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Polymerization of Diphenylbutadiyne by Gamma Rays Irradiation in the Molten State

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Diphenylbutadiyne was irradiated with Gamma ray in the molten state (90° C), and its polymerization process was studied. The amorphous product has a number average molecular weight of around 1300. The yield reached around 20% with a dose of 3000 kGy, which is far greater than that in the case of irradiation in the solid state at room temperature. From the number of spins and molecular weights the product is thought to be mainly composed of cyclic oligomers. The third order nonlinear optical susceptibility of the products was found to be 3–6 × 10^{-10} esu determined by the Z-scan technique.

Keywords Diphenylbutadiyne; Gamma-irradiation; oligomerization; Z-scan

I. Introduction

Oligoynes are high carbon-content compounds and are considered to be unique as precursors for nano-carbon materials. In recent years there are many studies on oligoynes having more than 10 conjugated acetylene groups [1]. However, these oligoynes are extremely high-energy compounds and their synthesis is accompanied with the risk of explosion. The most stable and readily prepared compound, diphenylbutadiyne (DPB) has a carbon content of 95%, Its unstable analogues, diphenyloctatetrayne (DPOT) and diphenyldodecaoctayne (DPDO) have carbon contents of 96% and 97% respectively. We see that the carbon content of DPB is just

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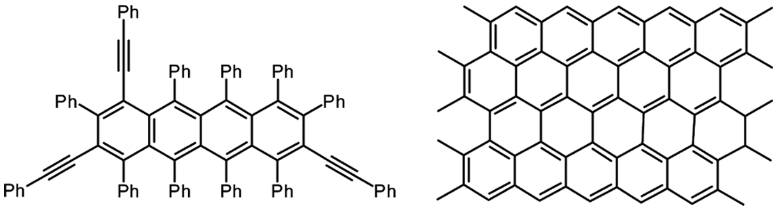
as high as that of the other unstable diphenyl oligoynes thus making it a better and safer material to work with. The synthesis of DPB is simple, but the synthetic difficulty increases with the increase in the number of acetylene groups. DPB is an interesting compound with its conjugated butadiyne groups. It interacts with transient free radicals stabilizing them to be detected by ESR spectroscopy at the temperature of reactions. For example, it was found previously, when vinyl monomers such as acrylate and methacrylates are polymerized in the presence of DPB, ESR signals of the propagating radicals are observed during polymerization [2,3], but DPB is not incorporated in the polymers. DPB is one of the diacetylenes, which do not undergo topochemical polymerization in the solid state, because it does not have a crystal structure adequate for the solid state polymerization [4]. It has a structure with benzene rings overlapping each other [5].

The polymerization of DPB has previously been investigated [6–11] and different structures have been proposed for the products. The thermal polymerization of DPB was investigated in 1960s by Davidov *et al.* [6] and Berlin *et al.* [7] and they proposed 1,2-polymerization as well as acenic structures although concrete evidence is not available. Later, Wiley *et al.* [8] have also reported thermal polymerization of DPB in solution, and they proposed a mechanism of second order addition polymerization similar to free radical vinyl polymerization, but they did not mention a probable structure of the product. Kojima *et al.* also reported its polymerization of DPB at temperatures 210–250°C under high pressure [9,10]. More recently, Zimmermann and Baranovic reported two-dimensional (2-D) infrared spectroscopic studies on the structures of polymerized DPB at 250°C [11]. In these previous studies 1,2- and 1,4-oligomers are said to be formed, and also acenic cyclic and amorphous graphite structures are suggested for the soluble and insoluble fractions, respectively as shown in Scheme 1, depending on the temperature at which DPB is heated. According to the differential scanning calorimetry (DSC), DPB melts at 88–89°C and starts the exothermic reaction to open its acetylenic bonds at temperature above 200°C. At higher temperatures such as 250°C DPB reacts randomly producing an intractable material and its characterization is difficult.

