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THEORETICAL INVESTIGATION ON THE TOPOCHEMICAL POLYMERIZATION OF DIACETYLENES

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Key Words: Topochemical polymerization; Woodward–Hoffmann's rules; Solid-state reactions; Diacetylenes; Polydiacetylenes

ABSTRACT

The solid-state polymerization of diacetylenes (MDA-PBT-PDA) is studied with a concerted reaction model and the calculation method of EHMO-ASED and EHCO-ASED, where MDA = crystalline molecular diacetylenes, PBT = polybutatrienes, and PDA = polydiacetylenes. As the reaction goes on, the symmetry of frontier orbitals inverts at state PBT, HOCO from C_2-antisymmetry to C_2-symmetry and LUCO from C_2-symmetry to C_2-antisymmetry, which means completion of the 1,4-addition. Two necessary conditions must be satisfied for the reaction to take place: 1) the geometric parameters must undergo a series of concerted changes to make the conformation suitable for the intermolecular 1,4-addition, which should overcome an energy barrier E_b; 2) the symmetry match between the frontier crystal orbitals of the reactant and the product must be satisfied—electrons of the reactant should be excited from HOCO (C_2-antisymmetry) into LUCO (C_2-symmetry), which faces an energy gap E_g. At state MDA, there is $E_g(\mathrm{MDA}) \approx 5.6$ eV. If MDA and PDA are analyzed according to Woodward–Hoffmann's rules, this reaction would be considered photochemically allowed but thermochemically forbidden. It has been shown that the E_g gradually decreases along the reaction coordinate from state MDA to PBT. At state PBT there is $E_g(\mathrm{PBT}) \leq 0.1$ eV, and the electrons of the reactant can be easily excited

there. Since $E_b \approx 1.0$ eV is not very large and $E_g(\mathrm{PBT}) \leq 0.1$ eV is very small, the two necessary conditions mentioned above can be satisfied thermally. Therefore, thermal polymerization can take place smoothly. By this pathway the apparent activation energy of the reaction will be $E_a \approx 1.0$ eV, which is consistent with the activation energies of the polymerizations of diacetylenes in the literature.

INTRODUCTION

The main difference between reactions in the solid state and those in the gaseous or liquid state is that the molecules of reactants and products cannot move and orientate freely. For organic reactions in the solid state, the larger size of molecules and their motions are restricted further. The solid-state polymerization of crystalline molecular diacetylenes $(\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R})_n$ (MDA) by intermolecular 1,4-addition to form polybutatrienes $({}^{\mathrm{R}}{\rangle}\mathrm{C{=}C{=}C{=}C}{\langle}_{\mathrm{R}})_n$ (PBT) and then polydiacetylenes $({}^{\mathrm{R}}{\rangle}\mathrm{C{-}C{\equiv}C{-}C}{\langle}_{\mathrm{R}})_n$ (PDA) is a typical example of lattice-controlled reaction. In this reaction the lattice is conserved and a nearly perfect single crystal with a fully conjugated planar backbone is produced [1]. A variety of polydiacetylenes with useful properties have been obtained by changing the substituent R. Today the study of polydiacetylenes is very active in polymer science, physical chemistry, material science, biomimetic chemistry, and many other fields [2, 3]. Additional research on the polymerization reaction itself is fundamentally important for theory and practical applications.

The polymerization reaction of diacetylenes can be initiated photochemically (by UV, x-ray, γ-ray) or thermally. Many papers have been published on photochemical polymerizations which are known to be chain reactions, and a large amount of research has been carried out on the intermediate states [4]. As for thermal polymerization, which has a considerable period of induction and autoacceleration [5], research is far from complete. A chain mechanism analogous to photochemical polymerizations has been reported for thermal polymerizations [6]. A theoretical problem was raised in the late 1970s, for which a satisfactory answer has not been obtained. From the Woodward-Hoffmann Conservation Principle of Orbital Symmetry, these reactions seem to be photochemically allowed by thermally forbidden [7, 8]. Yet in many diacetylene-polydiacetylene systems, thermal polymerization takes place smoothly and conversion can reach 100%. This paper attempts to shed some light on the problem mentioned above.

