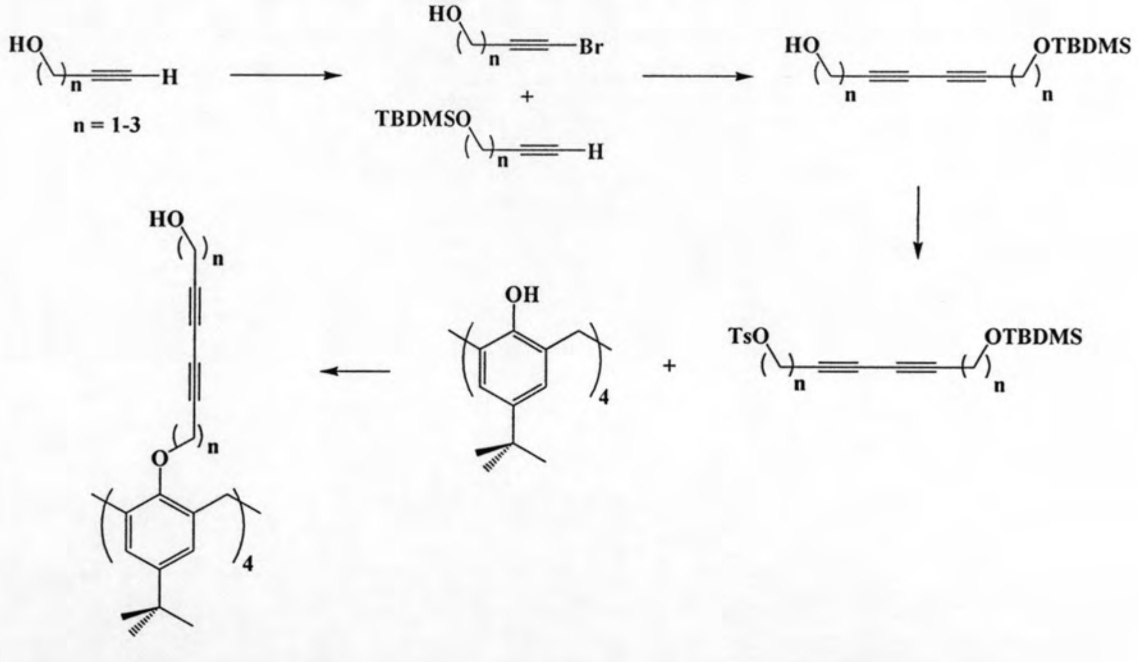
CHAPTER III

RESULTS AND DISCUSSION

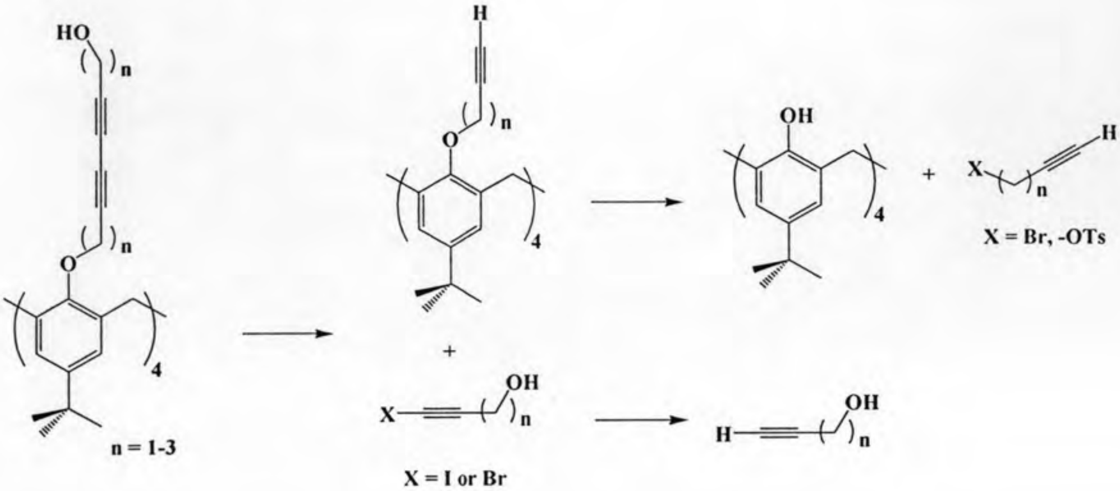
3.1 Synthesis

The synthesis of *tert*-butylcalix[4]arene containing four diyne units was devided in two pathways. In the first pathway, the unsymmetrical conjugated diynes, having tosylate group on one end and a silyl protected hydroxyl group on the other, are prepared first followed by attachment of four equivalents of these diyne chains to the hydroxyl groups of *tert*-butylcalix[4]arene (Scheme 3.1).



Scheme 3.1 Synthesis of the first pathway to *tert*-butylcalix[4]arene containing four diyne units.

In the second pathway, tetra(terminal alkyne) *tert*-butylcalix[4]arene is constructed first and it is then coupled to bromoalkyne to form *tert*-butylcalix[4]arene containing four diyne units.

