Polymerization of Diphenylbutadiyne Derivatives in Solution by Free Radical Initiator

MIRIAM F. BERISTAIN,[1] EDUARDO MUÑOZ,[2] and TAKESHI OGAWA[1]

[1]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico*
[2]*Instituto de Física, Universidad Nacional Autónoma de México, Mexico*

In order to study free radical reactions of aromatic diacetylenes, the reaction of diphenyldiacetylene with di-*t*-butylperoxide was carried out in 1,2-dichlorobenzene. The presence of *t*-butoxy radicals considerably accelerated product formation, and oligomers with number average molecular weights of 700−2000 were obtained. There is no fragment of the *t*-butyl group in the oligomers obtained according with the ¹H-NMR spectrum. Furthermore, it is impossible that the *t*-butoxy radicals would have initiated the oligomerization. The intense ESR spectra observed during the reaction at 130°C are due to the diradicals of oligomeric diphenylbutadiyne. It was concluded that the oligomerization proceeds via coupling of diradicals, and not the successive addition of radicals to monomers. The purified product oligomers did not contain carbonyl groups indicating there was no oxidation, and their ESR spectra have revealed that these oligomers contained a substantial amount of living free radicals stable in air at room temperature. The reason why high polymers are not obtained is the steric effect of oligomeric diradicals for coupling, as well as probable cyclization.

Keywords: aromatic diacetylenes; stable carbon diradicals; ESR spectroscopy; oligomerization mechanism

1 Introduction

The polymerization of diacetylenes (DAs) in solution is not an easy process because they are not very susceptible to free radical addition. Earlier, Chauser, et al. (1) carried out the thermal polymerization of diphenylbutadiyne (DPB) at 150°C, and later Wiley and Lee (2) also reported the thermal polymerization of DPB at 120−140°C in benzene and dimethylformamide, and they obtained soluble oligomers of unknown structure with molecular weights of 600−1700, and proposed a mechanism of bimolecular initiation and the successive addition of radical species to monomer for propagation. Kojima and coworkers (3) have reported thermal polymerization of DPB at 210°C under elevated pressures, and they proposed structure model of graphite. Under such conditions the real structures of products are difficult to be evaluated, as DPB undergoes thermal reactions when heated at temperatures above 150°C.

Free radical reactions of DAs are represented by their solid-state polymerization, which is said to be free radical propagation (4). An excited monomer diradical adds to the adjacent monomer in the crystal lattice to form dimeric diradicals, which then adds to the adjacent monomer to continue the propagation. However, very little is known about free radical reactions of DAs in solution. The light sensitive DAs, which undergo solid-state polymerization, usually do not polymerize in solution by irradiation or free radical initiator, although Paley, et al. (5) once reported photopolymerization of a diacetylene in solution, and this is the only case. There are free radical addition reactions to acetylenes, but they are mainly concerned with terminal acetylenes (6), and disubstituted acetylenes such as tolan, are usually inert to free radical addition.

The present authors have previously studied in detail the free radical polymerization of some vinyl monomers in the presence of aromatic DAs (7−8). It was found that the aromatic DAs interact with transient propagating polymer radicals, thus the propagating radicals are stabilized and can be detected by ESR spectroscopy at polymerization temperature. The rate and degree of polymerization decrease in general in the presence of aromatic DAs, and the effects depend on the type of monomers. The polymerization of the monomers such as acrylates, which give unstable propagating radicals, are more retarded, or inhibited. The interaction is weak for the aromatic DAs having electron donor groups at the *para*-positions (7). Surprisingly, the polymers obtained do not contain any fragment of DPB (8), indicating that the

Address correspondence to: Takeshi Ogawa, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Ciudad Universitaria, DF 04510, Mexico. E-mail: ogawa@servidor.unam.mx

polymer radicals do not add to DPB. The aromatic DAs only temporarily and reversibly trap the transient radicals without bond formation. Such phenomena could not be observed for aliphatic diacetylenes or for tolan. The photochemical $[2+2]$ addition of olefins to DPB has been reported (9). However, this is not an ordinary free radical reaction.