CALCULATION MODEL

In order for the polymerization of crystalline monomer (MDA) to proceed, the first and fourth carbon atoms of the adjacent diacetylenes must be located at a suitable distance from each other; this geometric restraint exists in order for the addition reaction to take place both photochemically and thermally (see Fig. 1). The reactions require each monomer molecule involved to rotate simultaneously accompanied by the following parametric changes: 1) the magnitude of the translation vector of the lattice (d); 2) the angle between the translation vector and the

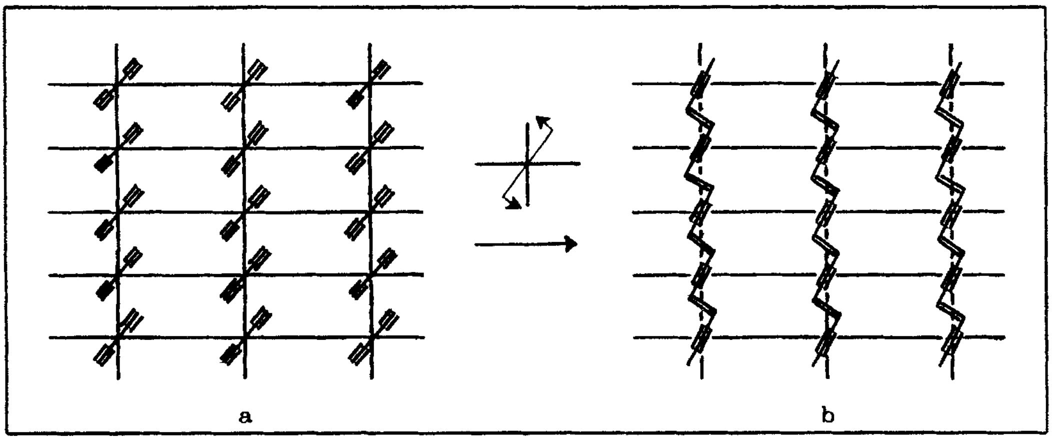

FIG. 1. Scheme of the concerted reaction from (a) MDA to (b) PDA [9].

conjugated rod of the repeat units (θ); and 3) the bond lengths and angles in the repeat units (see Figs. 1 and 2). In order to focus attention on the topochemical characteristics of the fully conjugated backbone of the polymer, only the substituent H is considered. Since θ and d of PBT are located between those of MDA and PDA (see Fig. 2), a pathway of MDA–PBT–PDA is also adopted. The reaction coordinates of MDA and PDA are 0 and 1, respectively. In this paper the structural parameters shown in Fig. 2 are obtained from referring to *ab initio* optimization [10].

In the MDA crystal, the diacetylene molecules form well-aligned molecular columns along the packing direction. Because of the large intercolumn distance, the molecular interaction between adjacent columns can be neglected in the calculation. The system can be treated as a quasi-one-dimensional system as can the crystals of PBT and PDA [11].

CALCULATION METHOD

Calculation for the periodic structural systems is based on the EHCO (Extended Hückel Crystal Orbital, i.e., tight binding EHMO) method. Anderson et al. recently made some modifications on the Extended Hückel method by adding the contribution of interatomic repulsion to the total energy of the system [12, 13]. At present, the modified EHCO is one of the most useful methods in the calculation of organic periodic structural systems. For the sake of the study of the potential energy curve of the reaction, in the present paper the contribution of the interatomic repulsion is included in the EHCO method utilizing modifications of Anderson. In this way the EHCO is extended to the EHCO-ASED (Atom-Superposition and Electron-Delocalization) program. Accordingly, the repulsive energy E_R between atom A and B in the system is

$$E_R = Z_b\left[\frac{Z_a}{|\mathbf{R}_b - \mathbf{R}_a|} - \int \frac{\rho_a(\mathbf{r})}{|\mathbf{R}_b - \mathbf{r}|}\,d\mathbf{r}\right] \tag{1}$$

