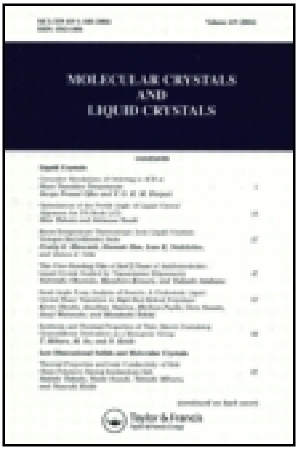


Molecular Crystals and Liquid Crystals

Thermal Reactions of Aromatic Diacetylenes: An Insight to Amorphous State Polymerization of Diacetylenes

Miriam F. Beristain [a], Sergei Fomine [a], Takeshi Ogawa [a], Eduardo Muñoz [b] & Angel Marcos [c]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, México, DF, México

[b] Instituto de Física, Universidad Nacional Autónoma de México, Ciudad Universitaria, México, DF, México

[c] Instituto de Ciencia y Tecnología de Polímeros (CSIC), Madrid, Spain

Version of record first published: 23 Aug 2006

To cite this article: Miriam F. Beristain, Sergei Fomine, Takeshi Ogawa, Eduardo Muñoz & Angel Marcos (2006): Thermal Reactions of Aromatic Diacetylenes: An Insight to Amorphous State Polymerization of Diacetylenes, Molecular Crystals and Liquid Crystals, 447:1, 251/[569]-263/[581]

To link to this article: http://dx.doi.org/10.1080/15421400500377271

Mol. Cryst. Liq. Cryst., Vol. 447, pp. 251/[569]–263/[581], 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500377271

Thermal Reactions of Aromatic Diacetylenes: An Insight to Amorphous State Polymerization of Diacetylenes

Miriam F. Beristain
Sergei Fomine
Takeshi Ogawa
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, México DF, México

Eduardo Muñoz
Instituto de Física, Universidad Nacional Autónoma de México, Ciudad Universitaria, México DF, México

Angel Marcos
Instituto de Ciencia y Tecnología de Polímeros (CSIC), Madrid, Spain

Several aromatic diacetylenes were heated in molten state, and the formation of diradicals was studied by ESR spectroscopy. Intense ESR signals were observed even at temperatures as high as 180°C. The formation of radical species at such low temperatures was explained by the formation of oligomeric species. The numbers of unpaired electrons in the molten state reached to 10^{21} electrons per mole of diacetylene, when heated to 180°C, and deep red materials were obtained. Surprisingly the radicals did not disappear when exposed to air showing that the radicals are stable in air.

Keywords: aromatic diacetylenes; diradicals; ESR spectra; oligomerization

I. INTRODUCTION

The polymerization of diacetylenes (DAs) in the solid state, which is often called as topochemical polymerization, is well known and the

This work was supported by the DGAPA grant from our university with the contract number IN102401. Thanks are also due to Mr. Miguel A. Canseco for his assistance in thermal analysis.

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

polymerization mechanism has been more or less established as free radical propagation in the crystal lattice [1]. It is said that the butatriene diradical is first formed on carbons 1 and 4 by irradiation or heating below their melting points, which then adds to the adjacent DA molecules, and the propagation species is said to be the dicarbene [2]. The polydiacetylenes (PDAs) thus obtained are totally crystalline highly conjugated materials, and they were thought to be the principal candidates for third order nonlinear optical (3-NLO) applications. However, it is practically impossible to obtain thin films with satisfactory optical quality due to its crystalline nature, and the interest in PDAs as 3-NLO materials has faded recently. It is of interest to obtain amorphous PDAs with a defined structure from the point of view of optical quality of films, and the polymerization of DAs in solution or in amorphous state was thought to be an alternative route. However, very little has been reported on the polymerization of DAs in solution or in molten state because the majority of topochemically polymerizable DAs do not give polymers under other conditions except in the crystalline state. Wiley and Lee [3] reported the polymerization of diphenylbutadiyne (DPB) in a concentrated DMF solution, and oligomers with unknown structure have been obtained. Paley, *et al.* [4] has reported photopolymerization of a DA in solution, and it is said that the PDA formed is insoluble in the solvent and deposits on a substrate in the form of a thin film.