DPB does not possess crystal structure adequate for the well-known topochemical polymerization, as reported by Surette *et al.* [5], and the solid-state polymerization of DPB does not take place by heating to temperatures below its melting point or by UV irradiation. Such an observation has been made also by Baughman [12]. Large doses of Gamma ray or electron beam in the solid-state produce a dark colored product but the yield is low. The authors have previously reported the oligomerization of DPB under various conditions, and found that it forms stable oligomeric triplet *sp*-butatriene diradicals by UV irradiation [13], heating at temperatures between its melting point and the temperature at which random thermal reaction



Scheme 1. Suggested structures of DPB polymerization at 250°C [11].

initiates [14], or in the presence of free radicals at 130°C [15]. The yields of reactions in solution and of thermal reaction at temperatures below 180°C are very low. However, the yield of methanol- and hexane-insoluble products (oligomers) in the presence of a large amount of *t*-butylperoxide was as high as 75% after the reaction for a few weeks, and amazingly the main product oligo-DPB did not contain fragments from *t*-butyl peroxide. In these studies the products were found to contain free radicals stable at the reaction temperature and in air. In these mild conditions the products were soluble in solvents such as chloroform and tetrahydrofuran, and insoluble in hexanes and methanol. It is important to obtain soluble products not only for characterization but also for their applications as a precursor for synthesis of novel highly conjugated materials. As mentioned above, the yields of thermal polymerization at temperatures below 200°C and of Gamma ray irradiated polymerization at room temperature, are low, therefore in order to increase the yield, DPB was irradiated with Gamma ray in the molten state (90°C). The products were analyzed, and the mechanism of the polymerization of DPB under mild conditions is discussed. The third order nonlinear optical property of the products mixed with 10% of polystyrene was also studied by the Z-scan technique.

II. *Experimental*

DPB is a known compound and it was prepared by the oxidative coupling reaction of phenylacetylene. Colorless needle crystals (3 g) were placed in Pyrex glass ampoules with 1 cm inner diameter and the ampoules were sealed off in vacuum. They were irradiated at 90°C (mp of DPB is 86°C) with a dose rate of 10 kGy/h. This temperature was chosen because the thermal reactions of DPB to form an intractable carbon material start at about 160°C, and also to avoid a possible risk of explosion because all diacetylenes are potentially dangerous when heated abruptly. After irradiation, the amorphous parts were separated by extraction with methanol and hexanes, in which DPB is soluble.

The crystallinity was determined using an X-ray diffractometer Siemens D500 with Cu $K\alpha_{1,2}$ and a graphite secondary monochromator. The molecular weight of amorphous part was determined by GPC, using a Waters 2695 ALLIANCE Separation Module equipped with a refraction index detector Waters 2414, using tetrahydrofuran as a solvent. A set of two Waters HPLC columns: HSP gel HR MB-L with Mw range of 5×10^2 to 7×10^3 and HSP gel HR MB-M with Mw range of 1×10^3 to 4×10^6, was used. NMR spectra were taken using a Bruker Avance 400 MHz NMR spectrometer. FT-IR spectra were recorded on a Perkin Elmer Spectra 100 with Universal ATR system. The differential scanning calorimetry was performed using a calorimeter Model 910 of DuPont Instruments. ESR spectra were taken using a JEOL ESR spectrometer Model RE3X. The samples were placed in quartz tubes with an inner diameter of 3 mm supplied by Wilmad LabGlass, and the spectra were taken in air. The number of spins (radicals) was calculated with the double numerical integration of the first derivative of the resonance curve from equation [16]

$$A = \int_{HA}^{HB} dH \int_{HA}^{H} dH' S(H')$$

where H_A and H_B are the initial and final parts of the resonance curve, and $S(H')$ is the value of the absorption at field H'. The NaCl:Mn^{++} crystal calibrated by atomic absorption spectroscopy, taking both spectra under the same conditions.

The third order nonlinear optical (3-NLO) properties of the products were determined by closed aperture Z-scan technique with 25 ps laser pulses, with a repetition rate of 20 Hz, from a Nd:YAG laser at wavelength 1064 nm.