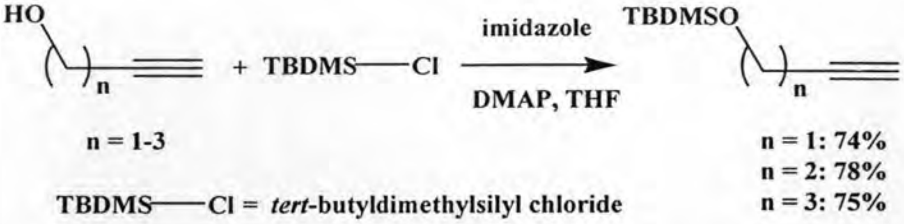


Scheme 3.2 Synthesis of the second pathway to *tert*-butylcalix[4]arene containing four diyne units.

3.1.1 The first synthetic pathway

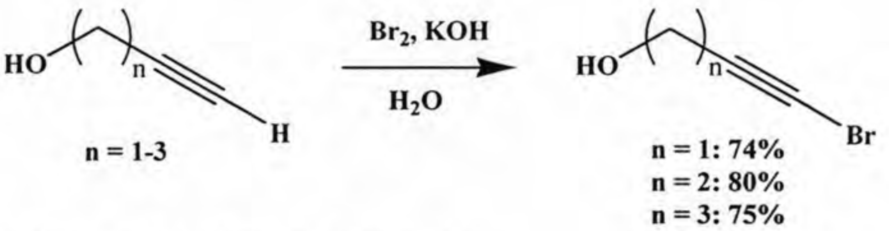
- **Synthesis of unsymmetrical 1,3-diynes**

tert-Butyldimethylsilyl (TBDMS) [87] group is one of the most frequently used protecting groups for the hydroxyl function in organic synthesis because of its easy preparation [88] and general stability to basic and mildly acidic reagents [87]. The first step in the synthesis of unsymmetrical diyne involved a protection of each alkynol, *i.e.* propargyl alcohol, 3-butynol and 4-pentynol, by reacting it with *tert*-butyldimethylsilyl chloride (TBDMS) in tetrahydrofuran at room temperature using imidazole as a base and 4-dimethylaminopyridine (DMAP) as a catalyst to furnish *tert*-butyldimethylsilyloxy-2-propyne, *tert*-butyldimethylsilyloxy-3-butyne and *tert*-butyldimethylsilyloxy-4-pentyne in good yields (Scheme 3.3).



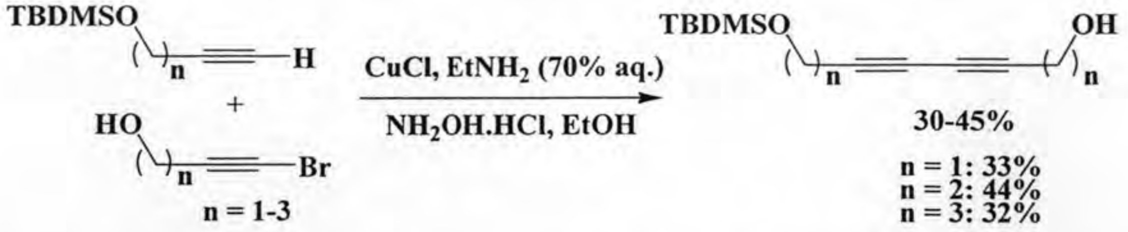
Scheme 3.3 Protection of alkynols with *tert*-butyldimethylsilyl group.

Another part of the unsymmetrical diyne was derived from one of the bromoalkynols. Terminal alkynol *i.e.* propargyl alcohol, 3-butynol and 4-pentynol were brominated with potassium hypobromite, generated *in situ* from bromine and potassium hydroxide solution, to afford 3-bromo-2-propynol, 4-bromo-3-butynol and 5-bromo-4-pentynol in good yields (Scheme 3.4).



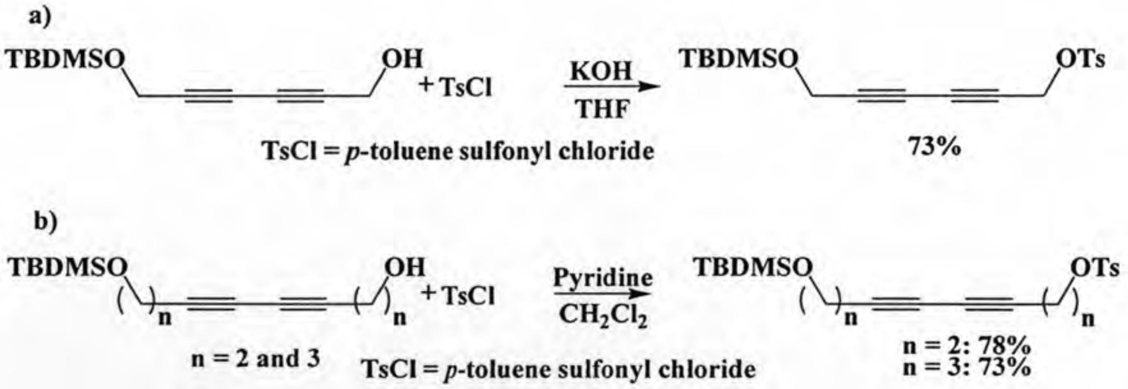
Scheme 3.4 Bromination of terminal alkynols.