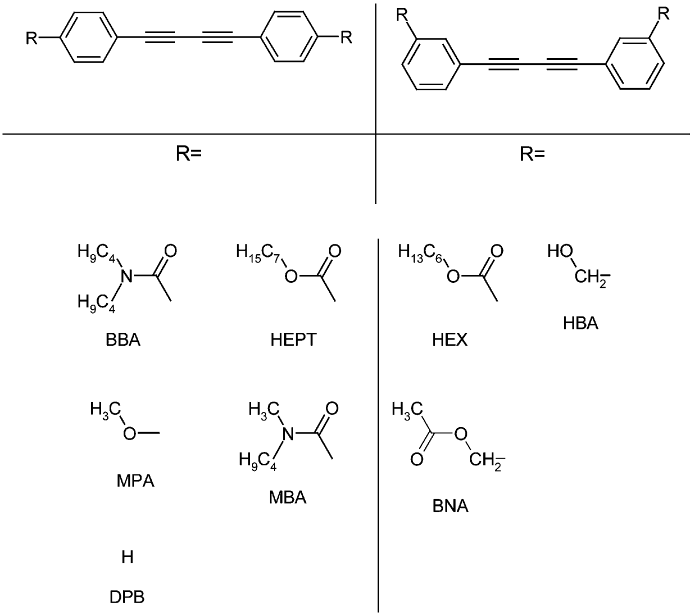
There are very few studies on ESR signals of aromatic DAs. The present authors found that aromatic DAs form free radical species on heating [5] or irradiating with UV light [6], which are detected by ESR spectroscopy and the radicals do not quench on standing almost indefinitely under inert atmosphere. In the case of irradiation of UV light it seems that *sp* diradicals are formed [6]. Murata and Iwamura [7] reported an ESR study of 1,3-butadiyne-1,4-diylbis(phenylnitrenes), in which nitrene radicals are detected at temperature below 10 K. However, they do not mention any radical species from the diacetylene group. Iwase, *et al.* [8] have studied the thermal polymerization of 1,4-bis(4-benzylpyridinium) butadiyne triflate, and detected an ESR signal when its DMF solution was heated to 80°C, and they assumed that the signal is that of dicarbene species, probably because the dicarbene propagation has been accepted as the mechanism of topochemical polymerization of aliphatic DAs by Sixl [2]. The present authors have previously reported that aromatic DA-containing polymers films develop deep red color when heated and irradiated at 180°C, and their third order nonlinear optical susceptibility of 10^{-10} esu could be obtained [9], and this is a case where the DA groups in the polymer chains couple each other to from a conjugated system. In this work, the thermal formation of diradicals of some aromatic DAs are reported, and possibility of obtaining amorphous PDAs, is discussed.

II. EXPERIMENTAL

DAs

The aromatic DAs were synthesized by the oxidative coupling reaction of respective aromatic acetylenes. Diphenylbutadiyne (DPB) was prepared by oxidative coupling of phenyl acetylene supplied by Farchan. In the cases of the benzoates and benzamides, bromobenzoic acid (Aldrich) was used as starting material. The bromo derivatives were converted to the corresponding ethynyl derivatives by Sonogashira reaction using trimethylsilyl acetylene [10]. Di(*p,p′*-methoxyphenyl)-butadiyne (MPA) was prepared from 4-iodo anisole by Sonogashira reaction, followed by oxidative coupling reaction. The DAs were characterized by FTIR and NMR spectroscopy, and elemental analysis. They are shown in Table 1. BBA: *p,p′*-N,N,N′,N′,-tetra-*n*-butyldi-

TABLE 1 Aromatic Diacetylenes used in this Work



aminocarbonyl diphenylbutadiyne. MBA: *p,p′*-N,N′-dimethyl-N,N′,-di-*n*-butyldiaminocarbonyl diphenylbutadiyne. HEPT: *p,p′*-diheptyloxycarbonyl diphenylbutadiyne. HEX: *m,m′*-dihexyloxycarbonyl diphenylbutadiyne. HBA : *m,m′*-dihydroxybenzyl diphenylbutadiyne. BNA: *m,m′*-diacetoxybenzyl diphenylbutadiyne.