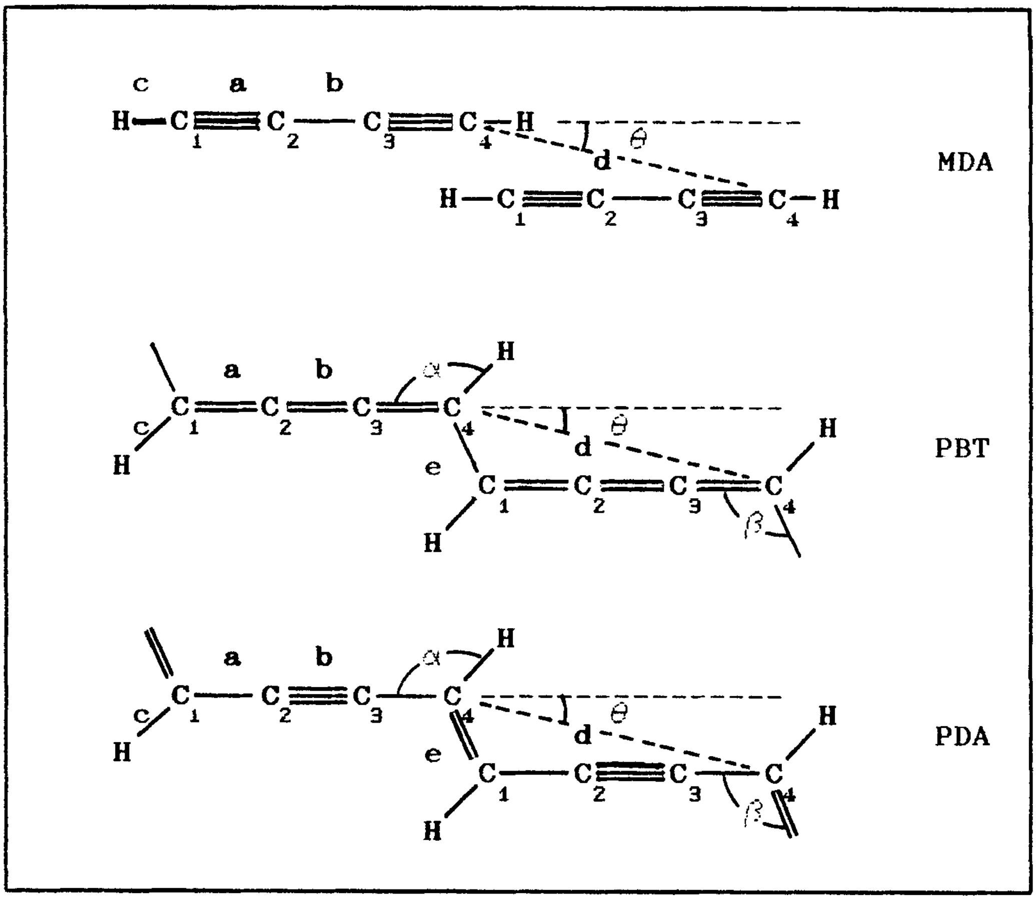

FIG. 2. Geometric parameters of the polydiacetylene system (a–e in Å; α, β, and θ in degrees. MDA: $a = 1.191$, $b = 1.377$, $c = 1.056$, $d = 4.362$, $\theta = 55.75$. PBT: $a = 1.328$, $b = 1.244$, $c = 1.073$, $d = 4.838$, $e = 1.433$, $\alpha = 118.70$, $\beta = 123.40$, $\theta = 14.32$. PDA: $a = 1.411$, $b = 1.204$, $c = 1.094$, $d = 4.920$, $e = 1.359$, $\alpha = 116.72$, $\beta = 124.12$, $\theta = 13.22$.

where Z_a, Z_b and $\mathbf{R}_a$, $\mathbf{R}_b$ are the nuclear charges and position vectors of atoms A and B, respectively. $\rho_a(\mathbf{r})$ is the charge density of atom A at $\mathbf{r}$. Integration is done over all space. Here the electronegativity of atom A is greater or equal to that of B. The off-diagonal element H_{ij}^{ab} of the Hückel matrix is of the form

$$H_{ij}^{ab} = \frac{K}{2}\left(H_{ii}^{aa} + H_{jj}^{bb}\right) S_{ij}^{ab} \exp\left(\delta R_{ab}\right) \tag{2}$$

where i and j denote the number of atomic orbitals, S is the overlap integral, and R_{ab} is the distance between atoms A and B. $K = 2.25$ and $\delta = -0.13$. The diagonal element $H_{\mathrm{ii}}^{\mathrm{aa}}$ of the Hückel matrix is still set to be the negative of Valence State Ionization Potentials (VSIP) of the respective atomic orbitals. The VSIP and the Slater orbital exponents are taken from Ref. [14].