The Cadiot-Chodkiewicz cross-coupling of 1-bromo alkynol with the silyloxy protected terminal alkynes in the presence of copper(I) iodide salt and an aliphatic amine has been reported to be a useful route to unsymmetrical conjugated diynes [89]. In this work, this coupling was used to synthesize 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynol (n = 1), 8-*tert*-butyldimethylsilyloxy-3,5-octadiynol (n = 2) and 10-*tert*-butyldimethylsilyloxy-4,6-decadiynol (n = 3). However, the reactions produced the desired unsymmetrical diynes in only moderate yields (Scheme 3.5) due to the competitive formation of the symmetrical diynes from the homo-coupling reaction of 1-bromoalkynol (40-50%).



Scheme 3.5 Synthesis of unsymmetrical diyne by Cadiot-Chodkiewicz cross-coupling reaction.

To connect the unsymmetrical diyne to the phenolic oxygen of *tert*-butylcalix[4]arene, nucleophilic substitution (S_N) to the primary alkoxy carbon of the diyne looked attractive. It was however a poor leaving group for the S_N reaction. The hydroxyl group was thus converted into a better leaving group by reacting with tosyl chloride in the presence of a suitable base, KOH or pyridine, to give tosylate esters. Three tosylate esters of the unsymmetrical diynes, 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate (n = 1), 8-*tert*-butyldimethylsilyloxy-3,5-octadiynyl tosylate (n =20) and 10-*tert*-butyldimethylsilyloxy-4,6-decadiynyl tosylate (n = 3), were obtained in good yields (Scheme 3.6).



Scheme 3.6 Tosylation of alkynol a) for n = 1 and b) for n = 2 and 3.

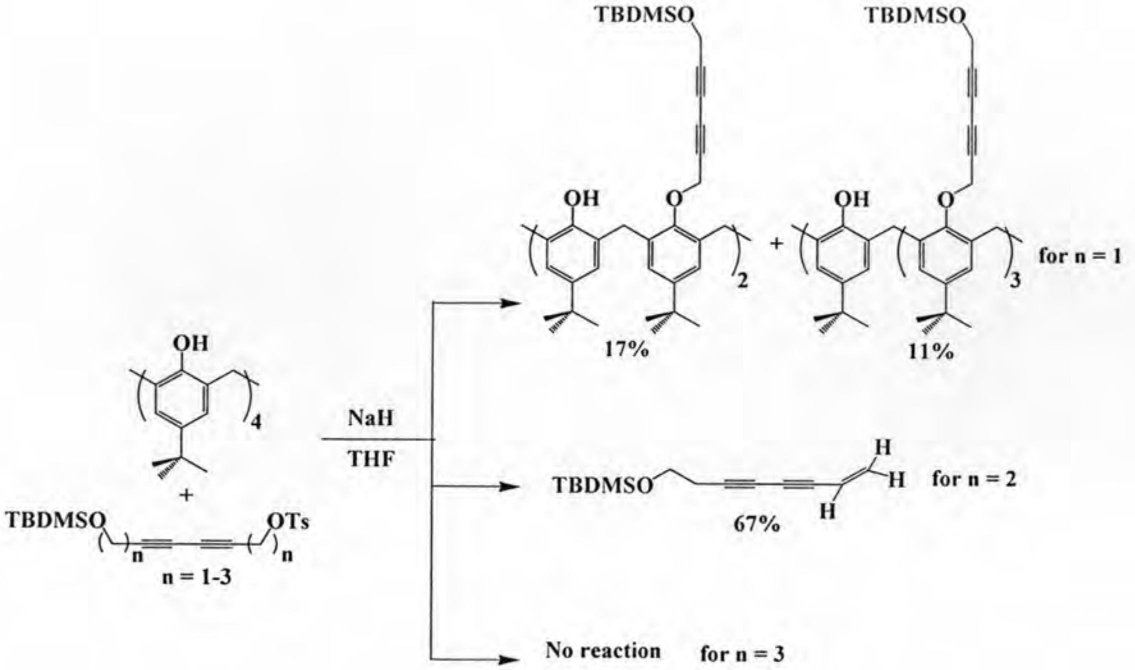
- **Attempt in synthesis of *tert*-butylcalix[4]arene containing four diyne units**

The diyne chains were introduced onto the hydroxyl rim of *tert*-butylcalix[4]arene by *O*-alkylation via the S_N reaction of the tosylate diynes in the presence of sodium hydride base. The S_N reaction of 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate (n = 1) using the phenolate anion of *tert*-butylcalix[4]arene as a nucleophile yielded only the di- and trisubstituted calix[4]arene in relatively low yields (Scheme 3.7). The desired tetrasubstituted product was not observed. The poor substitution observed in this reaction may be attributed to the low aspect ratio between the reactive and nonreactive sites of substrate and the nucleophile leading to high portion of unsuccessful collisions between the two reagents and thus the slow reaction. Furthermore, 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate also decomposed under the reaction condition. The decomposition of 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate to an unidentified mixture of colored materials was observed when it was stirred with sodium hydride in tetrahydrofuran at room temperature (Appendix A).