ESR Measurement

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 after degassing the system the tubes were sealed off in vacuum. In the case of thermal reaction, the tubes were heated in an oil bath or in the cavity of ESR spectrometer. The number of radicals was calculated with the double numerical integration of the first derivative of the resonance curve from the equation [11].

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

where H_A and H_B are the initial and final parts of the resonance curve, respectively, and $S(H')$ is the value of the absorption 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.

Characterization

NMR spectra of the compounds were recorded on a Brucker Avance 400 (400 MHz) spectrometer. FT-IR spectra were recorded using a Nicolet 510P spectrophotometer. DSC was carried out using a Perkin-Elmer DSC 7 calorimeter.

III. RESULTS AND DISCUSSION

Figure 1 shows ESR spectra of the products heated at 165°C (molten state) for 110 hours in vacuum-sealed tubes. The spectra were taken in tetrahydrofuran (THF) solution, and they are apparently identical to those observed for the aromatic DAs with UV-irradiation, having the same shape and g values of free electron, and it is difficult to discuss them because of their high delocalization. It is surprising that the reaction products were exposed to air when dissolved in THF but intense ESR signals were observed, indicating that the radicals are

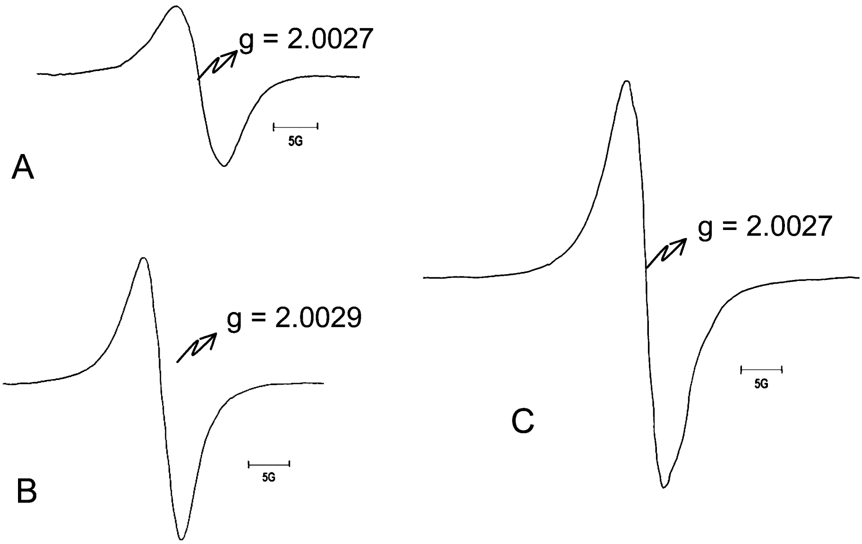
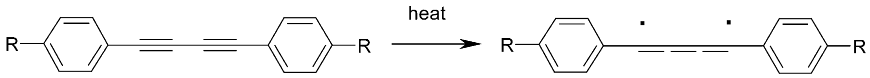


FIGURE 1 ESR signals of the products heated at 165°C in sealed tubes, and exposed to air and dissolved in THF. A: Oligo-BNA, B: Oligo-MPA and C: Oligo-DPB. Microwave frequency: 9.070 GHz, power: 4 mW, central field: 3220 Gauss, receiver gain: 1 × 10. Frequency modulation: 100 KHz.

stable in air. This is a rare example of a new type of stable carbon radicals. It was proposed previously by the theoretical calculations that *sp*-diradicals (Scheme 1) are formed by the irradiation of UV light [6]. Therefore, in this case also, *sp*-diradicals are assumed to be formed. However, the energy gap between the ground state and excited state calculated for the UV irradiation system was about 4 eV, which is more then sufficient to excite DAs from S0 to T0 state. However, the conversion of this energy to corresponding thermal energy indicates that temperature over 46,000 K is required for the formation of dicarbenes, and therefore the formation of monomeric diradical at moderate temperatures such as below 100°C, shown in Scheme 1, is rather impossible for a single DA molecule. However, it was found that the all the aromatic DAs give ESR signals at moderate temperatures around 100°C, and this cannot be explained only by the