In order to observe the energy variation of the polydiacetylene system with the increase of repeat units (n) in the polymer chains, the EHMO-ASED method (developed from EHMO) is employed. The plotting of total energy E per repeat unit vs $1/n$ is extrapolated to $1/n \rightarrow 0$ ($n \rightarrow \infty$). When $n \geq 3$, a very good straight line appears with the correlation coefficients greater than 0.999 (see Fig. 3). The stars in Fig. 3 represent the corresponding energies obtained from the EHCO-ASED. These results indicate that the two methods mentioned above are equivalent.

RESULTS AND DISCUSSIONS

The Variation of Total Energy and Repulsive Energy

The variation of the total energy E and the repulsive energy E_R (per unit) with the number of unit n is shown in Table 1 and Fig. 3. As mentioned above, when $1/n \rightarrow 0$, the results from EHMO-ASED and those from EHCO-ASED are equivalent. For MDA, both E and E_R stay constant in spite of the change in n, indicating that the interaction between units is very limited in the monomer. The slope for PDA (see Fig. 3) is greater than that for PBT, which is consistent with the fact that as the unit number increases from n to $n + 1$, one more double bond appears for PDA, and only one more single bond is formed for PBT. From Table 1 it can be seen that with the increase of n, the increase in repulsive energy (E_R) for PDA is greater than that for PBT. This is probably due to the smaller distance between

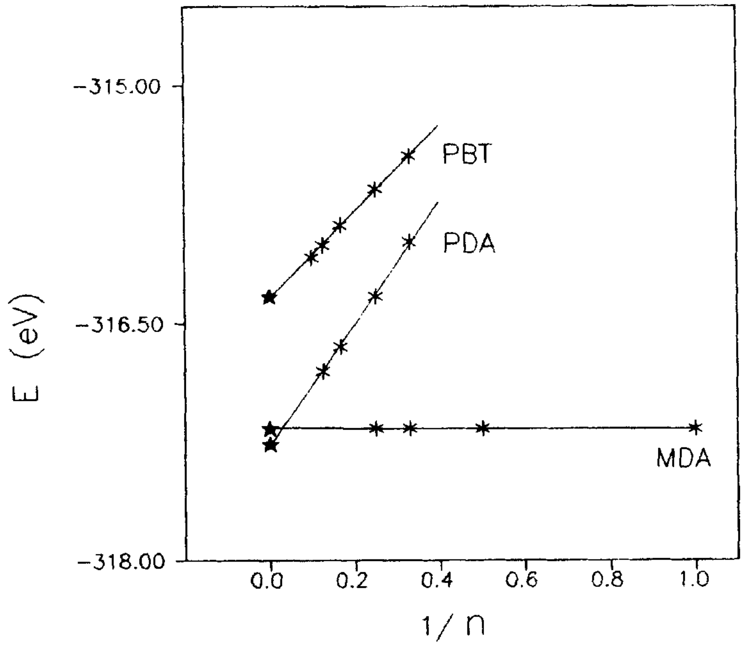

FIG. 3. Total energy E vs $1/n$ by EHMO-ASED. The stars indicate values from EHCO-ASED.

TABLE 1. The Variation of E and E_R with n (E and E_R in eV)

	MDA		PBT		PDA	
n	E	E_R	E	E_R	E	E_R
1	−317.169	21.302	−315.201	16.924	−314.520	14.748
2	−317.167	21.302	−315.128	17.886	−315.274	16.338
3	−317.167	21.302	−315.444	18.206	−315.984	16.868
4	−317.167	21.302	−315.654	18.366	−316.326	17.133
6			−315.882	18.527	−316.647	17.398
8			−316.006	18.607	−316.803	17.530
10			−316.083	18.656	−316.896	17.609
∞	−317.166	21.302	−316.330	18.847	−317.268	17.928

adjacent units of PDA (double bond) which leads to greater repulsion among atoms of adjacent units relative to that of PBT (single bond). However, it can also be seen that the magnitude of repulsive energy of the intra-PBT is greater than that of the intra-PDA for the same n which may be related to the larger size of the repeat unit for PDA. The results mentioned above are consistent with the fact that PDA is more stable than PBT.