When the same S_N reaction was performed on 8-*tert*-butyldimethylsilyloxy-3,5-octadiynyl tosylate (n = 2), only the elimination product, 8-*tert*-butyldimethyl silyloxy-3,5-octaene, was obtained (Scheme 3.7). The results were not entirely unexpected as the S_N2 process of this particular substrate is likely to be even slower than that of propargyl tosylate ester. Its 1,2-elimination is also promoted by the formation of the thermodynamically favored conjugated alkene product. The same reaction of 10-*tert*-butyldimethylsilyloxy-4,6-decadiynyl tosylate also gave no observable desired products but only the starting materials even after prolonged treatment of large excess of sodium hydride. This longer chain of tosylate ester should have even lower reactivity probably due to the bulky group of tosylate.

To avoid the decomposition of the diyne tosylate esters, a weak base, potassium carbonate, was used in place of sodium hydride for the *O*-alkylation. The alkyltion of *tert*-butylcalix[4]arene with the shortest diyne tosylate ester, 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate, using potassium carbonate gave only the di-*O*-alkylated *tert*-butylcalix[4]arene. The two longer diyne chains were thus not tested.

Even though tosylate group is a highly reactive leaving group for displacement, its use for *O*-alkylation of *tert*-butylcalix[4]arene seems to be successful only for the disubstitution as found in most literature reports [90]. Furthermore, bromide leaving group have been more extensively used for the alkylation of *tert*-butylcalix[4]arene at the phenoxide rim, especially for longer alkyl chain [91].



Scheme 3.7 Nucleophilic substitution of *tert*-butylcalix[4]arene with 6-*tert*-butyldimethylsilyloxy-2,4-hexadiynyl tosylate (n = 1), 8-*tert*-butyl-dimethylsilyloxy-3,5-octadiynyl tosylate (n = 2) and 10-*tert*-butyldimethyl-silyloxy-4,6-decadiynyl tosylate (n = 3), respectively.

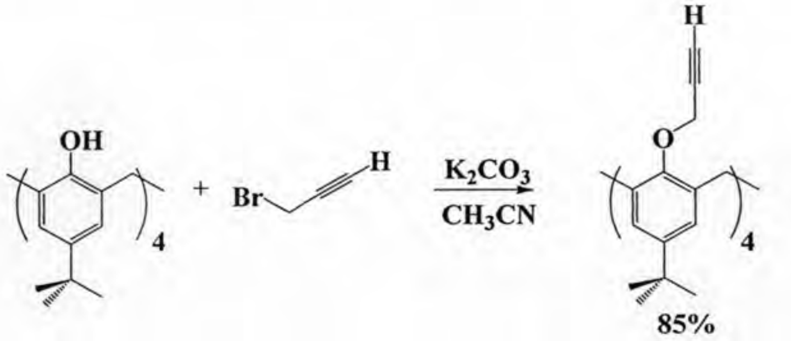
As described above, all attempts based on the first approach did not lead to the desired *tert*-butylcalix[4]arene containing four diyne units. Hence, the second synthetic pathway was devised based on the multiple *O*-alkylation of *tert*-butylcalix[4]arene followed by the Cadiot-Chodkiewicz coupling. In this approach, the protection and deprotection of the hydroxyl group by the silyl group are also avoided.

3.1.2 The second synthetic pathway

- **Synthesis of *tert*-butylcalix[4]arene containing four propargyl groups**

In the second approach, *tert*-butylcalix[4]arene was alkylated with excess propargyl bromide in the presence of potassium carbonate as a base at reflux temperature of acetonitrile. The desired tetra-*O*-alkylated product, 25,26,27,28-

tetra(propargyloxy)-*tert*-butylcalix[4]arene was readily obtained in one step (Scheme 3.8).

