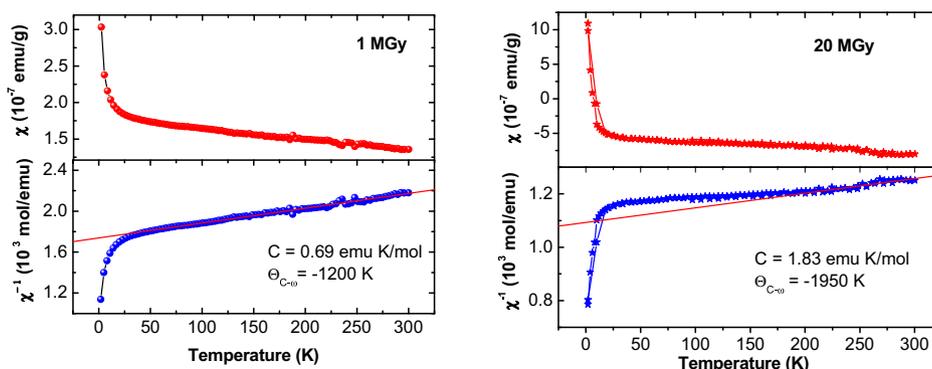


Fig. 11. Temperature dependence of the magnetic susceptibility of irradiated-DPOT with doses of 1 and 20 MGy.

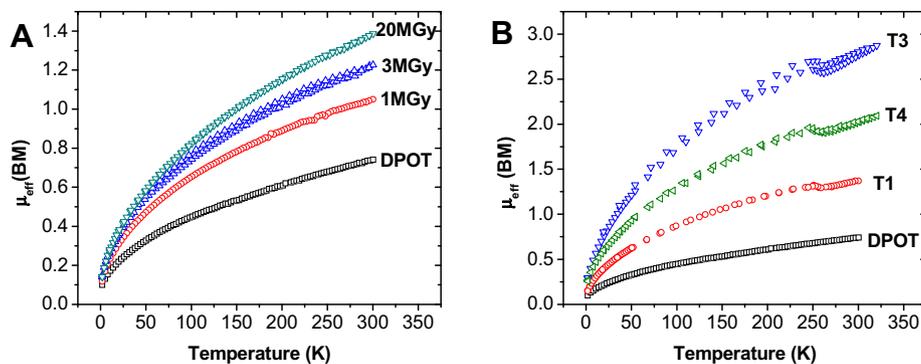


Fig. 13. Temperature dependence of the magnetic moment of (A) irradiated-DPOT, and (B) heated-DPOT.

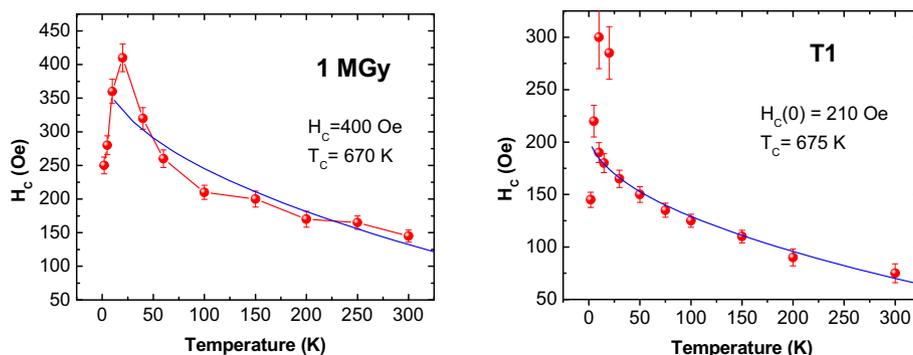


Fig. 14. Coercive field behavior for 1 MGy and T1 samples.

indicating that the both compounds are basically the same type of carbon material, independent of preparation method, even though the H_c is somewhat different due to difference in morphology of each system, showing higher magnetic ordering in irradiated-DPOT than heated-DPOT. Thus, the former is more crystalline as prepared at lower temperature and its spins are more orientated while the latter prepared at around the melting point is amorphous and has more spin frustration. At very low temperature decrease in the coercive field was observed, which could be related to the competition between the two magnetic processes; canted antiferromagnetism and weak ferromagnetism.

4. Conclusions

DPOT heated near its melting point gives an amorphous carbon material with sp^2 configuration, which contains stable radicals in the order of 10^{20} radicals g^{-1} , indicating that one radical is distributed over 10–20 DPOT molecular units, and the g values corresponds to that of free electrons (2.0023). The radicals are stable due to their highly conjugated nature, and do not decay with time in air. The reaction products of irradiated- and heated-DPOT showed weak but intrinsic ferromagnetism with a similar Curie temperature suggesting that the same magnetic ordering can be obtained by both methods, although, the magnetic susceptibility, effective magnetic moment and radical concentration of the heated-DPOT were greater than those of irradiated-DPOT. A novel organic ferromagnetic material could be readily obtained by a simple process of a crystalline compound.

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