On the other hand, the aromatic diacetylenes form diradicals stable under inert atmosphere when irradiated with UV light in solution (10) or heated in the molten state (11) and the radicals are detected by ESR spectroscopy as signals of free electrons. The theoretical calculation suggested that the radical species are sp-diradicals rather than sp^2 diradicals. They undergo coupling to form dimeric and trimeric diradicals, which give ESR signals, but no high molecular weight polymer is obtained probably due to the steric effect for recombination reactions.

The above two findings are important for the studies not only on the polymerization, but also in general on free radical reactions of aromatic diacetylenes. Aliphatic diacetylenes, which do not have resonance stabilization by adjacent group, on the other hand, are completely different from aromatic diacetylenes. The free radical vinyl polymerization was not affected at all by the presence of aliphatic diacetylenes, and they did not show any ESR signals in solution when heated or irradiated with UV light. This paper deals with the reaction of aromatic diacetylenes principally diphenylbutadiyne (DPB) in solution in the presence and absence of peroxide, using ESR signals during the reaction, and provides a new understanding on the non-topochemical polymerization of diacetylenes, as well as on the novel stable carbon free radicals.

2   Experimental

DPB was prepared by the oxidative coupling reaction of phenyl acetylene (Farchan) in acetone using copper (I) chloride and N,N,N',N'-tetramethylethylenediamine (colorless fine needle crystals melting at 83°C). p,p'-di(N,N,-dibutyl-laminocarbonyl)diphenyl-butadiyne (BBA) was prepared by the Sonogashira reaction of p-bromo-N,N-dibutylbenzamide with trimethylsilylacetylene, followed by the oxidative coupling reaction of the ethynylbenzamide (colorless fine powder crystals with mp. $112-113^\circ$C). m,m'-di(hexyloxycar-bonyl) diphenylbutadiyne (HEX) and p,p'-di(heptyloxycarbo-nyl)diphenylbutadiyne (HEPT) were prepared from the respective m- and p-bromobenzoates with the Sonogashira reaction with trimethylsilylacetylene, followed by the oxi-dative coupling reactions (fine powder crystals melting at 62°C and 53°C, respectively). Their purity was confirmed by elemental analysis, and from NMR (Bruker Avance 400) and IR spectroscopy. t-Butylperoxide (t-BPO) was supplied by Aldrich, and it was used as received.

The polymerization of DPB was carried out in pyrex tubes in which 1,2-dichlorobenzene and t-BPO were placed, and the tubes were sealed off in vacuum after repeated freeze and thaw degassing. The tubes were then placed in a flask containing boiling n-butanol (boiling at 110°C at an altitude of 2300 m of Mexico City). After the reaction, the content was poured into methanol and the polymer obtained was washed several times with methanol and hexanes to remove the unreacted DPB. The NMR Spectra were taken using a Bruker 400 MHz NMR spectrometer in $CDCl_3$, and molecular weights were determined by GPC in tetrahydrofuran (THF) using a poly-styrene standard. The inherent viscosity was measured in dichloroethane dimethylformamide (DMF) at 30°C.

2.1   ESR Measurement

ESR spectra were taken at 130°C using a JEOL ESR spec-trometer Model RE3X. The samples were placed in quartz tubes with an inner diameter of 3 mm, supplied by Wilmad Lab Glass, and after degassing the system by the freeze and thaw process, the tubes were sealed off in vacuum. The temp-erature, 130°C, was chosen, because aromatic DAs undergo thermal reactions; opening of triple bonds at temperatures above 150°C. The number of free radicals was calculated with the double numerical integration of the first derivative of the resonance curve from the equation (12);

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

where H_A and H_B are the initial and final parts of the reson-ance curve, respectively, and $S(H')$ is the value of the absorp-tion at field H'. The free radical concentrations were measured by comparison with a NaCl:Mn^{++} crystal calibrated by atomic absorption spectroscopy, taking both spectra under the same ESR spectrometer conditions.