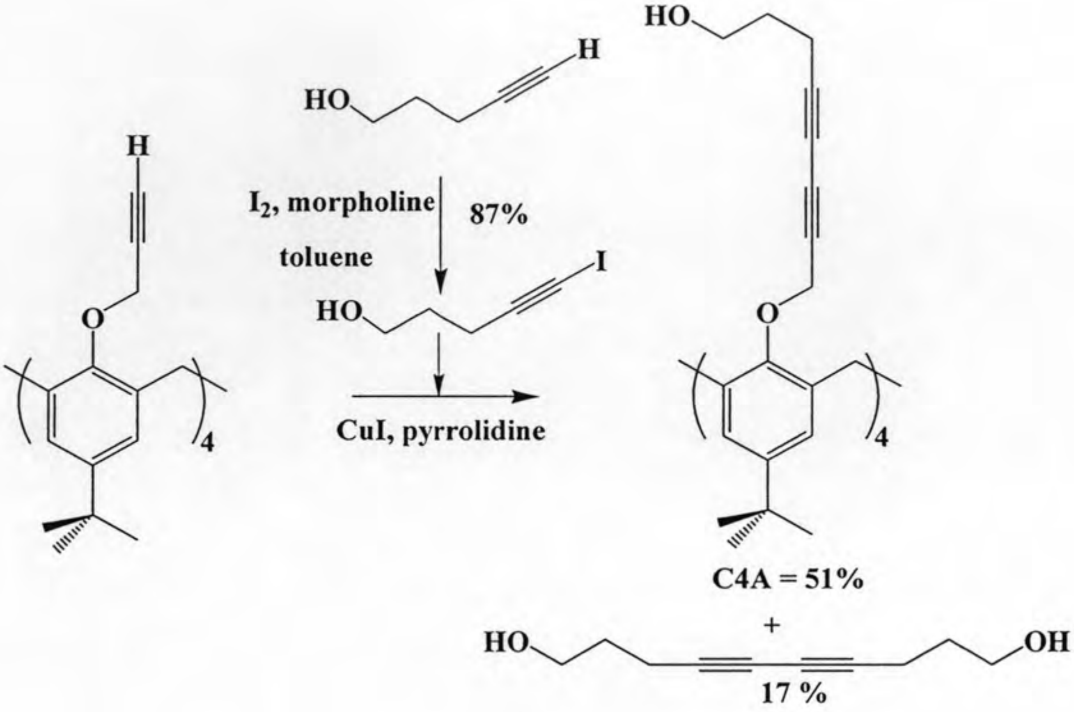


Scheme 3.8 Nucleophilic substitution of *tert*-butylcalix[4]arene with propargyl bromide.

- **Synthesis of *tert*-butylcalix[4]arene containing four diyne units**

Initially, this key step utilized a typical Cadiot-Chodkiewicz coupling involving the reaction of a terminal alkyne with a bromoalkyne catalyzed by copper(I) chloride (Scheme 3.5). As a result, the desired product, 25,26,27,28-tetra(octa-4,6-diyn-1-ol)oxy-*tert*-butylcalix[4]arene, was obtained from the cross-coupling reaction of 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]arene and 5-bromo-4-pentynol in low yield (14%) along with considerable amount of the symmetrical diyne major product, 4,6-decadiyn-1,10-diol (56% yield).

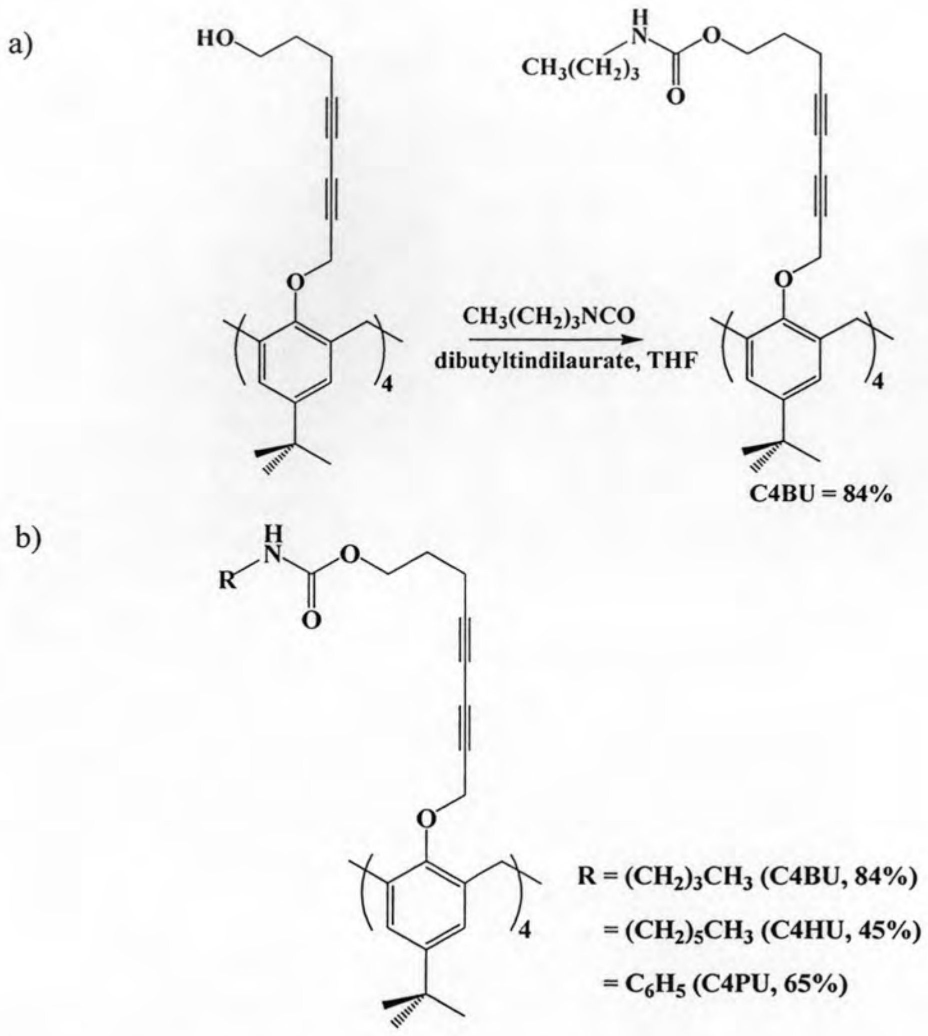
In 1996, Alami and co-workers reported a modified condition of Cadiot-Chodkiewicz cross-coupling using iodoalkynes in pyrrolidine [30]. The iodoalkyne was synthesized via a reaction of a terminal alkyne with iodo-morpholine complex, generated in-situ from slow addition of morpholine to a well-stirred iodine solution at 45 °C. Using Alami's protocol, 5-iodo-4-pentynol was obtained in excellent yield (87%) and its cross-coupling with 25,26,27,28-tetra(propargyloxy)-*tert*-butylcalix[4]arene gave acceptable yield of 25,26,27,28-tetra(octa-4,6-diyn-1-ol)oxy-*tert*-butylcalix[4]arene (**C4A**) (Scheme 3.9). The symmetrical diyne side product, 4,6-decadiyn-1,10-diol, resulted from the homo-coupling of 5-iodo-4-pentynol was obtained as a minor product (17% yield).