III. Results and Discussion

Figure 1 shows differential scanning calorimetry (DSC) diagrams of DPB and its oligomerization product. The endothermic peak at around 89°C is due to melting, and the large exothermic peak starting at around 200°C corresponds to the thermal opening of acetylene bonds forming an unknown intractable material. Therefore, in order to obtain soluble products, the reaction temperature was kept 90°C, thus no insoluble product was obtained. It should be mentioned that DPB produces a significant product at 90°C without irradiation. The DSC curve of the product oligomer showed a broad exothermic peak (B) indicating that oligomers react with each other to form more conjugated materials.

Figure 2 shows relationship between radiation dose and the formation of amorphous product obtained from the X-ray diffraction. The percentage of amorphous part increased with irradiation dose, but it did not increase linearly and the increase declined with the dose. The crystalline part extracted by hexane and methanol was the unreacted DPB. The slow down in the reaction rate at about 20% conversion shown in Fig. 2, suggests that the polymerization is not a normal addition polymerization. The amorphous product is soluble in the molten DPB and the viscosity of the system increases when the concentration of the product (oligomers) exceeds 10%. If the polymerization mechanism were of an addition polymerization where the reactive species, diradicals add to the monomer, such decline in the propagation would not be observed. In general in free radical addition polymerization process, the increase in viscosity will retard the termination reactions between two polymer radicals. In the previous studies, where DPB was treated with UV light [13], heat [14] or free radicals [15], 1,4-diradicals are formed, and their coupling was considered for the oligomerization mechanism. Scheme 2 shows the coupling of

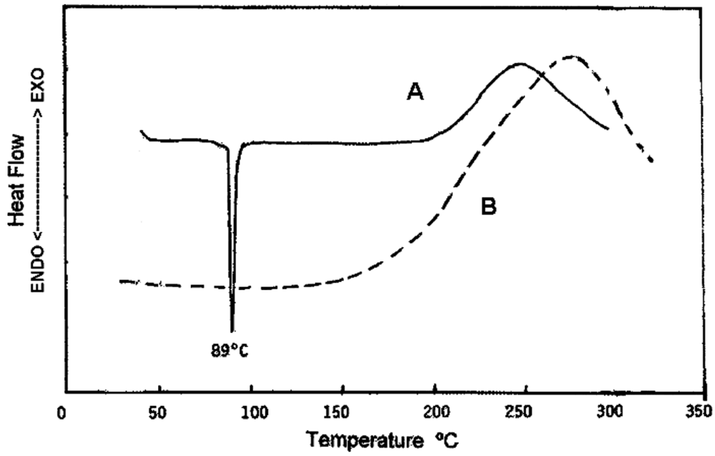


Figure 1. Differential scunning calorimetry of DPB (A) and its amorphous reaction product (B).

