CHAPTER V
CONSTRUCTING THE Π-ELECTRON-CONJUGATED DIARYLBUTADIYNE-BASED POLYDIACETYLENE UNDER THE MOLECULAR FRAMEWORK CONTRIBUTED BY HYDROGEN-BOND AND SIDE-CHAIN SUBSTITUENT POSITION

Abstract

Diarylbutadiyne derivative is one of the ideal monomers that can provide the π-electron-conjugated system of polydiacetylenes (PDAs). The geometrical parameters for diacetylenetopochemical polymerization are known. However, how to control the molecules under those parameters is yet to be answered. The present work shows that by simply tailoring diarylbutadiyne with amide side chain substituent, the molecules are in the preferable framework under the hydrogen bond and the substituent position arrangement leading to the π-electron conjugated polydiacetylene.

5.1 Introduction

Polydiacetylenes (PDAs) are the unique linear π-electron-conjugated polymers derived from the topochemical polymerization of the corresponding diacetylene monomers by a solid-state polymerization when exposed to a UV, X-ray, γ-ray, and electron beam.[1] PDAs have attracted the great interest for their electronic and optical properties for many unique applications, especially to light emitting diodes (OLEDs)[2] and sensors.[3] In fact, PDAs are potential sensing materials because of their possible colour changes responsive to various external stimuli such as temperature,[4] pH,[4a, 5] solvent,[6] and host-guest interaction.[7]

It was reported that the preparation of PDAs by photochemical polymerization requires the imbalance of electronic density distribution and assembly of diacetylene monomers in an appropriate arrangement to favour 1,4-addition polymerization.[1a, 1b, 8] In addition, the crystal structure parameters available for topotactic polymerization are; the translational period (d) in the range of 4.7 to 5.2 Å and the tilt angle (γ) between the diacetylene rods close to 45°.[1a, 1b, 9] It should be noted that the well-known PDA are butadiynes with flexible chains which favour the abovementioned parameters,[10] whereas diarylbutadiynes are still the rare cases.

In fact, PDAs from diarylbutadiyne are the π-conjugated systems (Scheme 5.1) which are ideal for very pure and well-defined conjugated polymer with high efficient opto-electrical properties. By simply designing the butadiyne monomer with the aryl groups instead of the flexible chains at both ends, PDAs from diarylbutadiyne can be easily obtained. Based on this concept, few works were reported.[28-31] However, according to Baughman *et al.*, the diarylbutadiyne molecule is rather photostable[11], which leads to the limitation of photopolymerization. It appears, up to now, that the reports of diarylbutadiynetopochemical polymerization are the cases when the aryl groups attached directly to butadiyne.[12] For example, Diegelman *et al.* revealed the solid-state polymerization of benzylamide derivatives with oligopeptide on the butadiyne at *para*-position, leading to the nanofibrous morphology under

the hydrogen bond network.[13] Néabo*et al.* reported that diarylbutadiyne bearing the long alkylamide at *meta*-position together with the alkyl alcohol unit at *ortho*-position performs topochemical polymerization in both solid state and gel.[12c] Tashiro *et al.* succeeded to analyse the crystal structures of monomer and polymer species for fluorine-substituted diarylbutadiyne species to clarify the reservation of space group symmetry between the initial monomer and the resultant polymer crystals or topotactic reaction. The fluorine atoms that join directly to the phenyl group were considered to be the key factor for withdrawing π-electrons from the benzene-acetylene bonds, and thus the $C\equiv C$-phenyl part becomes relatively flexible to cause the easier transformation from linear sp-type structure to sp^2-type bent structure.[14] As a result, topochemical polymerization is favoured. It should be noted that the reports in the past were relied on the semi-empirical studies. The way to control the molecular arrangement to favour the topochemical polymerization was not in the scope of discussion. In other words, the possibility to control the molecules for diaryl-substituted π-conjugation PDAs from diarylbutadiyne derivatives is yet to be answered.

To our idea, the fact that diarylbutadiynes, which represents the π–conjugated PDAs, can be verified with the substituent positions at *ortho-* (o-), *meta-* (m-), and *para-* (p-) positions; and at that time if the substituents are also under hydrogen bond network, the specific molecular framework can be constructed. It is possible that the substituents provide the intermolecular hydrogen bond to bring the packing framework be satisfied with the abovementioned parameters and consequently favours the topochemical polymerization. In contrast, the rigid framework may obstruct the packing and retard the polymerization. To answer this point, the present work focuses on (i) a series of diarylbutadiynes of which the substituents are varied to o-, m-, and p-positions (oDA, mDA, and pDA, respectively), and at the same time, the substituents contain the amide group to allow the hydrogen bond framework formation and (ii) the investigation of their crystal structures and the consequent topochemical polymerization.