Scheme 3.9 Cadiot-Chodkiewicz cross-coupling reaction: the letter C and A stands for calix[4]arene and alcohol, respectively.

- **Synthesis of *tert*-butylcalix[4]arene containing four diyne units with carbamate groups**

In order to convert hydroxyl group in diyne backbone into the group providing stronger hydrogen bonding, *tert*-butylcalix[4]arene derivatives containing four diynol chains were treated with various isocyanate groups to form carbamate (urethane) groups. **C4A** obtained in the previous section was hence treated with butylisocyanate in the presence of catalytic amount of dibutyltindilaurate in tetrahydrofuran at room temperature. The desired carbamate product, **C4BU**, was obtained in excellent yield (84%) (Scheme 3.10a). Using the same synthetic approach *tert*-butylcalix[4]arene derivatives containing four diyne carbamates, **C4HU** and **C4PU** was obtained in 45 and 65% yield, respectively (Scheme 3.10b).



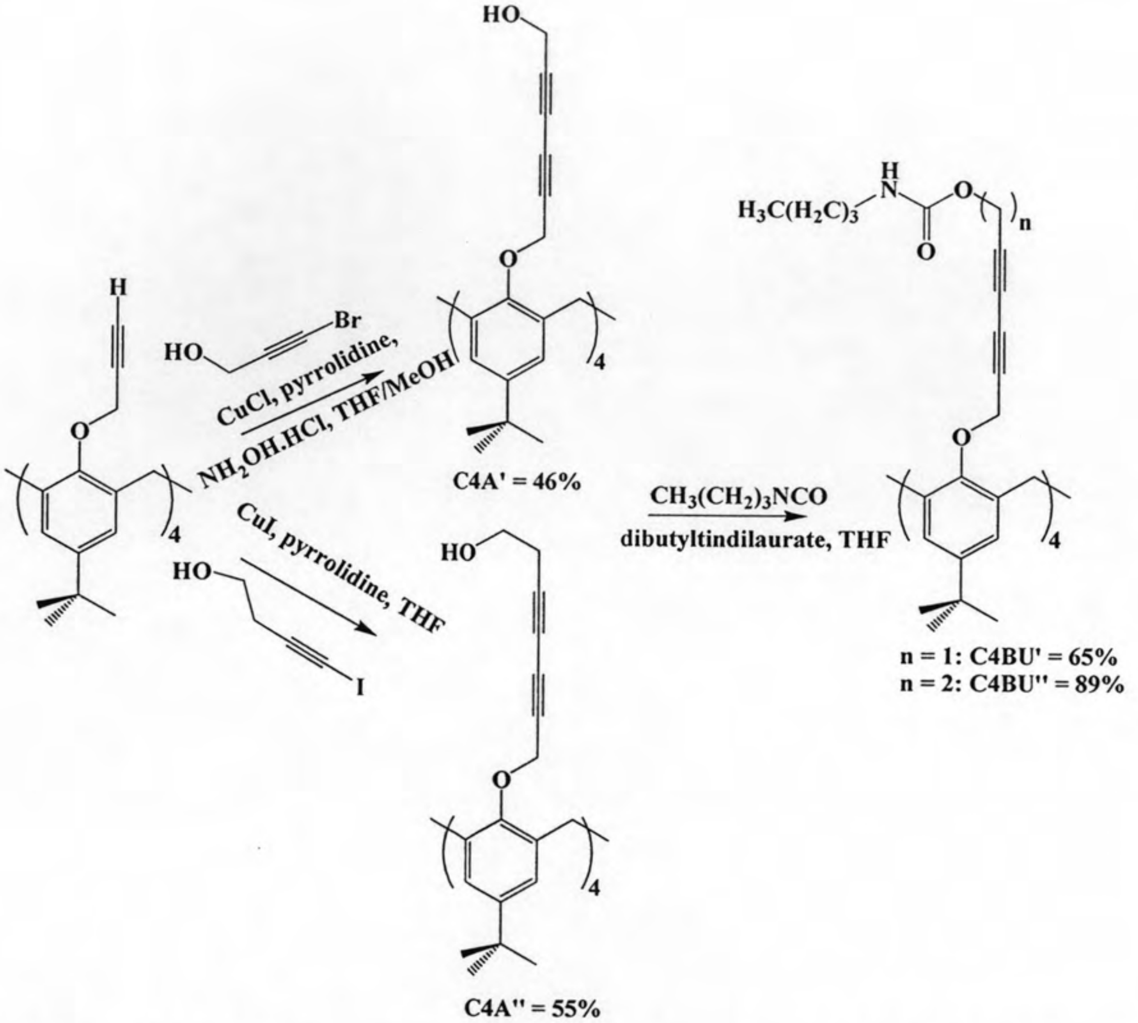
Scheme 3.10 a) Carbamate formation of **C4A** with butylisocyanate b) yields of **C4HU** and **C4PU**: the letter B, H, P and U stands for butyl, hexyl, phenyl and urethane (carbamate), respectively.