Potential Energy Curve of the Reaction

The potential energy curve of the polydiacetylene system is shown in Fig. 4 where E and R.C. stand for the total energy per unit and reaction coordinate, respectively. State 1 represents the crystalline molecular monomer state of MDA for which the structural parameters of the solitary monomer are adopted. Going forward along the reaction coordinate, the gradually decreasing energy at states 2, 3 and 4 implies a certain relaxation of interaction among the molecules of MDA in the solid state. Beyond state 5, the energy increases and reaches its maximum at state 7 and then reaches an energy plateau at states 9 to 11 (PBT); the energy finally decreases to state 17 (PDA). Corresponding to state 11, the hybrids of the first and fourth carbon atoms are thoroughly changed from the original sp to sp^2, and meanwhile the symmetries of frontier orbitals are inverted. This means that the system undergoes 1,4-addition, which will be discussed further in the next section. The corresponding energy barrier $E_b(E_7 - E_1) = 1.02$ eV (97.9 kJ/mol).

The Symmetry of Frontier Orbitals

When the C_2(I) axis, in the middle of the $C_2—C_3$ bond and perpendicular to the conjugated chain, is taken as the symmetry element, it can be seen that for state 1 (MDA) to 10 (R.C. = 0.68) the highest occupied crystal orbitals (HOCOs) are antisymmetric (A), and the lowest unoccupied crystal orbitals (LUCOs) are symmetric (S) (see Table 2, Figs. 5 and 6). On the contrary, for states 11 to 17 (PDA), the symmetry of HOCOs and LUCOs are S and A, respectively. In other words, the symmetry for states 1-10 and 11-17 are of the MDA and PDA types. There is a symmetric/antisymmetric inversion of the frontier orbitals at state 11.

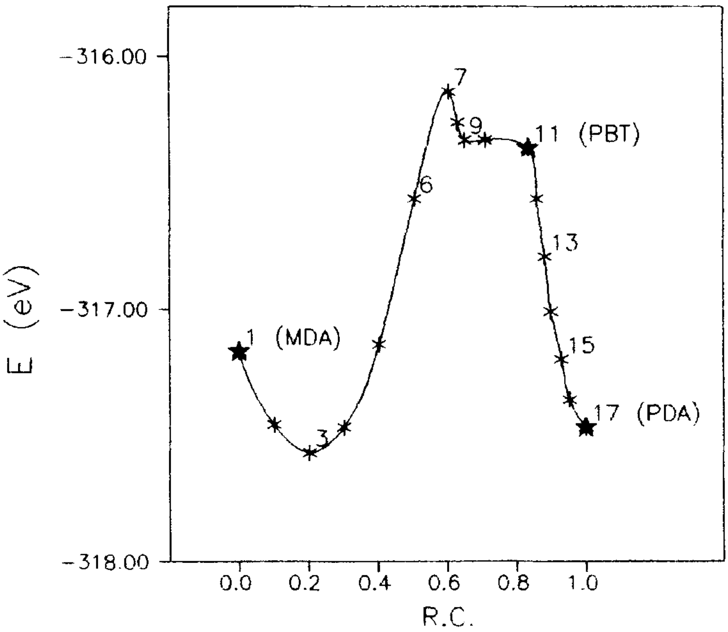

FIG. 4. The potential curve. R.C. is the reaction coordinate.

In order to understand such a transformation, a closer look at the components of the HOCOs in MDA and PDA is required. For PDA the p_z orbital of C_4 in unit (2) and that of C_1 in unit (3) have the same phase (as shown in Fig. 6), i.e., S with respect to the $C_2(II)$ axis which is in the middle of $C_4—C_1$ bond and perpendicular to the planar conjugated backbone. Such symmetry (S) is necessary for the creation of a p—π bond by a 1,4-addition reaction between adjacent monomers. Furthermore, owing to the characteristic of translational symmetry, the p_z orbitals of atom C_1s in different units are in the same phase and so are those of C_4s. Therefore, for each unit the contributions from the p_z orbitals of atom C_1 and C_4 to the HOCO are symmetric with respect to $C_2(I)$ as are the contributions from the other carbon atoms. Thus the symmetry within one unit [with respect to $C_2(I)$] essentially represents that between adjacent units [with respect to $C_2(II)$] (see Fig. 6). Similarly, it can be seen that in MDA the p_z orbitals of atoms C_1 and C_4, appearing in the HOCO, are of opposite phases, so that the two p_z orbitals are antisymmetric with respect to both $C_2(I)$ and $C_2(II)$. On the other hand, it can be seen that the p_z orbitals of atoms C_1 and C_4 appearing in LUCO for PDA and MDA are, respectively, antisymmetric and symmetric with respect to both $C_2(I)$ and $C_2(II)$.