3   Results and Discussion

Figure 1 shows ESR signals of DPB and HEX in the absence and presence of t-BPO. The other DAs also gave similar spectra. The g values (in Table 1) are of free electrons, being in the range of 2.0024−2.0031, indicating that the radicals are highly conjugated carbon radicals, and their detailed analysis is difficult due to their highly delocalized nature. The signals are identical to those of the sp diradicals observed for the UV irradiated system (10) and for the molten system (11), and they are considered to be oligomeric diradicals. The formation of the 1,4-butadiynyl sp-diradical was found to be the most stable form by the theoretical calcu-lation (10). It is clearly seen that the signals are much more intense (higher radical concentration) in the presence of peroxide. As can be seen from Table 1 and Figure 2, which is the plots of the number of diradicals against reaction time for the system of DPB for example, in the absence of the peroxide the numbers of radicals did not increase significantly with heating time, while the numbers of radicals in the presence of peroxide increased by more than one order. The t-butoxy (t-BO) radicals are not detectable by ESR under
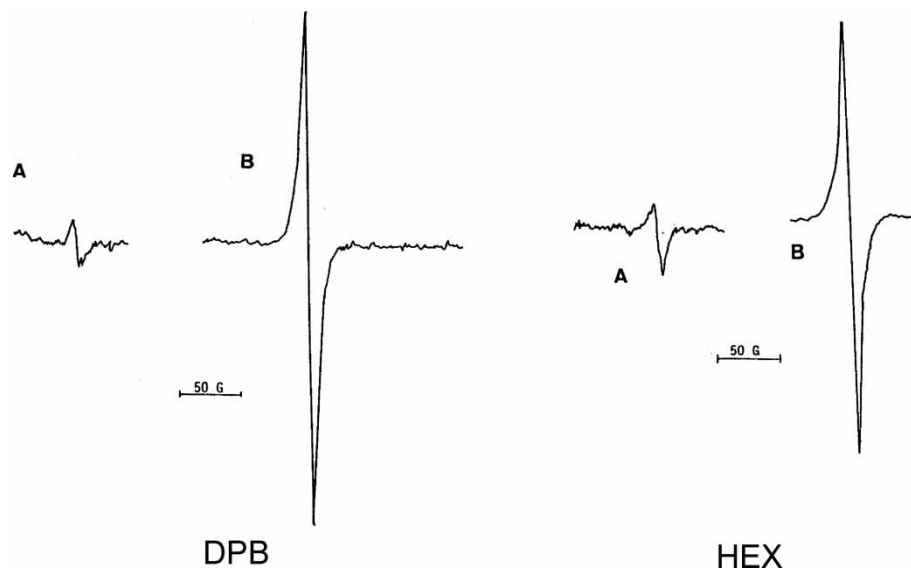
Fig. 1. ESR spectra of DAs heated at 130°C for 40 min. (DPB) and 30 min. (HEX) in the absence (A) and presence (B) of *t*-BPO.

the experimental conditions of this work. The systems in the presence of peroxide became reddish brown indicating that conjugated materials are formed, while the systems without the peroxide only became yellow. The ESR signals do not quench, or change very little after being left to stand for several months at room temperature, suggesting that they are very stable.

The reason why more radicals are formed in the presence of *t*-BO radicals is intriguing. One can simply imagine that *t*-BO radicals would add to the triple bonds of DAs. However, as mentioned before, when free radical polymerization of ethylacrylate was carried out in the presence of DPB, the polymerization was retarded and almost inhibited, but no fragment of DPB was found in the obtained polymers, indicating the transient radicals did not add to the triple bonds. However, the ESR signals of propagating polymer radicals were observed during polymerization. This indicates that the transient free radicals do not add to the triple bonds, but simply interact to stabilize the transient radicals (8). If the *t*-BO radicals are added to the acetylenes, the product oligomers should have aliphatic groups arising from the *t*-butyl group. Figure 3 shows ^{1}H-NMR spectrum of the polymerization product obtained in vacuum in the presence of the peroxide at 110°C for 60 days. It can be seen that there is no aliphatic proton from the *t*-butyl group at 1−2 ppm region. The number average molecular weight of this oligomer measured by GPC was also about 1400 (7 DPB units) and the inherent viscosity was 0.32 dl g in DMF. FT-IR spectrum of the product is shown in Figure 4. There is no carbonyl group at the 1650−1700 cm^{-1} region, indicating that no oxidation of the radicals took place, although the reaction product was exposed to air during purification, filtering, drying and storage for three years. Furthermore, an intense ESR signal was observed indicating that the radicals are still alive. The number of radicals was found to be 7×10^{21} radicals per