- Synthesis of *tert*-butylcalix[4]arene containing four butylcarbamate-substituted diyne units with varying methylene spacers

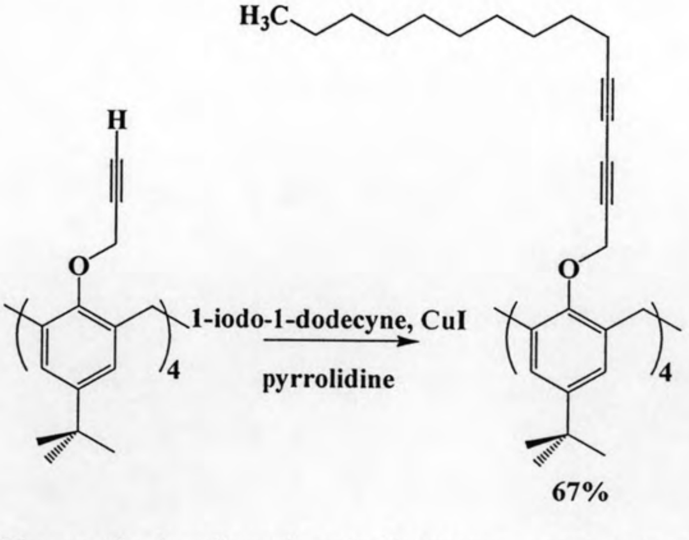
There have been literature reports that the length of methylene spacer between the hydrogen bond forming head group and the diyne unit can affect the reactivity on the diacetylene monomer and the optical properties of the resulting polydiacetylene [92]. **C4BU** synthesized in the previous section contains three methylene units between the carbamate head group and the diyne unit. To study the effect of the length of methylene spacer between the carbamate head group and the diyne unit, **C4BU′** and **C4BU″** containing one and two methylene units, respectively, were synthesized through **C4A′** and **C4A″** using similar procedures as those in the synthesis of **C4BU** (Scheme 3.11).

For **C4A′**, tetra(propargyloxy)calix[4]arene was coupled with 4-iodo-3-butynol using pyrrolidine as base catalyzed by copper(I) iodide to obtain **C4A′** in 55% yield. In the synthesis of **C4A″**, tetra(propargyloxy)calix[4]arene was initially coupled with 3-iodo-2-propynol catalyzed by copper(I) iodide in pyrrolidine as a base. The coupling was not successful as many products were observed by thin layer chromatography. This is due to the instability of 3-iodo-2-propynol which is readily decomposed at the ambient condition. Using the same synthetic protocol, tetra(propargyloxy)calix[4]arene was therefore coupled with the more stable halo alkyne, 3-bromo-2-propynol to afford **C4A″** in 46% yield. The subsequent reactions of **C4A′**and **C4A″** with butylisocyanate readily afforded **C4BU′** and **C4BU″** in 65% and 89% yield, respectively (Scheme 3.11).

The *tert*-butylcalix[4]arene derivative containing diyne hydrocarbon chain with 15 carbons equal to the number of atoms in the diyne unit of **C4BU** was synthesized for comparative study in solid-state polymerization. Using Cadiot-Chodkiewicz cross-coupling reaction of tetra(propargyloxy)calix[4]arene with 1-iodododecyne, 25,26,27,28-tetra(pentadeca-2,4-diynoxy)-*tert*-butylcalix[4]arene (**C4PD**), was obtained in 67% yield (Scheme 3.12).



Scheme 3.11 The synthesis of *tert*-butylcalix[4]arene containing butylcarbamate-substituted four diyne units with varying alkyl chain length.