Let us return to Figs. 4 and 5. As mentioned above, the symmetry of HOCO and LUCO for states 1 to 10 is of the MDA type and that for states 11 to 17 is of the PDA type (Fig. 5). In other words, at state 11 there is an inversion of the symmetry for HOCO and LUCO. From states 11 to 17 only bond lengths and angles are changed continuously, but the hybrid and the symmetry of frontier orbitals remain unchanged. This inversion should imply the completion of intermolecular 1,4-addition and the formation of the conjugated backbone. Correspondingly, the

TABLE 2. The Frontier Crystal Orbitals of the Polydiacetylene System

		CO							
		STATE 1 (MDA)		STATE 10		STATE 11 (PBT)		STATE 17 (PDA)	
AO		HOCO	LUCO	HOCO	LUCO	HOCO	LUCO	HOCO	LUCO
C_1	s	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_y	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_z	−0.5260	0.6683	−0.5596	0.5574	0.5519	0.5667	−0.5385	−0.5841
C_2	s	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_y	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_z	−0.3685	−0.4806	−0.4563	−0.4793	−0.4727	0.4594	0.4580	−0.4687
C_3	s	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_y	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_z	0.3685	−0.4806	0.4563	−0.4793	−0.4727	−0.4594	0.4580	0.4687
C_4	s	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_y	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	p_z	0.5260	0.6683	0.5596	0.5574	0.5519	−0.5667	−0.5385	0.5841
H_5	s	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_6	s	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

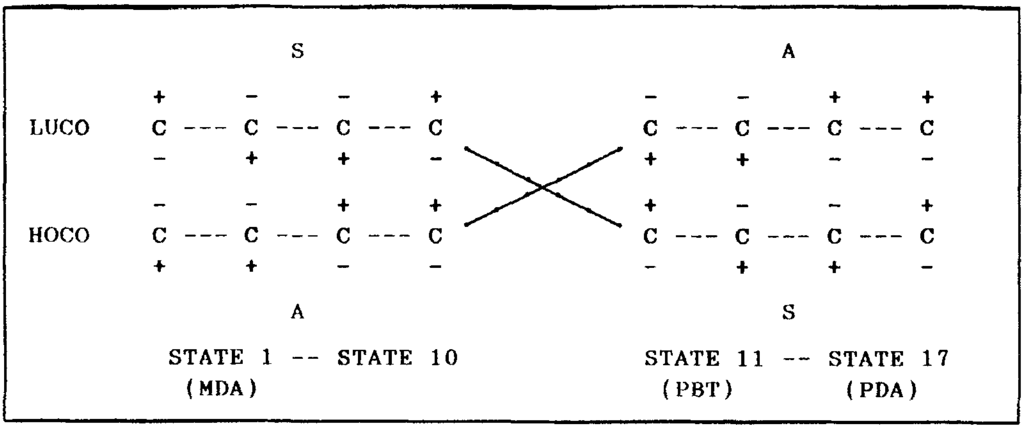

FIG. 5. The symmetry of the frontier crystal orbitals.