Scheme 5.1 (a) Photopolymerization of Diacetylene and (b) Synthesis of DA.
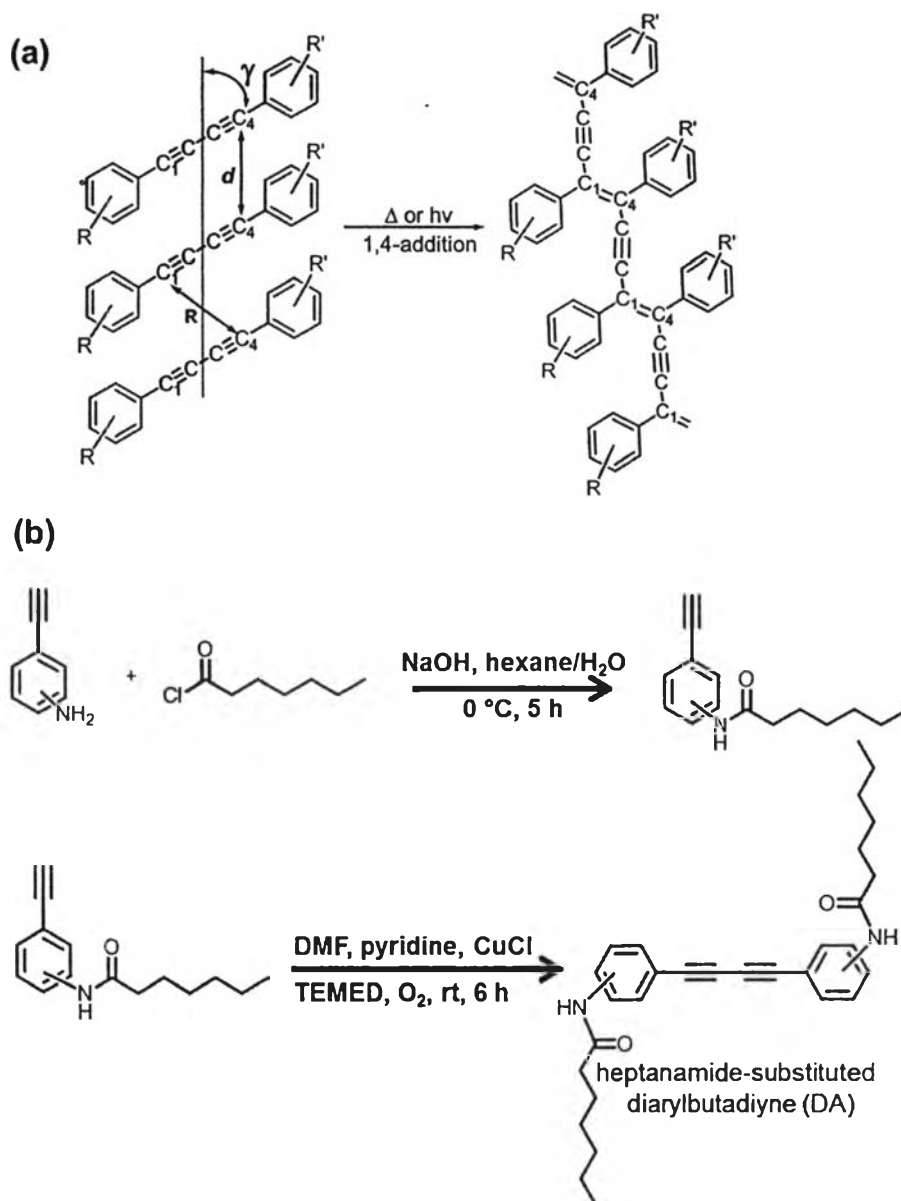
5.2 Experimental Section

5.2.1 Materials

2-Ethynylaniline, 3-ethylnylaniline, 4-ethylnylaniline, *N,N,N',N'*-Tetramethylethylenediamine (TEMED), and heptanoyl chloride were purchased from Aldrich, Germany. n-Hexane, pyridine, sodium hydroxide (NaOH) and were

obtained from Fisher, USA. Copper (I) chloride (CuCl) was purchased from Across, Belgium. Dimethylsulfoxide (DMSO) was received from Labscan, Ireland. All chemicals were used as received.