SCHEME 1 *sp* Diradicals of aromatic diacetylene.

excitation energy. If the monomeric diradicals were formed, they would not be stable in air, and therefore the radicals formed by heating are thought to be highly conjugated oligomeric diradicals. The numbers of the radicals were found to be in the order of 10^{21} radicals per mole of DA, which are in the same order to those shown in Table 2

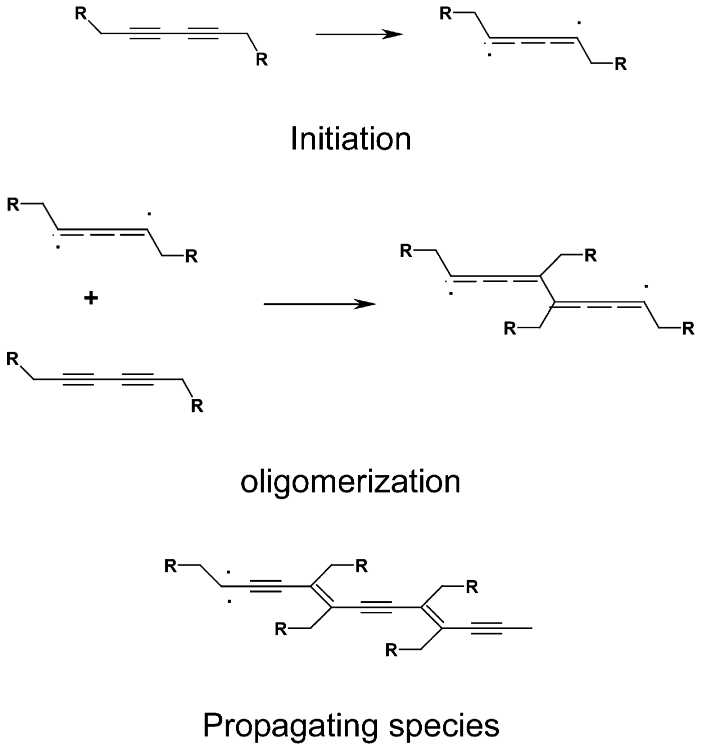
TABLE 2 Radical Formation of Aromatic Diacetylenes above their Melting Point

DA	mp [°C]	T [°C][a]	Rad/mol$_{DA}$ × 10^{19}	Color of heated system at 180°C	Temperature of thermal opening of DA group °C[#] Initial[b]	Max
BBA	112–113	RT	*	Brown	210	301
		160	1.7			
		170	2.2			
		180	6.7			
BNA	79–80	RT	*	Deep red	215	261
		160	9.2			
		170	25			
		180	190			
DPB	82–84	RT	*	Red black	180	247
		160	31			
		170	320			
		180	440			
HBA	153–154	RT	0.5	Brown	210	261
		160	6.1			
		170	2.5			
		180	5.0			
HEPT	53	RT	*	Brown	220	273
		160	0.24			
		170	1.2			
		180	4.6			
HEX	62–63	RT	*	Brown	210	278
		160	0.27			
		170	0.9			
		180	3.5			
MPA	140–141	RT	0.46	Deep red	200	273
		160	1.8			
		170	3.4			
		180	47			

[a] Time intervals between temperatures = 15 minutes. Heated in the cavity.
[b] Approximate temperature at which the DSC curves started to rise.
[*] Undetectable from ESR.
[#] From DSC. Heating rate = 10°C/min under N_2.

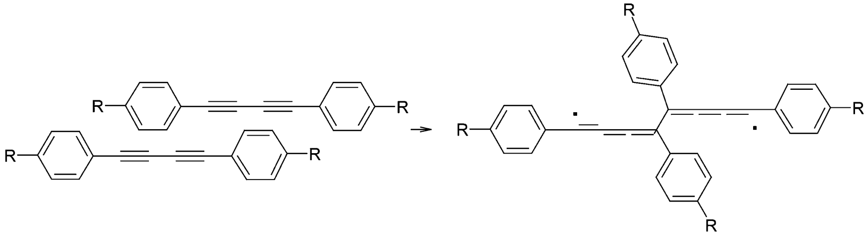
for sealed tube samples unexposed to air. The number average molecular weights determined by GPC in THF using polystyrene standard, were only 1000–1500, which indicate that the number average degree of polymerization is only 5–7. The degree of polymerization calculated from the number of radicals assuming that every molecules were diradicals, is in the order of 100, which means that the molecular weights are in the order of 20,000. This discrepancy cannot be explained in this moment, but macrocyclic products might be formed.