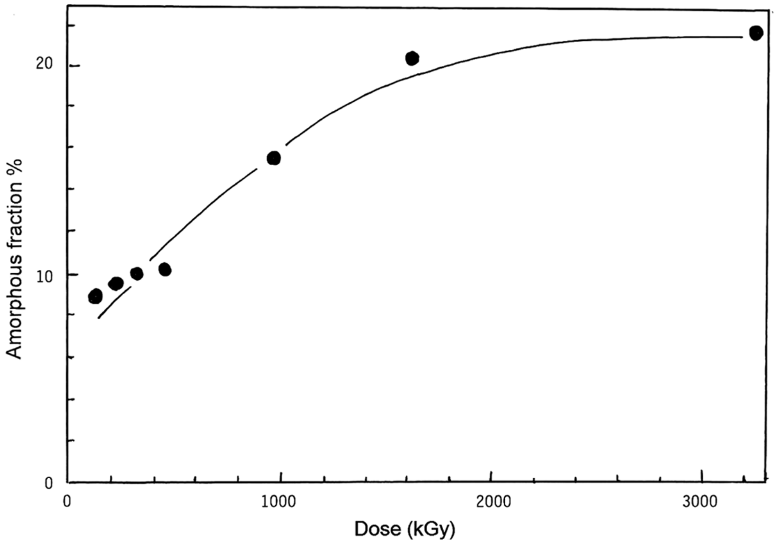
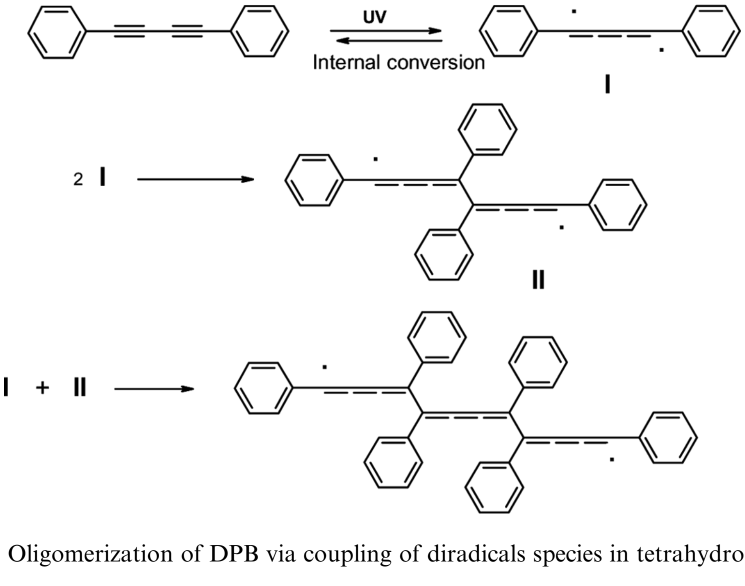


Figure 2. Relationships between doses and crystallinity.

diradicals for the UV irradiated system in solution. The oligomeric diradicals are stable in air and do not suffer oxidation as they are highly conjugated. However, the monomeric diradical (**I**) is not stable and if it does not couple with the other, it will return to DPB (Internal conversion process). Considering from these observations, it is thought that the Gamma-irradiated oligomerization of DPB in the molten state proceeds via coupling of diradicals. The increase in viscosity of the system retards the effective collision of diradicals to form the oligomeric diradicals, and therefore the rate decrease as the viscosity increases.

The molecular weights of the amorphous products are shown in Table 1. They did not increase appreciably with increase in the dose, and the number average



Scheme 2. Oligomerization of DPB via coupling of diradicals species in tetrahydrofuran [13].

Table 1. GPC results of amorphous products

Dose (kGy)	Mn	Mw	PDI
440	1250	1770	1.4
940	1140	1650	1.45
1600	1160	1740	1.5
3240	1330	2115	1.6

molecular weight remained in the range of 1140–1330, indicating the formation of oligomers of 5–7 monomer units. The probable reason why the molecular weight does not increase is that the cyclization takes place. The oligomer structure is quite different from polystyrene (standard used in GPC), and therefore the determined molecular weights may not be accurate. Nevertheless, the molecular weights of poly-DPB so far reported in the literature do not exceed 2000, the majority being less than 1500 [8,15], and this obviously shows that the polymerization or oligomerization of DPB is not an addition process in which the propagating radicals add to the monomer.

The ESR spectra of the reaction products were of free electrons and identical to those observed previously in solution and other systems [13–15]. The number of radicals formed also showed the same tendency as that of the formation of amorphous product, as shown in Fig. 3. At the initial stage the amount of radicals increased linearly but the increase slowed down above 1500 kGy. As they are formed by irradiation, they are consumed by coupling. The radicals were contained only in the amorphous products, and from the numbers of spins of the amorphous products and their number average molecular weights, the numbers of radicals per mole can be calculated. For the sample irradiated with 3240 kGy for example, the oligomer contained 8.3×10^{16} spins per 0.0196 g, whose average molecular weight was 1326. Thus the number of spins is 5.6×10^{21} spins per mole of oligomer. From the