5.2.2 Preparation of *N*-(2-ethynylphenyl)heptanamide (oAc)

oAc was simply prepared by dissolving 2-ethynylaniline (117.15 mg, 1 mmol) in sodium hydroxide solution (40 mg, 1 mmol) 20 ml, a solution of heptanoylchloride (148.63 mg, 1 mmol) in hexane 20 ml was then dropwise added and stirred at 0°C for 5 hours. The oAc was collected by filtration and then recrystallization in isopropanol to get needle-like colorless crystals. ^{1}H NMR (CDCl$_3$), ppm: δ = 0.88 (*t*, CH$_3$), 1.29 (*t*, CH$_2$), 1.31 (*t*, CH$_2$), 1.63 (*t*, CH$_2$), 2.39 (*t*, O=CCH$_2$), 4.05 (*s*, C≡CH), 7.16 (*t*, HAr), 7.41 (*t*, HAr), 7.53 (*d*, HAr), 7.78 (*d*, HAr), and 10.01 (*s*, NH).

5.2.3 Preparation of *N*-(3-ethynylphenyl)heptanamide (mAc)

mAc was synthesized in the same procedure as oAc, but 3-ethynylaniline was used instead of 2-ethynylaniline. The needle-like colorless crystals were obtained. ^{1}H NMR (CDCl$_3$), ppm: δ = 0.87 (*t*, CH$_3$), 1.27 (*t*, CH$_2$), 1.67 (*t*, CH$_2$), 2.34 (*t*, CH$_2$), 3.03 (*t*, O=CCH$_2$), 3.68 (*s*, C≡CH), 7.08 (*d*, HAr), 7.55 (*d*, HAr), 7.70 (*s*, HAr), and 8.48 (*s*, NH).

5.2.4 Preparation of *N*-(4-ethynylphenyl)heptanamide (pAc)

pAc was synthesized in the same procedure as oAc, but 4-ethynylaniline was used instead of 2-ethynylaniline. The yellow powder was obtained. ^{1}H NMR (CDCl$_3$), ppm: δ = 0.87 (*t*, CH$_3$), 1.27 (*t*, CH$_2$), 1.67 (*t*, CH$_2$), 2.34 (*t*, CH$_2$), 3.03 (*t*, O=CCH$_2$), 3.68 (*s*, C≡CH), 7.66 (*d*, HAr), 7.53 (*d*, HAr), and 10.13 (*s*, NH).

5.2.5 Preparation of *N,N'*-(2,2'-(buta-1,3-diyne-1,4-diyl)bis(2,1-phenylene))diheptanamide (oDA)

oDA was prepared by dissolving oAc (229.3 mg, 1 mmol) in DMF 3 ml, adding 20 mg of copper (I) chloride, 0.1 ml of TEMED and 1 ml of pyridine, then the solution was kept stirring under room temperature and oxygen bubbling system for 6 hours. The obtained product was washed by distillated water and filtrated through silica gel. Thin needle-like colorless crystals were grown by recrystallization in isopropanol. (yield ca. 72.0%). ^{1}H NMR (CDCl$_3$), ppm: δ = 0.88 (t, CH$_3$), 1.29 (t, CH$_2$), 1.31 (t, CH$_2$), 1.63 (t, CH$_2$), 2.39 (t, O=CCH$_2$), 7.16 (t, HAr), 7.41 (t, HAr), 7.53 (d, HAr), 7.78 (d, HAr), and 10.01 (s, NH). ESI MS (m/z): 457.63 (M+H$^+$).

5.2.6 Preparation of N,N'-(3,3'-(buta-1,3-diyne-1,4-diyl)bis(3,1-phenylene))diheptanamide (mDA)

mDA was prepared in the same procedure as oDA, but mAc was used instead of oAc. The thin needle-like colorless crystals were grown by recrystallization in isopropanol. (yield ca. 80.0%). ^{1}H NMR (CDCl$_3$), ppm: δ = 0.87 (t, CH$_3$), 1.27 (t, CH$_2$), 1.67 (t, CH$_2$), 2.34 (t, CH$_2$), 3.03 (t, O=CCH$_2$), 7.08 (d, HAr), 7.55 (d, HAr), 7.70 (s, HAr), and 8.48 (s, NH). ESI MS (m/z): 457.63 (M+H$^+$).

5.2.7 Preparation of N,N'-(4,4'-(buta-1,3-diyne-1,4-diyl)bis(4,1-phenylene)) diheptanamide (pDA)

pDA was prepared in the same procedure as oDA, but pAc was used instead of oAc. The yellow powder was collected and cannot be dissolved in any solvent. (yield ca. 76.0%). ^{1}H NMR (CDCl$_3$), ppm: δ = 0.87 (t, CH$_3$), 1.27 (t, CH$_2$), 1.67 (t, CH$_2$), 2.34 (t, CH$_2$), 3.03 (t, O=CCH$_2$), 7.66 (d, HAr), 7.53 (d, HAr), and 10.13 (s, NH). ESI MS (m/z): 457.63 (M+H$^+$).