mol of oligo-DPB (estimated from the number average molecular weight from GPC), indicating that one out of a hundred exists as living radicals. In order to confirm the above results, the polymerization was repeated under the same previous condition, and the products were analyzed. The reaction product was precipitated in excess methanol, and the methanol soluble portion (22%) was found to be principally unreacted DPB contaminated with fragments of *t*-BPO. The methanol insoluble part was extracted with hexanes, and the hexane-soluble product (<5%) did not contain a DPB fragment and seems to be residues from *t*-BPO. The brown powder insoluble in methanol and hexanes, but soluble in chloroform, THF, etc. was obtained with a 72% yield. It had an inherent viscosity of 0.37 dl/g at 30°C in 1,2-dichloroethane and GPC in THF, gave Mn and Mw of 1450 and 2630, respectively, indicating the product is also heptamer in average. The oligomer was completely amorphous judging from its X-ray diffraction pattern. FT-IR spectrum of this part was identical to that shown in Figure 4, indicating that there is neither carbonyl group nor aliphatic groups. The ^{1}H-NMR spectrum of the oligo-DPB was also identical to that shown in Figure 3, confirming that there was no addition of *t*-BO radicals to the DPB. The ESR spectra of the oligomer showed an intense signal, and the calculation of diradical species assuming its Mn to be 1450, showed that one diradical oligomer exists for three non-radical oligomers. One possible explanation why products consist of living radicals and non-radical species is probably the cyclization of oligomeric diradicals. ^{13}C-NMR spectra of the product did not show the presence of acetylenic bonds, indicating that they maintain butatriene structure. The decrease in number of living radicals with lapse of time may be attributed to the recombination of diradicals to form cyclic species. The GPC was repeated for the same sample after 6 months, and the molecular weight did not change. Its

Table 1. Numbers of radical species formed in 1,2-dichlorobenzene at 130°C in vacuum-sealed ESR tube