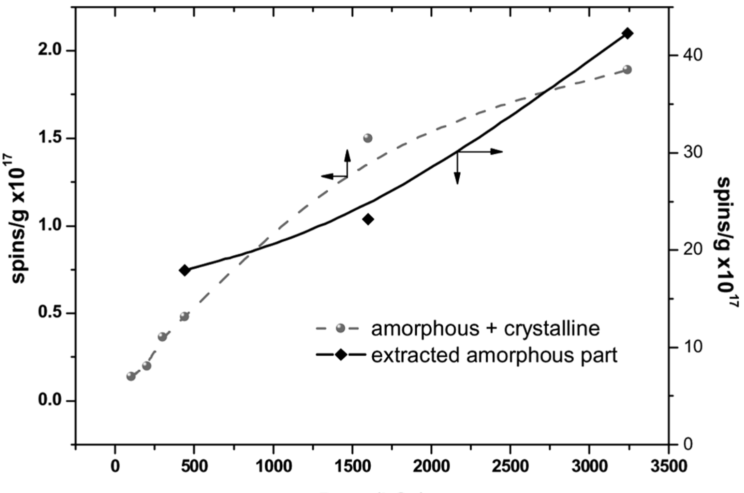
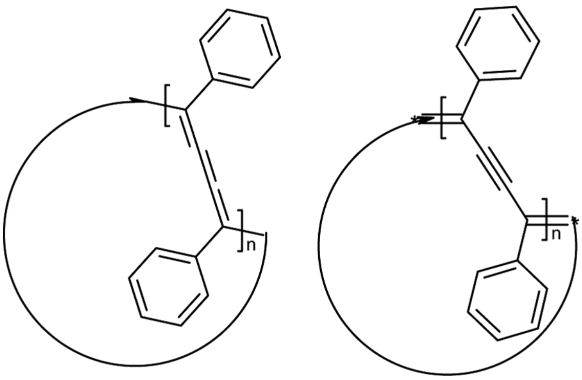


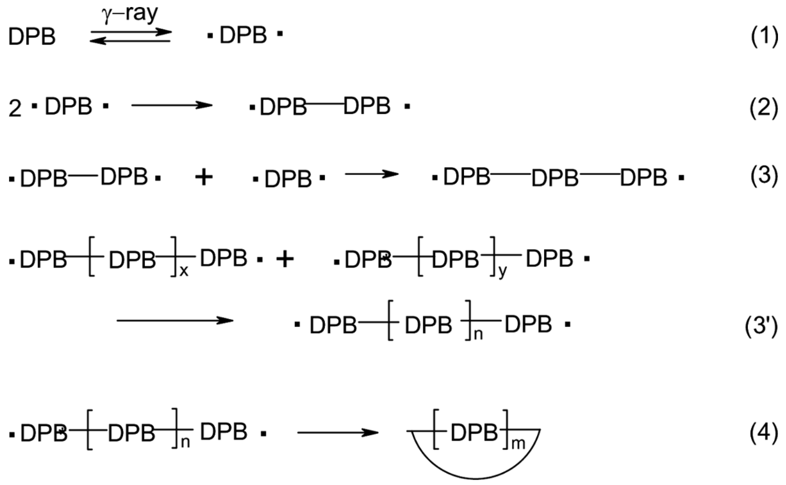
Figure 3. Relationships between doses and the formation of stable radicals.



Scheme 3. Cyclic oligomers of DPB.

Avogadro's number, 6.0225×10^{23} molecules per mole, it can be said that only one molecule exists as radicals per each 107 molecules. Considering that the radicals are diradicals, it can be estimated that approximately only one out of 200 molecules exists as diradicals. However, these radicals are stable, and after several months in air its decay was negligible. From these results it is thought that the main product is cyclic oligomer with average 6–7 DPB units. Only a small fraction exists as linear oligomers containing stable radicals at both terminals, similar to the product shown in Scheme 2.