5.3 Results and Discussion

In order to clarify how the substituent position and the hydrogen bond initiate the framework for totally π-electron conjugated PDAs, it is essential to consider a series of diarylbutadiyne with the side chains at o-, m-, and p-positions and can form the hydrogen bond framework. Here, heptanamide-substituted diarylbutadiyne derivatives (DA) were prepared and their packing structures, hydrogen bond framework, and topochemical polymerization were studied.

The molecular packing structures of oDA, mDA, and pDA are confirmed by single crystal X-ray analysis (Figure 5.1). The oDA, mDA, and pDA show the intermolecular hydrogen bond with the bond length of 2.976, 2.958, and 2.963 Å, respectively.
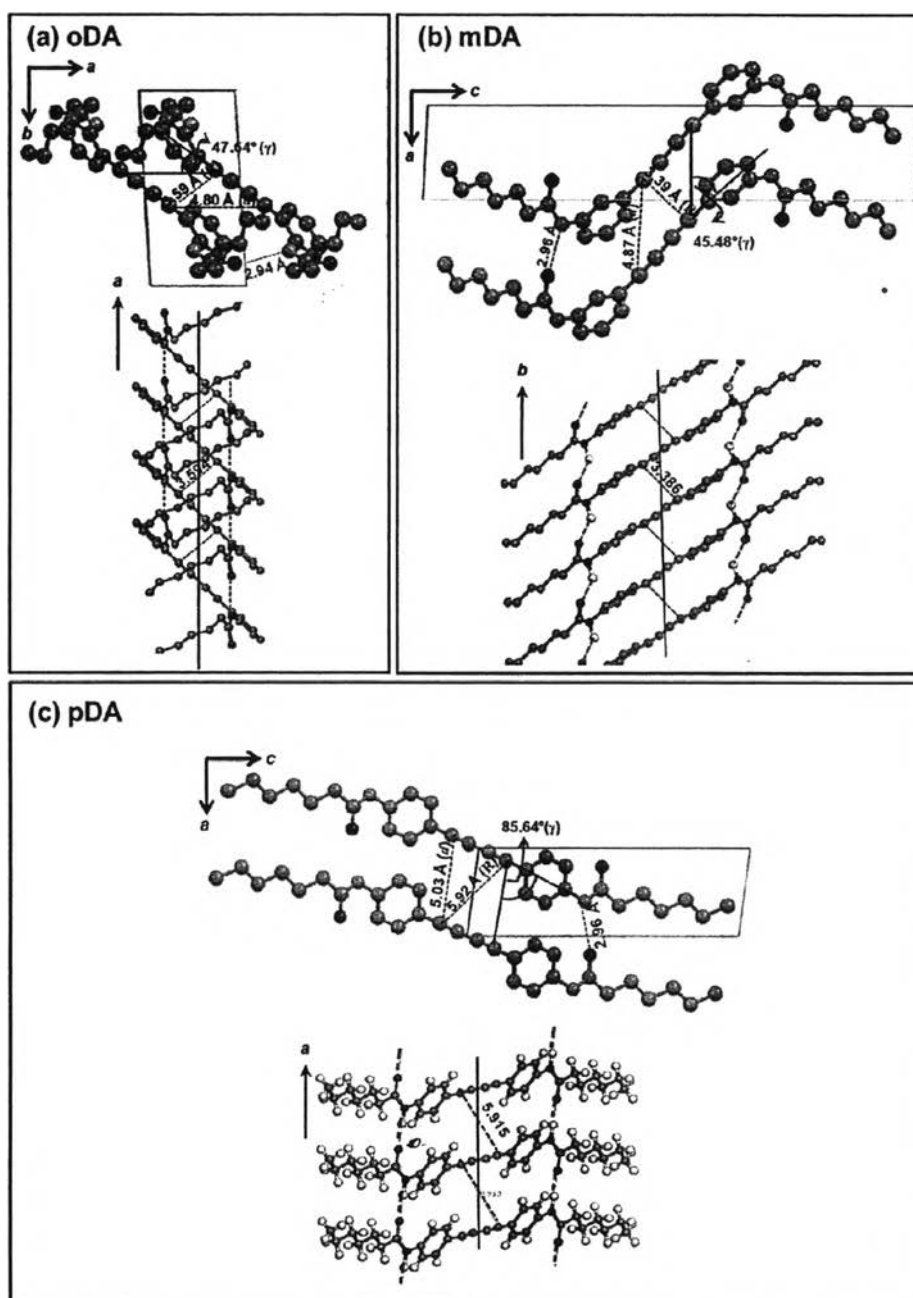
Figure 5.1 Crystal structures of (a) oDA, (b) mDA, and (c) pDA and the corresponding parameters, i.e. d, R, and γ.