As shown in Scheme 2, it has been established for the solid-state polymerization of DAs, that the first step of the polymerization is the formation of monomeric sp^2 butatriene diradicals [2], formed by irradiation, heating or pressure. They rapidly add to the adjacent monomers in the crystal lattice to form dimeric diradicals, trimeric and so on. It is said that when the chain length increases, the butatriene diradicals are transformed to the more stable dicarbene



SCHEME 2 The solid-state polymerization of diacetylenes.

species. However, the topochemically polymerizable DAs undergo polymerization also in dark even at temperatures below their melting points, which are often below 100°C. This is rather contradictory to the extremely large energy calculated from the photo-induced excitation energy, required for the thermal formation of DA diradicals. In fact, it was reconfirmed in our laboratory that the hexa-2,4-diynylene DAs (non-aromatic) which can undergo topochemical polymerization, do not polymerize in solution or in the molten state, even if they were heated and irradiated with UV light. Naturally, they do not give ESR signals during polymerization at normal polymerization temperatures. Therefore, the mechanism of the initiation of the thermally induced topochemical polymerization, established by the Wegner's group and currently accepted, cannot be the formation of monomeric diradicals. If such monomeric diradicals were formed, at least oligomerization of DAs should take place in solution or in molten state. Therefore, the reason why the majority of topochemically polymerizable DAs (aliphatic DAs) do not give polymers in solution or molten state, is that monomeric diradicals cannot be formed because they are not stable. However, in the crystal lattice of topochemically polymerizable DAs, each monomers are situated in the ideal position to form instantaneously dimers, trimers, and so on, and therefore, oligomeric diradicals can be formed to start the polymerization, instead of monomeric diradicals. Considering these facts, it can be assumed that the following speculation can be made: When two or three aromatic DA molecules are happened to be situated close together it may directly form dimeric or trimeric diradicals without forming the monomeric diradicals: Therefore, the observed ESR signals can be attributed to oligomers (dimers, trimers, etc.). To confirm this hypothesis theoretical calculations were carried out for DPB. The minimal energy structures have been located for diphenyldiacetylene, dimer and trimer using systematic conformational search method implemented in Titan suit of program. Located structures were minimized using B3LYP hybrid functional in combination with standard 6-31G(d) basis set. Triplet states were supposed for dimer and trimer. Frequency jobs were run for all structures to ensure that a minimum was located and to calculate the Gibbs free energy. Scheme showed that the Gibbs free energy of to form dimeric diradical requires 25.5 kcal/mol while to form the trimeric diradical out of dimer and monomer is only needed 9.3 kcal/mol. Therefore, the calculation proves the hypothesis that ESR signals correspond to the oligomeric diradicals, which can be formed at temperatures above 100°C. The ESR signal intensity naturally increased with temperature due to increase in kinetic energy, which promotes collisions to form more diradicals.

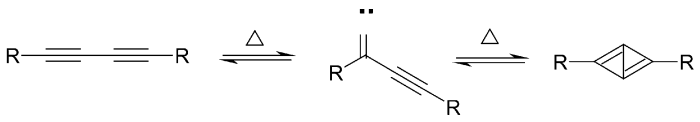


SCHEME 3 Formation of dimeric diradical by bimolecular reaction.