The ^{1}HNMR spectrum of the oligomer had only a broad peak of benzene rings in the region of 6–8 ppm. The ^{13}CNMR spectrum did not show any noticeable signals of C=C and C≡C bonds, because the material contained a significant numbers of free radicals, which would interfere with the magnetic field. Furthermore the C=C allenic bonds are delocalized by the benzene rings, and are difficult to be observed. The FT-IR spectra of the amorphous product did not give any useful information because the butatriene bond in general does not show any noticeable peak. Therefore, it is rather inconclusive whether the product has butatriene or en-yne structure,



$$\mathrm{DPB} \xrightleftharpoons{\gamma\text{-ray}} \cdot\mathrm{DPB}\cdot \qquad (1)$$

$$2\cdot\mathrm{DPB}\cdot \longrightarrow \cdot\mathrm{DPB{-}DPB}\cdot \qquad (2)$$

$$\cdot\mathrm{DPB{-}DPB}\cdot + \cdot\mathrm{DPB}\cdot \longrightarrow \cdot\mathrm{DPB{-}DPB{-}DPB}\cdot \qquad (3)$$

$$\cdot\mathrm{DPB}{-}[\mathrm{DPB}]_x{-}\mathrm{DPB}\cdot + \cdot\mathrm{DPB}{-}[\mathrm{DPB}]_y{-}\mathrm{DPB}\cdot \longrightarrow \cdot\mathrm{DPB}{-}[\mathrm{DPB}]_n{-}\mathrm{DPB}\cdot \qquad (3')$$

$$\cdot\mathrm{DPB}{-}[\mathrm{DPB}]_n{-}\mathrm{DPB}\cdot \longrightarrow [\mathrm{DPB}]_m \qquad (4)$$

Scheme 4. Mechanism of oligomerization of DPB by Gamma irradiation at 90°C.

Table 2. Third order nonlinear optical susceptibility of oligo-DPB determined by the Z-scan technique

ID	Heating conditions	Appearance	Thickness (μm)	$\lvert\chi^{(3)} \times 10^{-10}\rvert$ (esu)
T0	No heating	Yellow	1.5	1.3
T1	2 h at 180°C, N_2 (g)	Brown	1	3.69
T2	7 h at 180°C, N_2 (g)	Brown	1	2.92
T3	3 h at 240°C, N_2(g)	Dark brown	0.7	5.94

as shown in Scheme 3. Considering the above results and the previous studies on DPB [13–15], the mechanism shown in Scheme 4 is proposed for the oligomerization of DPB with gamma irradiation at 90°C. The reaction (1) is the monomeric diradicals formation by radiation. The addition of diradicals to DPB does not take place because they are very stable and the acetylenic bonds are resistant to free radical addition. Therefore the next step is the coupling reaction to form more stable dimeric diradicals (2). The reactions (3) and (3′) are the oligomerization steps. Since the concentration of diradicals species is not high, the cyclization takes place predominantly (reaction 4). The possible structures of cyclic oligomers are shown in Scheme 3. In the previous studies [8,15] also, the number molecular weights of soluble products do not exceed about 2000, and the cyclization apparently took place.

The spin-coated films of the oligomer were brittle, and therefore polystyrene was added to reinforce the films. A chloroform solution containing 90% oligomer and 10% polystyrene by weight was spin-coated on a glass substrate. The brown transparent films were heated under nitrogen atmosphere, the magnitude and sign of the 3-NLO susceptibility of the resulting films were determined by the Z-scan technique and found to be in the order of $3\text{–}6 \times 10^{-10}$ esu (Table 2) and negative. These results are common for highly conjugated organic compounds away from single photon resonance.

IV. Conclusion

The irradiation of Gamma ray in the molten state (liquid state) at 90°C, increased significantly the yield of oligomerization, compared with that in the solid state. The yield and numbers of spins did not increase lineally with dose, and these observations indicate that the oligomerization proceeds via coupling of diradicals formed, as shown in Scheme 4. The low molecular weights of the products indicate that the cyclization by the intramolecular recombination of radicals takes place predominantly. The oligo-DPB gives brittle films, but when added with 10% polystyrene, films with excellent optical quality were obtained by spin coating. They showed third order nonlinear optical susceptibility of about 6×10^{-10} esu.

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