DA	Time [min] 130°C	Absence of peroxide		Presence of peroxide		
		$\text{Rad/mol}_{DA} \times 10^{17}$	g	Molar ratio [DA]/[PO]	$\text{Rad/mol}_{DA} \times 10^{18}$	g
DPB	—	—	—	0.87	0.47	2.0032
	10	—	—		0.72	2.0031
	20	1.0	2.0031		1.5	2.0031
	30	1.5	2.0030		2.2	2.0030
	40	1.5	2.0032		2.8	2.0028
	50	1.5	2.0030		3.5	2.0029
	60	1.5	2.0031		4.3	2.0028
BBA	—	—	—	0.45	2.5	2.0030
	10	2.2	2.0024		5.3	2.0030
	20	2.5	2.0024		8.1	2.0030
	30	2.5	2.0024		10.3	2.0030
	40	2.5	2.0024		12.6	2.0030
	50	2.5	2.0024		14.4	2.0031
	60	2.5	2.0024		15.6	2.0031
HEX	—	2.3	2.0027	0.72	0.88	2.0030
	10	2.7	2.0027		2.9	2.0030
	20	3.4	2.0027		4.4	2.0030
	30	3.8	2.0027		5.9	2.0030
	40	4.2	2.0027		6.8	2.0030
	50	5.7	2.0027		7.7	2.0030
	60	5.7	2.0027		8.8	2.0030
HEPT	—	4.4	2.0027	0.68	1.0	2.0028
	10	5.4	2.0027		3.4	2.0029
	20	6.5	2.0027		4.6	2.0030
	30	6.7	2.0027		6.4	2.0030
	40	7.0	2.0027		7.5	2.0030
	50	8.0	2.0027		8.7	2.0030
	60	9.0	2.0027		9.4	2.0032
MPA	—	0		0.61	1.2	
	10	0			6.4	
	20	15.5	2.0026		10.1	2.0032
	30	17.6	2.0026		13.6	2.0032
	40	19.2	2.0026		19.0	2.0032
	50	21.4	2.0026		52.9	
	60	22.4	2.0026		70.7	
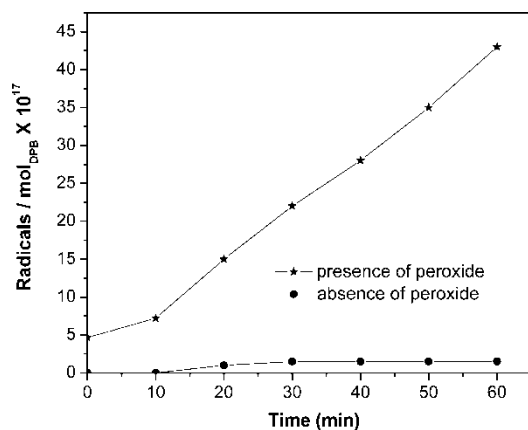
Fig. 2. Numbers of radicals against the reaction time for DPB (Plotted from the data of Table 1).
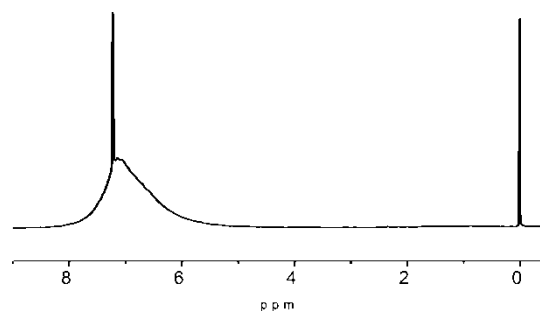
Fig. 3. ^{1}H-NMR Spectrum of oligo-DPB separated and purified from the reaction products of DPB in the presence of t-BPO.
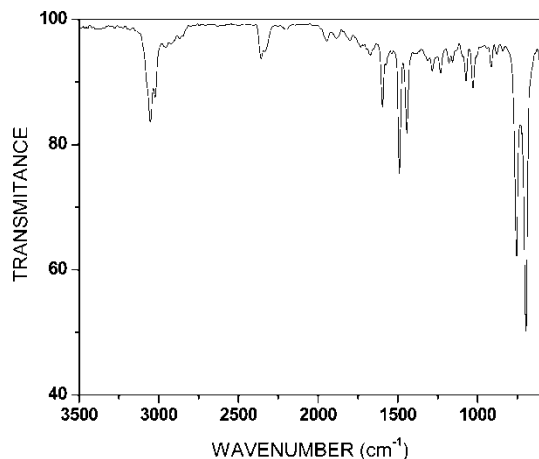
Fig. 4. FT-IR spectrum of oligo-DPB obtained by heating at 110°C for 2 months in *o*-dichlorobenzene in the presence of *t*-BPO.

FT-IR spectra did not show any change during the storage. The ESR measurement for the number of living radicals was also repeated, and it was found that the number decreased by about 30%, indicating one molecule exists as diradical for ten molecules. The results indicate that the cyclization is slowly taking place during the storage.