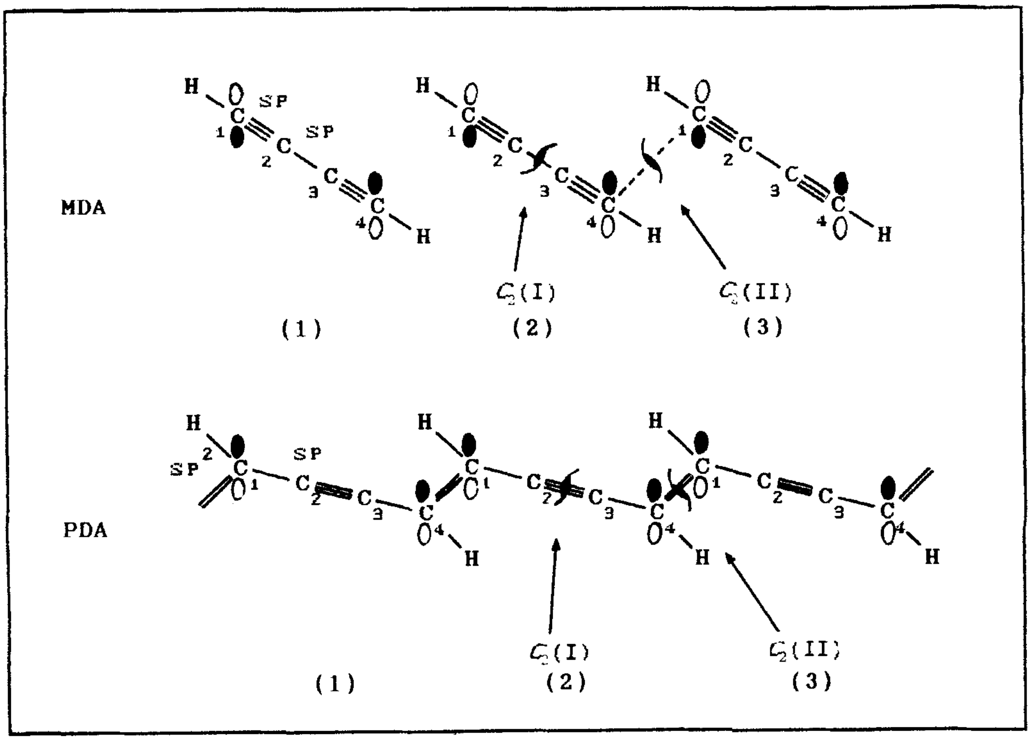

FIG. 6. Analysis of the symmetry of HOCOs for MDA and PDA.

hybrids of C_1 and C_4 are thoroughly changed from original sp to sp^2 (Fig. 6). Based on the reasons given above, it is reasonable to suggest that PBT corresponds to state 11 (geometric parameters in Fig. 2).

About Thermopolymerization and Photopolymerization

As mentioned above, the symmetry of frontier orbitals of MDA is opposite to that of PDA. Such polymerization would be considered as photochemically allowed but thermally forbidden according to the Woodward–Hoffmann Conservation Principle of Orbital Symmetry [7, 8], but the fact is that the thermopolymerization for many diacetylenes can also take place smoothly. This problem can be analyzed as follows.

According to the W-H principle [15], in an elementary chemical reaction, if the molecules of the reactant and the product are of the same symmetry with respect to a properly selected common symmetry element, and if the reaction is thermally allowed, then the HOMOs of the reactant and the product should have the same symmetry, i.e., are symmetry-matched, and so should the LUMOs. Under this condition, the activation energy of a reaction will generally not be particularly large, and the reaction can take place by proper heating. On the contrary, if the HOMOs for the reactant and the product molecules are of the opposite symmetry and so are the LUMOs, then the electrons of the reactant in the HOMO need to be excited into the LUMO to make frontier orbitals symmetry match for the reaction to be able to take place. In the case of MDA–PBT–PDA polymerization, two necessary conditions must be satisfied: 1) the geometric parameters of the reactant must undergo a series of concerted changes to make the conformation suitable for the intermolecular 1,4-addition reaction; 2) the frontier crystal orbitals of the reactant and the product must be symmetry-matched. The change of geometric parameters causes the energy of the system to increase gradually, which forms an energy barrier E_b. The symmetry match requires electrons of the reactant to be excited from HOCO into LUCO, which faces an energy gap E_g. It is interesting to show that the energy gap (E_g) decreases along the reaction coordinate (R.C.) gradually and reaches the minimum at state 11 (Fig. 7). There are $E_g(1) \approx 5.6$ eV, $E_g(7) \approx 1.0$ eV, and $E_g(11) \leq 0.1$ eV. If electrons are excited from HOCO into LUCO at state 1, they must cross $E_g(1)$, which is too large for the thermopolymerization but not too large for the photopolymerization. Therefore, the polymerization would be considered as photochemically allowed but thermochemically forbidden, which is just the conclusion from the analysis of the orbital symmetry of MDA and PDA by the rules of Woodward–Hoffmann [7, 8]. But if electrons cross E_g at state 11, the situation will be quite different. Since $E_b \approx 1.0$ eV is not very large and $E_g(11) \leq 0.1$ eV is very small, they can be obtained thermally. Therefore, these two necessary conditions of reaction can be satisfied thermally and the thermopolymerization can take place smoothly.