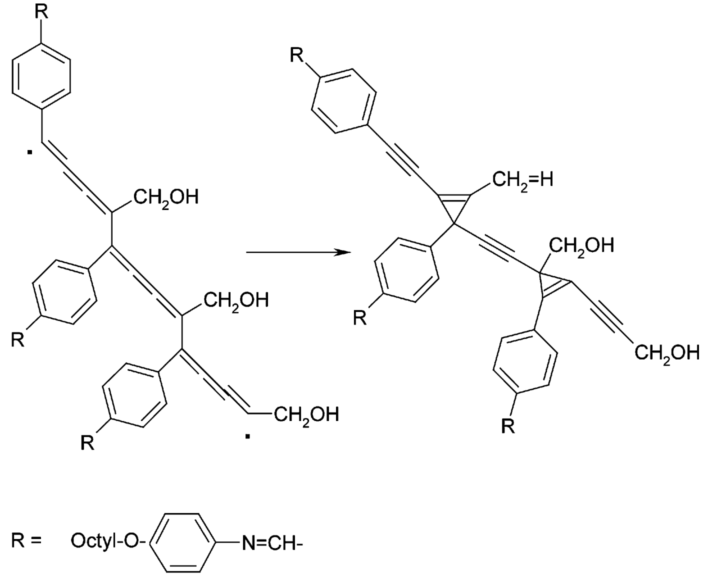
The numbers of radicals formed in the molten state are shown in Table 2. It can be seen that the radicals are formed at relatively low temperature. However, the numbers of radicals per mole of DAs are smaller by one order than those in the case of UV irradiation [6]. It can be seen from the table that more radicals are formed for the DAs with smaller substituent groups. In the case of UV irradiation, more radicals are formed for DAs with substituent groups due to expanded conjugation [6]. This is because in the case of irradiation the monomeric diradicals can be formed, while in the thermal system, dimeric and trimeric diradicals are first formed, and this is influenced by the steric effect.

There exists a possibility that a bicyclopropenyl compound is formed from diacetylenes [12], as shown in Scheme 4. However, the reaction conditions (high temperature) are very much different from that of this work, and it is unlikely that such unstable intermediates are formed at temperatures below 200°C. Sugawara and coworkers have reported that a cyclopropenyl derivative is formed when a liquid crystalline forming aromatic DA was heated at its nematic temperature (139°C) as shown in Scheme 5 [13]. Theoretical calculation showed this compound is rather stable, and it is likely to be formed. However, these cyclic compounds do not give ESR signals.

In order to study the thermal behaviors of these DAs, DSC was carried out and the data are shown in Figure 2. The endotherm peaks are due to melting and the strong exotherm peaks are due to the thermal reaction of DA groups. The temperature at which the thermal reaction



SCHEME 4 Bicyclo formation of diacetylenes [12].



SCHEME 5 Formation of biscyclopropenyl derivative [13].

starts differs among the DAs (Table 2). It is difficult to see what type of reaction takes place, but it is assumed that in addition to the diradical formation, the opening of diacetylenic triple bonds takes place to form three-dimensional polymers, giving hard reddish black intractable solids. Table 2 shows the numbers of radicals formed when heated at temperatures at 160–180°C, which are below the temperatures at which this exothermic reaction starts. As mentioned before, DPB that has no substituted group, showed more radicals than other DAs, probably because it has less steric hindrance to form the diradicals. There was no relationship between the diradical formation and the melting points. The numbers of radicals at 180°C of DPB, BNA and MPA, which give more conjugated systems, are considerably greater than those of others. It can be seen that DPB and MPA have lower onset temperatures at which this thermal reaction initiates compared to others. The other DAs initiate their thermal polymerization at above 210°C while DPB starts the thermal polymerization at 180°C. Those having radicals more than 10^{20} radicals/mole developed deep red color on heating, suggesting more expanded conjugated systems are being formed by the coupling of diradicals. The behavior of BNA showing a large number of radicals and forming highly conjugated system cannot be understood, as its analogue HBA did not show such behaviors.