Wiley and coworkers have reported that poly-DPB with maximum 2,000 molecular weight, can be obtained by thermal polymerization in a concentrated solution in benzene and DMF at 120−140°C (2). They suggested from their kinetic study of polymerization, that the initiation is a bimolecular reaction, although no indication was made on the initiating species. They presumed that the radicals add to monomer DPB to form polymers. In the case of photo-excitation of aromatic diacetylenes to form diradicals, the energy of visible region is sufficient to form monomeric diradicals, shown in Scheme 1. However, this energy is very high when converted to the thermal energy, and the thermal unimolecular reaction to form the monomeric diradical is not possible. However, if two or three molecules with sufficient kinetic energy collide in such a manner that the more stable dimeric or trimeric diradicals are formed, the required energy is considerably reduced. Theoretical calculation showed that the Gibbs free energy to form dimeric diradical requires 25.5 kcal/mol, while to form the trimeric diradical out of dimer and monomer only 9.3 kcal/mol is needed (11). Furthermore, the thermal reaction system has extra energy coming from collision, and the dimeric diradical can be formed by a bimolecular reaction of two DPB molecules. In the presence of *t*-BPO, there are plenty of active molecules in the solution such as *t*-BO radicals, and they pass their
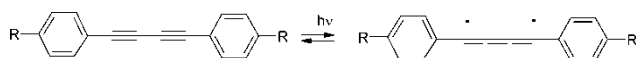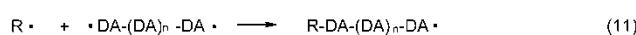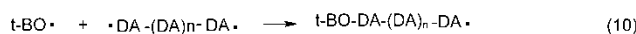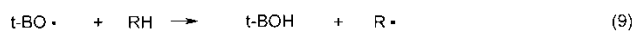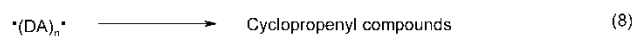
kinetic energy by collision to DPB molecules, forming more diradicals, possibly monomeric diradicals, which combine to form dimeric diradicals which are detected by ESR spectroscopy. It can be concluded that aromatic diacetylenes form their dimeric and oligomeric diradicals by the collision at elevated temperatures.

As can be seen in Table 1, although precise comparison cannot be made due to the difference in the relative quantity of the peroxide in each case, it can be generalized that the numbers of radicals of the substituted DAs were greater than those of DPB. This may be due to the increased stabilization of diradicals by the expansion of conjugation by the substituents, the carbonyl groups. The larger quantity of radicals in the case of P,P′-dimethoxydiphenylbutadiyne (MPA) is probably due to the stabilization by increase in electronic density of MPA diradicals by the electron donor methoxy groups. However, the yield of oligomers of DPB in the presence of *t*-BPO was high after several weeks, but in the cases of the substituted DAs, the yields of methanol insoluble fractions were very low, and it was almost impossible to isolate the products, although they form more diradicals. This indicates that the steric effect is very important for the coupling of diradicals, and the substituted DAs apparently cannot give large oligomers that precipitate in methanol, and they stay as small diradicals. Therefore, as a whole the substituted DAs contained more radicals, as less coupling could take place.

From the above findings, the following steps are suggested for the thermal polymerization of aromatic diacetylenes in solution as shown in Scheme 2. The reaction 1 is the formation of dimeric diradicals independently of the peroxide, and the reaction 2 is the formation of monomeric diradicals by the collision with the high-energy *t*-BO radicals. The monomeric diradical is not stable and deactivates itself to return to DPB (reaction 3) or undergoes coupling to form dimeric and trimeric diradicals (reaction 4). When the *t*-BO

$$2DA \xrightarrow{\triangle} {}^{\bullet}DA\text{-}DA^{\bullet} \quad (1)$$

$$t\text{-}BO^{\bullet} + DA \longrightarrow {}^{\bullet}DA^{\bullet} + t\text{-}BO^{\bullet} \quad (2)$$

$${}^{\bullet}DA^{\bullet} \longrightarrow DA \quad (3)$$

$$2\ {}^{\bullet}DA^{\bullet} \longrightarrow {}^{\bullet}DA\text{-}DA^{\bullet} \quad (4)$$

$${}^{\bullet}DA\text{-}DA^{\bullet} + {}^{\bullet}DA^{\bullet} \longrightarrow {}^{\bullet}DA\text{-}DA\text{-}DA^{\bullet} \quad (5)$$