The compounds give clear needle crystals and after UV irradiation at room temperature for 48 hours, the oDA, and mDA show the purple and amaranth color,

respectively. In the case of pDA, the crystals do not show any color change even the irradiation time was extended to 168 hours (Figure 5.2 (A)). This implies the topochemical polymerization for oDA and mDA.
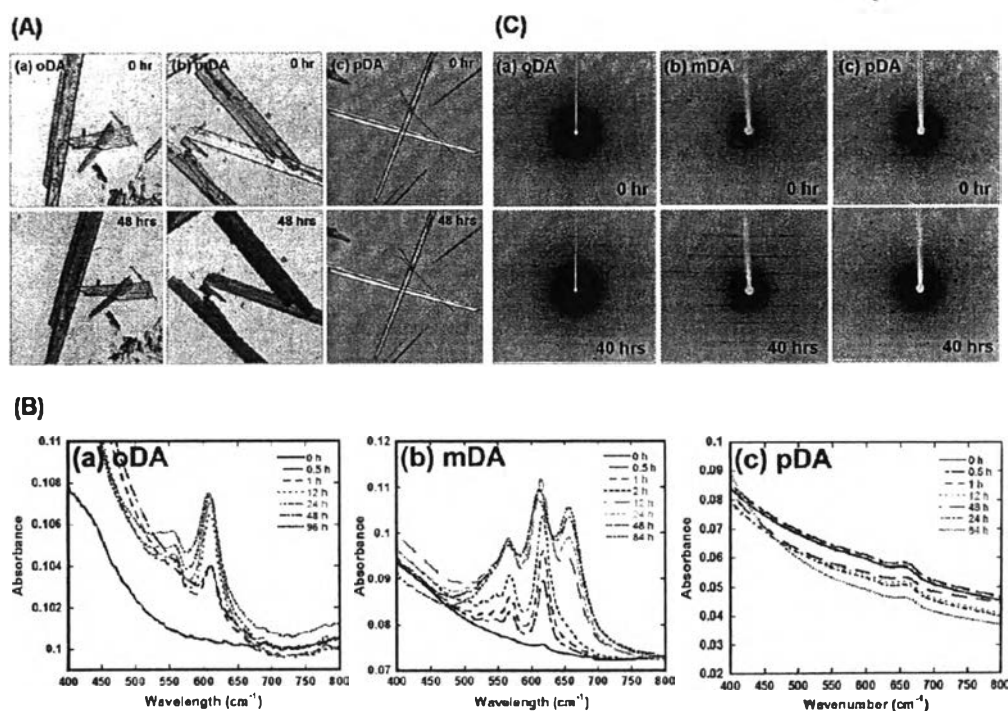

Figure 5.2 (A) Appearances of crystals of (a) oDA, (b) mDA, and (c) pDA before (0 hr) and after UV radiation (48 hrs); (B) time dependence UV spectra of (a) oDA, (b) mDA, and (c) pDA measured by a solid-state UV-vis spectrophotometer at room temperature; (C) time dependence X-ray diffraction patterns of (a) oDA, (b) mDA, and (c) pDA single crystals measured by an imaging plate system at room temperature.

The ene-yne conjugated backbone was confirmed by Raman spectroscopy technique. The oDA clearly shows the characteristic vibration band of $-C\equiv C-C\equiv C-$ at 2200 cm^{-1}. After irradiation, the peak at 2100 cm^{-1} becomes significant implying the ene-yne backbone (Figure 5.3 (a)). In fact, the peak at 2100 cm^{-1} was observed before UV irradiation and this suggested that a certain topochemical polymerization of oDA was already occurred. The fact that mDA did not show any 2200 cm^{-1} but

only 2100 cm^{-1} (Figure 5.3 (b)) , this implies the polymerization was proceeded during the sample preparation. For pDA, there is no change in Raman spectrum at all (Figure 5.3 (c)).
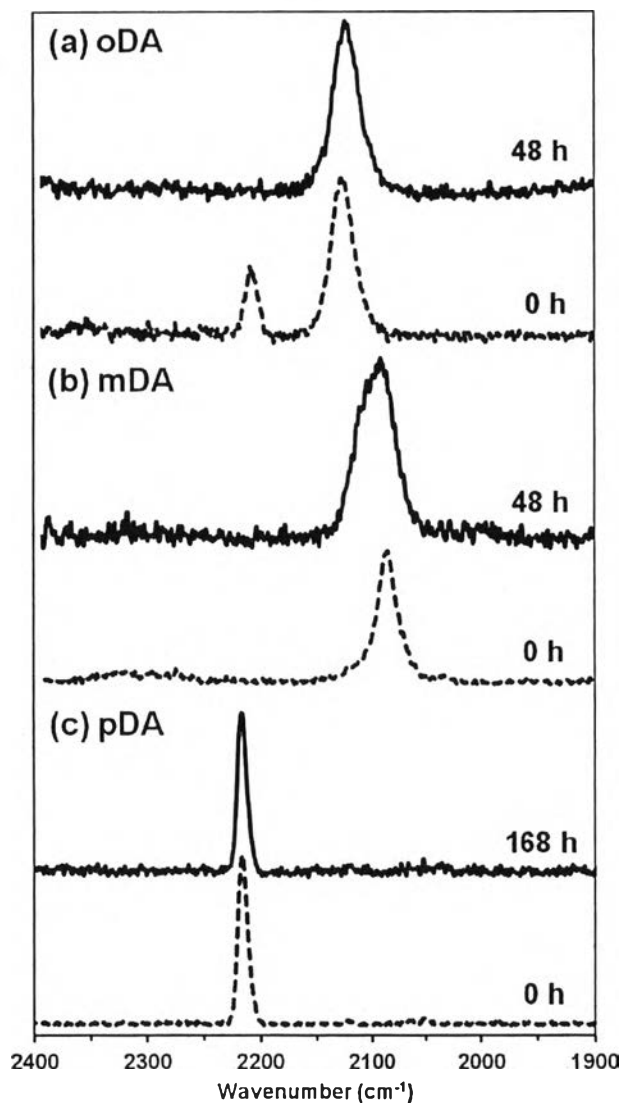