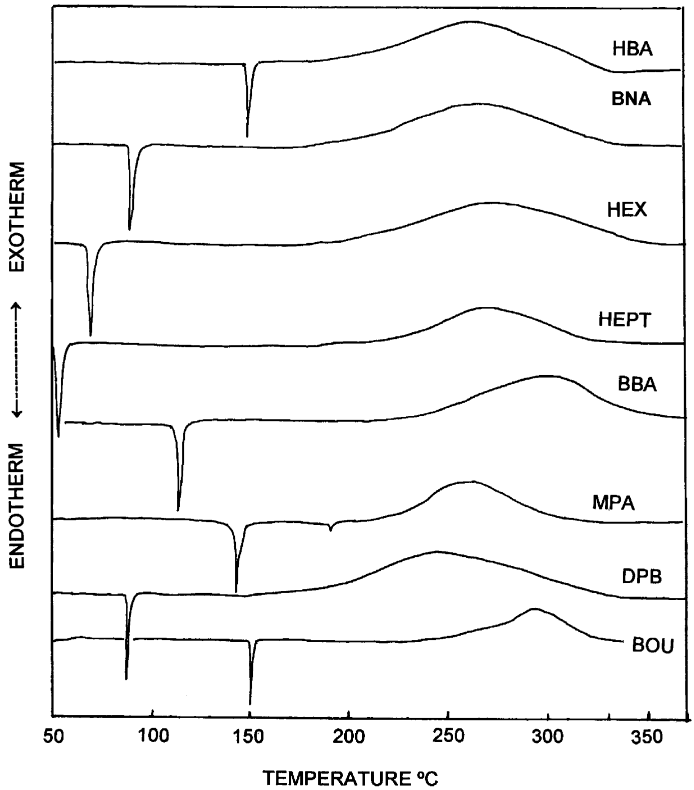


FIGURE 2 DSC Curves of aromatic diacetylenes. Under nitrogen. Heating rate: 10°C/min.

However, it seems that the smaller the substituted groups, the more radicals are formed. If the diradical formation is bi- or tri-molecular reaction where two or three DA molecules are involved, smaller substituents favor the effective collision. Figure 2 includes the thermal behavior of BOU, an aliphatic topochemically polymerizable DA, N,N′-di-n-butyl octa-3,4-diynylene diurethane (BOU). It can be seen that the temperature at which this DA opens its diacetylenic bonds is much higher than the aromatic DAs, and no ESR signal was observed.

UV/Visible absorption spectra of some of these DAs heated at 165°C in vacuum-sealed tubes, are shown in Figure 3. In all the cases the formation of conjugated systems are observed, but the products consist of mixtures of various oligomers with low molecular weights.

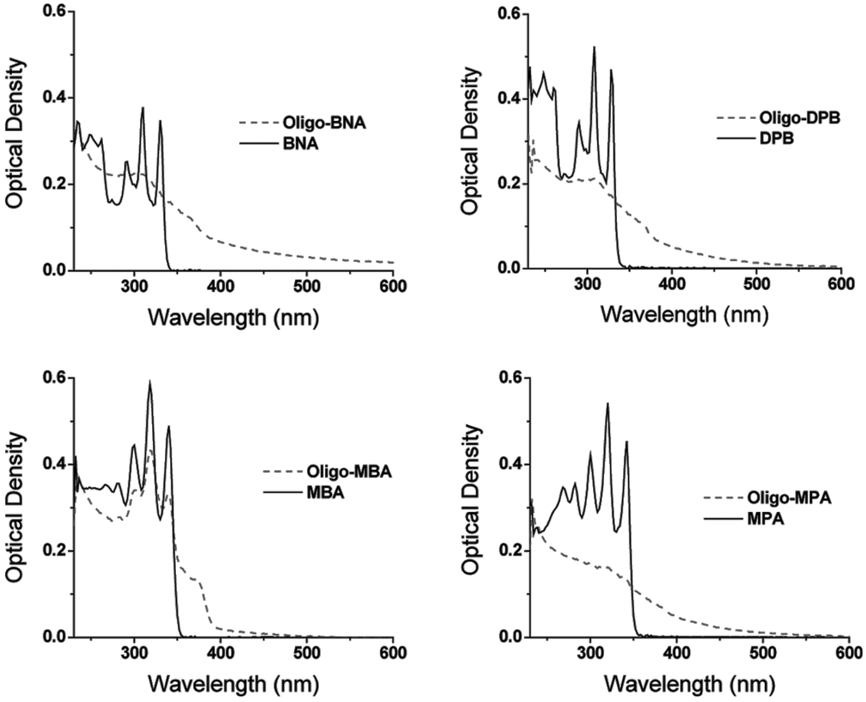


FIGURE 3 UV/Visible absorption spectra of some aromatic DAs treated at 165°C for 109 hours. In THF. Concentration: 1×10^{-5} mole of DA per liter.