$$2\ {}^{\bullet}DA\text{-}DA^{\bullet} \longrightarrow {}^{\bullet}DA\text{-}DA\text{-}DA\text{-}DA^{\bullet} \quad (6)$$

$${}^{\bullet}DA\text{-}DA\text{-}DA\text{-}DA^{\bullet} \longrightarrow \begin{matrix} DA\text{—}DA \\ | \quad | \\ DA\text{—}DA \end{matrix} \quad (7)$$

$${}^{\bullet}(DA)_n{}^{\bullet} \longrightarrow \text{Cyclopropenyl compounds} \quad (8)$$

$$t\text{-}BO^{\bullet} + RH \longrightarrow t\text{-}BOH + R^{\bullet} \quad (9)$$

$$t\text{-}BO^{\bullet} + {}^{\bullet}DA\text{-}(DA)_n\text{-}DA^{\bullet} \longrightarrow t\text{-}BO\text{-}DA\text{-}(DA)_n\text{-}DA^{\bullet} \quad (10)$$

$$R^{\bullet} + {}^{\bullet}DA\text{-}(DA)_n\text{-}DA^{\bullet} \longrightarrow R\text{-}DA\text{-}(DA)_n\text{-}DA^{\bullet} \quad (11)$$
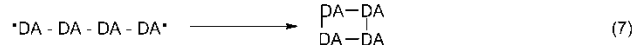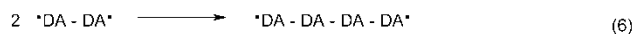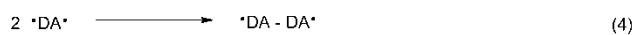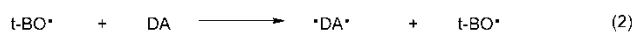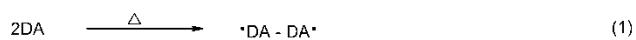
Sch. 2. Mechanism for the oligomerization of aromatic diacetylene.

Sch. 1. *sp*- Diradical of DPB formed by UV irradiation.
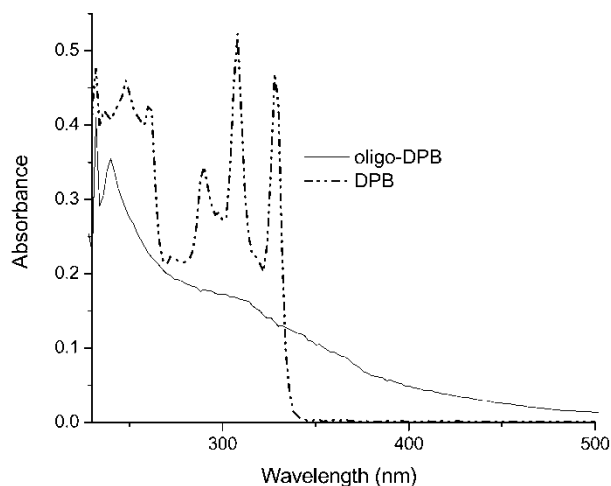
Fig. 5. UV/Visible spectra of DPB and oligo-DPB in THF solution.

Sch. 3. A butatriene structure of oligo-DPB obtained in the presence of peroxide at 110°C.

radical collides with diradicals, they can combine, and the small amount of aliphatic groups contained in the methanol soluble products are due to the reaction 5. However, the frequency factors of the reactions 6 and 7, must be very small because of the steric effect, and therefore the oligomerization (or polymerization) is very slow. Reaction 8 is the formation of cyclopropenyl compounds between the diradical and acetylene group (13), however this is unlikely because no acetylenic bonds are present in the product of this work. Reaction 9 is the result of the *t*-BO radicals. They abstract hydrogen from *t*-butyl groups and the resulting radicals combine with each other. The small amounts of *t*-BO fragments found in the polymerization products soluble in hexanes are thought to be due to the recombination of diradicals with *t*-BO radical and R· (reactions 10 and 11).