Until now there is no experimental observation of activation energy of the solid-state reaction from MDA to PDA (R being H) in the literature, but some researchers have pointed out that the experimental activation energy of the polymerization of diacetylenes with a variety of substituents is approximately 1.0 eV [16, 17]. By the latter pathway mentioned above, there will be $E_a \approx E_b \approx 1.0$ eV, where E_a is the apparent activation energy of the reaction. This value is in quite good agreement with the experimental activation mentioned above [16, 17].

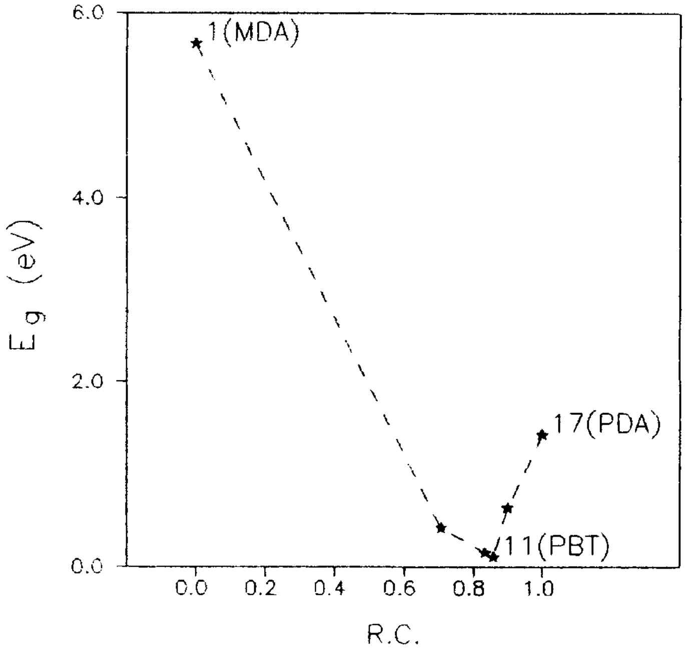

FIG. 7. Energy gaps vs reaction coordinate.

CONCLUSIONS

1. In order for the solid-state polymerization of diacetylene to take place, two necessary conditions must be satisfied: 1) the geometric parameters of the reactant must undergo a series of concerted changes to make the conformation suitable for intermolecular 1,4-addition (energy barrier E_b); 2) the symmetry match between the frontier crystal orbitals of the reactant and the product must be satisfied–electrons of the reactant must be excited from HOCO into LUCO (energy gap E_g).

2. As the reaction goes on, the symmetry of frontier crystal orbitals inverts at a certain state, which implies completion of the 1,4-addition and the formation of a conjugated backbone. It is reasonable to suggest that PBT corresponds to this state, but not the state at which the energy barrier has just been crossed.

3. $E_g(1) \approx 5.6$ eV at state 1 (MDA), so that if MDA-PBT-PDA polymerization is analyzed at this initial state (MDA) according to Woodward-Hoffmann's rules, the reaction would be considered as photochemically allowed but thermochemically forbidden. E_g decreases along the reaction coordinate, $E_g(11) \leq 0.1$ eV at state 11 (PBT), so that if electrons of the reactant are excited at state 11, the situation will be quite different. Because $E_b \approx 1.0$ eV is not very large and $E_g(11) \leq 0.1$ eV is very small, the two necessary conditions of reaction can be satisfied thermally. Therefore, the thermal polymerization can take place smoothly. Following this pathway, the apparent activation energy of reaction will be $E_a \approx 1.0$ eV, which is in agreement with the experimental activation energies for the polymerization of diacetylenes in the literature.

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