IV. CONCLUSION

The formation of very unique semi-stable diradicals of aromatic diacetylenes was described. These new class of radicals are stable in inert atmosphere even at elevated temperature. It seems that the only quenching in inert atmosphere is due to the combination of diradicals to form oligomeric species, but it seems difficult to obtain high polymers by the coupling of these diradicals probably due to steric effect and probable side products. The formation of diradicals is a second order reaction that takes place only when DAs collide in such a manner to form dimeric diradicals, which are more stable than the monomeric diradicals.

Some physical and chemical properties of these products are being investigated, and will be reported in future.

REFERENCES

[1] Sixl, H. (1984). Polydiacetylenes. In: *Adv. In Polym. Sci.*, Cantow, H.-J. (Ed.), Springer-Verlag: Berlin, 63.

[2] Sixl, H. (1985). Photopolymerization reaction intermediates in diacetylene crystals. In: *Polydiacetylenes*, Bloor, D. & Chance, R. R. (Eds.), NATO ASI Series, Martinus Nijhoff Pub.: Dordrecht, 41.

[3] Wiley, R. H. & Lee, J. Y. (1971). Thermal polymerization of diphenyldiacetylene. *J. Macromol. Sci.*, *A5*(3), 513.

[4] Paley, M. S., Frazier, D. O., Abdeldeyem, H., Armstrong, S., & McManus, S. P. (1995). Photodeposition of amorphous polydiacetylene films from monomer solutions onto transparent substrates. *J. Am. Chem. Soc.*, *117*, 4775.

[5] Canizal, G., Burillo, G., Boldu, J. L., Muñoz, E., & Ogawa, T. (1997). Radicals of diphenylbutadiynes and their interactions with diphenylpicrylhydrazyl. A suggestion for the nontopochemical polymerization mechanism of diacetylene. *Polym. J.*, *29*, 230.

[6] Beristain, M. F., Fomine, S., Salcedo, R., Muñoz, E. & Ogawa, T. (2005). UV-irradiated formation of diradicals of diphenylbutadiyne and some of its *p,p′*-disubstituted derivatives. *Bull. Chem. Soc. Japan, 78*, 1986–1993.

[7] Murata, S. & Iwamura, H. (1991). Magnetic interaction between the triplet centers in ethynylenebis(phenylnitrenes) and 1,3-butadiyne-1,4-diylbis(phenylnitrenes). *J. Am. Chem. Soc.*, *113*, 5547.

[8] Iwase, Y., Kondo, K., Kamada, K., & Ohta, K. (2002). 1,4-Addition polymerization of 1,4-bis(4-benzylpyridinium)butadiyne triflate in a dipolar aprotic solvent. *J. Polym. Sci. Part A: Polymer Chemistry*, *40*, 3534.

[9] Carreón, M. P., Fomina, L., Fomine, S., Rao, D. V. G. L. N., Aranda, F. J., & Ogawa, T. (1995). Third-order nonlinear susceptibility of polydiacetylene-containing polymeric systems. Chapt. 14. In: *Photonic and Optoelectronic Polymers*, Jenekhe, S. A. & Winne, K. J. (Eds.), ACS Symp. Ser., ACS: Washington, DC, 672.

[10] Sonogashira, K., Tohda, Y., & Hagihara, N. (1975). A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes, and bromopyridines. *Tetrahedron Lett.*, *50*, 4467.

[11] Chang, T. & Vahn, A. H. (1978). *Electron Paramagnetic Resonance Intensity Standard: SRM-2601; Description and Use*, National Bureau of Standards Special Publication, National Bureau of Standards: Washington, DC, Pub. No. 260–59.

[12] Mabry, J. & Johnson, R. P. (2002). Beyond the roger brown rearrangement: Long-range atom topomerization in conjugated polyynes. *J. Am. Chem. Soc.*, *124*, 6497.

[13] Izumioka, A., Okuno, T., Sato, N., & Sugawara, T. (1989). Abstract. 39th Symposium on Organic Reaction Chemistry (Yuki Hanno Kagaku Toronkai, Japan) page 243.