Figure 5.3 Raman spectra of (a) oDA,(b) mDA, and (c) pDA before (0 h) and after UV irradiation.

The topochemical polymerization of all samples in thin film forms was also followed by using a UV-Vis spectrophotometer. For oDA, the new peak at 615 nm

can be observed after radiation for 30 min, and it gradually increases with the UV irradiation time for 24 hours (Figure 2B (a)). For mDA, the three new peaks at 570, 620, and 670 nm are also observed as the irradiation time increased (Figure 2B (b)). However, for pDA, no change of UV spectra was observed (Figure 2B (c)). The UV spectra suggest the solid-state polymerization for only the cases of oDA and mDA.

It comes to the question why the polymerization of pDA is not observed despite the hydrogen bond direct the molecules to align and the steric effect is less than those of o-, and mDA. Based on the information obtained from single crystal X-ray analysis (Figure 5.1 and Table S1), it is clear that the framework is more or less different from those of oDA and mDA. It is known that for diacetylene formation via solid-state polymerization, the framework of the monomer needs to be satisfied with the three geometrical parameters (Scheme 5.1(a)), i.e. the translational period (d) between the monomers in the array, the tilt angle (γ) between the diacetylene rod and the stacking axis, and the distance between C1 and C4 of the adjacent molecule (R).[1a, 1b] Here, the oDA and mDA show the parameters, i.e. d for 4.800 Å, 4.821 Å, γ for 47.64°, 46.80°, and R for 3.59 Å, and 3.48 Å, respectively, which are relevant to the requirement (Figure 5.1 (a), (b)). In the case of pDA, although the d (5.302 Å) and R (5.92 Å) are in the suitable range, the γ (85.64°) is too high (Figure 5.1 (c)).

The topochemical polymerization of oDA and mDA were carried out and during the time the diffraction patterns were recorded at a constant interval time by using an imaging plate system. In this way, how the framework favours the solid state polymerization can be confirmed. As shown in Figure 5.2C, the oDA and mDA crystals show their sharp reflection patterns, even when the measurement was taken at 40 hours. The amorphous halo is not observed in these X-ray diffraction patterns, indicating that the single crystal morphology was maintained even after polymerization. As the exposure time was increased, some streak lines are detected on the X-ray diffraction images, especially in the cases of oDA and mDA. The resultant polymer crystals consist of the disordered packing of polymer chains with respect to their relative height along the chain axis. Taking the differences in colours, i.e. purple for oDA,and amaranth for mDA, to our account (Figure 5.2A), the development of streak lines suggest the more favourable topochemical

polymerization condition of mDA. In the case of pDA, there is no change in X-ray diffraction pattern even after 40 hours X-ray irradiation.

The single crystal analysis is a good tool to let us visualize the PDAs developed under the framework. However, the preparation of polymer single crystals was not successful. Therefore, the simulation of polymerization under time-dependence X-ray crystal structure analysis using Cerius^2 software (Accelrys, USA) was carried out and the structures obtained were superimposed with these of the monomer structures (Figure 5.4 and Table 5.1).