The visible spectra of oligomerization products of DPB, are shown in Figure 5. The characteristic peaks of the π-π^* transitions of DPB in the region of 300−340 nm disappeared, and the spectrum did not show any absorption maximum at the visible region, giving a tailing slope from UV region to the visible region of 600 nm.
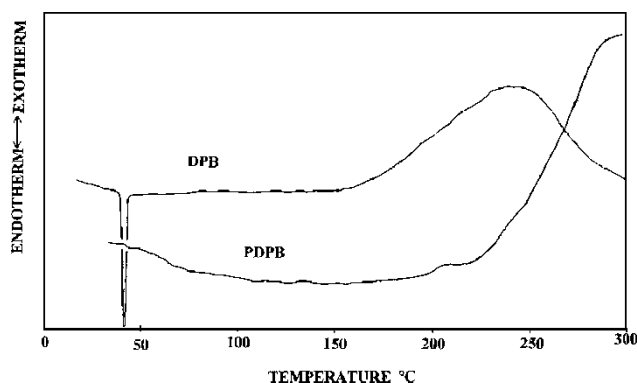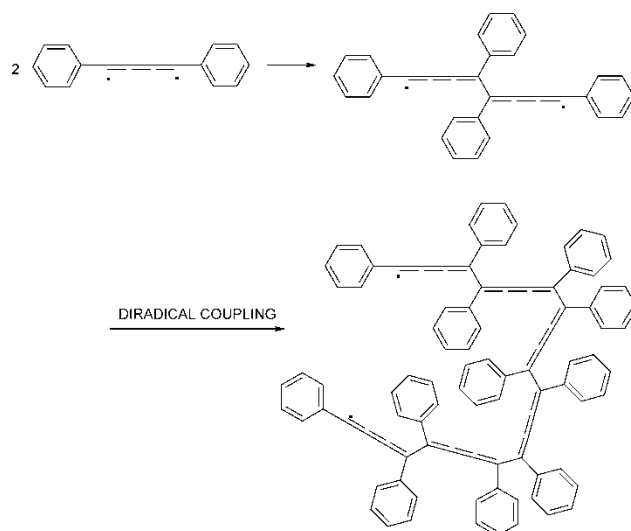
Figure 6 shows DSC curves for DPB and its oligomer. DPB starts its thermal reaction at around 150°C, and this is typical to aromatic diacetylenes, which do not undergo the topochemical polymerization, and the exotherm reaches its maximum at around 240°C. In contrast to this, the oligomer obtained at 110°C starts its thermal reaction at around 220°C, and at below 200°C it is stable and no thermal reaction is observed. The probable structure of the polymer is shown in Scheme 3. It does not contain an acetylenic bond in accordance with ^{13}C-NMR spectra. Kojima suggested the structure of their soluble polymer obtained at 210°C as polyacene to which benzene rings are attached (3). Although it is said that polydiacetylenes form the enyne structure, in the cases of aromatic diacetylenes, which do not undergo topochemical polymerization, the butatriene structure can be more stable for the oligomers. In the case of aliphatic diacetylenes, which undergo topochemical polymerization, the polymers formed at the initial stage are said to have a butatriene structure (4).

4 Conclusions

The free radical catalyzed oligomerization of aromatic diacetylenes in solution proceeds via coupling of diradicals formed by the collision with *t*-BO radicals, and not the successive addition propagation of radical species to DAs. The initiation is not the addition of *t*-BO radical to monomer, but it gives kinetic energy to form diradicals. The difficulty in obtaining high polymers is due to the steric hindrance and high stability of diradicals. The structure of the oligomers is considered to be butatriene because no acetylenic linkage is detected by ^{13}C-NMR and FT-IR spectra. The oligomeric diradicals are stable and are not oxidized by air under the ambient condition, and they probably undergo slow cyclization.

Fig. 6. DSC Curves for DPB and its polymerization product.

5 Acknowledgements

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