The geometry of the adjacent monomer molecules was carefully examined to find that the hydrogen bonds are along the axis to favour the polymerization. Although the hydrogen bond was also satisfied with the case of pDA, it was confirmed that the p-substitution control the packing structure to result in the unfavourable tilt angle (γ) for the polymerization. In other words, the position of the substituent chains and the hydrogen bonds network synergistically construct the framework for the topochemical polymerization.
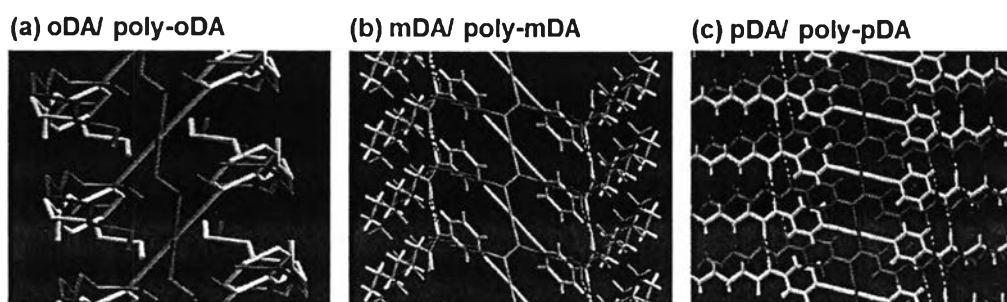
(a) oDA/ poly-oDA   **(b) mDA/ poly-mDA**   **(c) pDA/ poly-pDA**

Figure 5.4 Monomer crystals overlaid with polymer crystals simulated by Cerius^2 of; (a) oDA(white and yellow)/ poly-oDA (red), (b) mDA (white)/ poly-mDA (red), and (c) pDA (white)/ poly-pDA (red).

Table 5.1 Crystallographic data and structure refinement parameters of

diarylbutadiynes

Compound	oDA	mDA	pDA
Empirical Formula	$C_{30}H_{36}N_2O_2$	$C_{30}H_{36}N_2O_2$	$C_{30}H_{36}N_2O_2$
Formula weight	456.63	456.63	456.63
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimension			
a (Å)	4.8469(4)	4.865(8)	5.0320(12)
b (Å)	10.4394(10)	5.58(1)	8.866(2)
c (Å)	14.2693(13)	25.03(4)	15.658(5)
V (Å^3)	673.96(10)	667(2)	643.7(3)
α (°)	69.422(3)	93.02(3)	104.048(9)
β (°)	88.897(3)	92.12(2)	106.487(7)
γ (°)	85.642(30)	100.34(3)	100.34(3)
Z	1	1	2
D_{cal} (g cm^{-3})	1.125	1.091	1.255
μ (mm^{-1})	6.99	6.89	10.033
Reflections collected	5508	6393	5973
Independent reflections	2979 (R_{int} = 0.041)	3014 (R_{int} = 0.082)	2868 (R_{int} = 0.068) [a]
No. of reflections used in refinement [I > 2σ(I)]	1301	3014	697
Goodness of fit indicator	7.157	1.057	3.178
Final R index [I > 2σ(I)]	R^1 = 0.0906	R^1 = 0.1425	R^1 = 0.1014

5.4 Conclusions

In conclusion, although the geometrical parameters for topochemical polymerization of diarylbutadiynes are known, the success of the diaryl-substituted π-conjugation PDAs is few and rather relied on the semi-empirical trials. The present work demonstrates a unique approach to construct the . diarylbutadiynes based PDAs under hydrogen bond of amide. By simply applying oxidative coupling reaction of ethynylphenylheptanamide, a series of heptanamide-substituted diarlybutadiyne could be obtained. The detailed structural analyses and the simulated information clarified that the amide groups of DA formed the hydrogen bond and favoured the molecular alignment. At that time, the position of the substituent was another important factor to direct the molecules so that the packing structure can be satisfied with the parameters for topochemical polymerization. The exploration here is a good guideline to design the monomers with high possibility to give PDAs from diarylbutadiynes with fully conjugated systems and demonstrate the importance of hydrogen bond to framework the substituted diarlybutadiyne to favor the geometrical parameters for polymerization.

5.5 Acknowledgement

5.6 References

(1)   G. Z. Wegner, *Naturforschg. B* **1969**, *24*, 824.

(2)   G. Z. Wegner, *Pure Appl. Chem.* **1977**, *49*, 443.

(3)   R. R. Chance, G. N. Patel, *J. Polym. Sci. B Polym. Phys.* **1978**, *16*, 859.

(4)   M. Fujimoto, M. Ishida, A. Fujii, Y. Sakamoto, N. Fujita, S. Shinkai, M. Ozaki, *Synt. Met.* **2009**, *159*, 871.

(5)   E. Giorgetti, S. Sottini, T. del Rosso, G. Margheri, M. Alloisio, G. Dellepiane, *Synt. Met.* **2004**, *147*, 271.

(6)   I. S. Park, H. J. Park, J.-M. Kim, *ACS Appl. Mater. Interfaces* **2013**, *5*, 8805.

(7)   J. S. Kauffman, B. M. Ellerbrock, K. A. Stevens, P. J. Brown, W. T. Pennington, T. W. Hanks, *ACS Appl. Mater. Interfaces* **2009**, *1*, 1287.

(8)   T. H. Kim, B. Y. Lee, J. Jaworski, K. Yokoyama, W.-J. Chung, E. Wang, S. Hong, A. Majumdar, S.-W. Lee, *ACS Nano* **2011**, *5*, 2824.

(9)   M. A. Reppy, B. A. Pindzola, *Chem. Commun.* **2007**, *42*, 4317.

(10)   D. J. Ahn, E.-H. Chae, G. S. Lee, H.-Y. Shim, T.-E. Chang, K.-D. Ahn, J.-M. Kim, *J. Am. Chem. Soc.* **2003**, *125*, 8976.

(11)   S. Ampornpun, S. Montha, G. Tumcharern, V. Vchirawongkwin, M. Sukwattanasinitt, S. Wacharasindhu, *Macromolecules* **2012**, *45*, 9038.

(12)   G. J. Exarhos, W. M. Risen, R. H. Baughman, *J. Am. Chem. Soc.* **1976**, *98*, 481.

(13)   S. J. Kew, E. A. H. Hall, *Anal. Chem.* **2006**, *78*, 2231.

(14)   N. B. Kodali, W. Kim, J. Kumar, S. K. Tripathy, S. S. Talwar, *Macromolecules* **1994**, *27*, 6612.

(15)   L. Luo, C. Wilhelm, A. Sun, C. P. Grey, J. W. Lauher, N. S. Goroff, *J. Am. Chem. Soc.* **2008**, *130*, 7702.

(16)   X. Ouyang, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.* **2003**, *125*, 12400.

(17)   T. Shimogaki, A. Matsumoto, *Macromolecules* **2011**, *44*, 3323.

(18)   J. Deschamps, M. Balog, B. Boury, M. Ben Yahia, J.-S. Filhol, A. van der Lee, A. Al Choueiry, T. Barisien, L. Legrand, M. Schott, S. G. Dutremez, *Chem. Mater.* **2010**, *22*, 3961.

(19)   T. Kohji, H. Makoto, Y. Yoshinori, O. Takashi, K. Ryota, K. Toshiaki, N. Takashi, S. Sono, T. Masaki, *JPCS* **2009**, *184*, 012012.

(20)   F. L. Hirshfeld, G. M. J. Schmidt, *J Polym Sci A.* **1964**, *2*, 2181.

(21)   H. Sixl, "Spectroscopy of the intermediate states of the solid state polymerization reaction in diacetylene crystals", in *Polydiacetylenes*, H.-J. Cantow, Ed., Springer Berlin Heidelberg, 1984, p. 49.

(22)   V. Enkelmann, "Structural aspects of the topochemical polymerization of diacetylenes", in *Polydiacetylenes*, H.-J. Cantow, Ed., Springer Berlin Heidelberg, 1984, p. 91.   •

(23)   X. Pan, Y. Wang, H. Jiang, G. Zou, Q. Zhang, *J. Mater. Chem.* **2011**, *21*, 3604.

(24)   H. Jiang, X.-J. Pan, Z.-Y. Lei, G. Zou, Q.-J. Zhang, K.-Y. Wang, *J. Mater. Chem.* **2011**, *21*, 4518.

(25)   X. Yan, X. An, *RSC Adv.* **2014**, *4*, 18604.

(26)   R. Jelinek, M. Ritenberg, *RSC Adv.* **2013**, *3*, 21192.

(27)   R. H. Baughman, *J. Appl. Phys.* **1972**, *43*.

(28)   K. Tashiro, H. Yamamoto, M. Hanesaka, "Recent Progress in Static and Dynamic Structural Analysis of Crystalline Polymers Studied from a Microscopic Point of View", in *Encyclopedia of Polymers and Composites*, S. Palsule, Ed., Springer Berlin Heidelberg, 2014, p. 1.

(29)   G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty, R. H. Grubbs, *Angew. Chem. Int. Ed. (English)* **1997**, *36*, 248.

(30)   J. R. Néabo, K. I. S. Tohoundjona, J.-F. Morin, *Org. Lett.* **2011**, *13*, 1358.

(31)   Z. Li, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.* **2008**, *131*, 634.

(32)   S. R. Diegelmann, J. M. Gorham, J. D. Tovar, *J. Am. Chem. Soc.* **2008**, *130*, 13840.

(33)   S. R. Diegelmann, N. Hartman, N. Markovic, J. D. Tovar, *J. Am. Chem. Soc.* **2012**, *134*, 2028.

(34)   H. Yamamoto, K. Tashiro, S. Okada, *Polymer Preprints, Japan (English Edition)* **2011**, *60*, 720.

(35)   A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320.