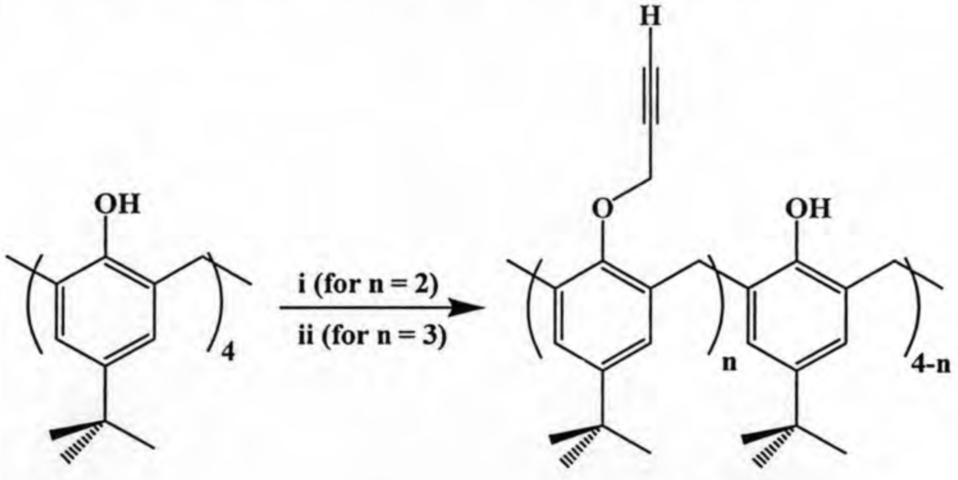
Scheme 3.12 The synthesis of *tert*-butylcalix[4]arene containing C15 hydrocarbon diyne chain (**C4PD**).

3.1.3 Synthesis of *tert*-butylcalix[4]arene containing two and three diyne units

To study the effect of number of diyne units in the solid-state topological polymerization, *tert*-butylcalix[4]arene derivatives containing two and three diyne units were synthesized. Using a similar approach as in the second synthetic pathway of tetrasubstituted calix[4]arene, di- and tripropargyl substituted calix[4]arenes were first synthesized followed by alkylation of the remaining phenoxyl groups and the eventual Cadiot-Chodkiewicz cross-coupling brought about the desired *tert*-butylcalix[4]arene containing two and three diyne units.

- **Synthesis of *tert*-butylcalix[4]arene containing two and three propargyl groups**

Di- and tripropargyloxy-*tert*-butylcalix[4]arene were prepared in 83% and 67% yields, respectively, *via* a nucleophilic substitution of *tert*-butylcalix[4]arene with two and three equivalents of propargyl bromide in the presence of potassium carbonate base at reflux temperature of acetonitrile (Scheme 3.13).



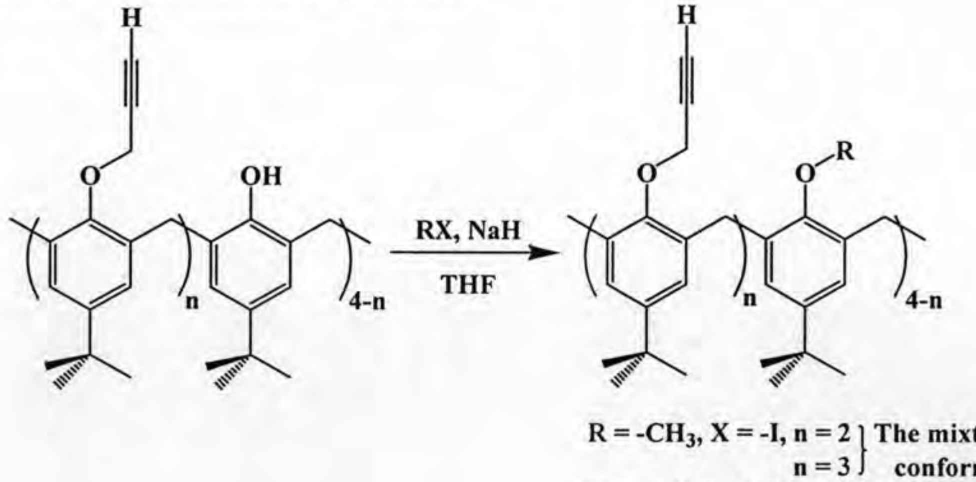
n = 2: 83%
n = 3: 67%

Scheme 3.13 Synthesis of di- and tripropargyloxycalix[4]arene via nucleophilic substitution i) propargyl bromide, K_2CO_3 and CH_3CN ii) propargyl bromide, BaO, $Ba(OH)_2 \cdot 8H_2O$ and THF.

- Alkylation of *tert*-butylcalix[4]arene containing two and three propargyl groups

To avoid the reaction of the phenolic hydroxyl groups with the isocyanate used in the final carbamate formation step, the remaining hydroxyl groups of di- and tripropargyloxy-*tert*-butylcalix[4]arene were alkylated. First, di- and tripropargyloxy-*tert*-butylcalix[4]arene were methylated with methyl iodide to form methyl ether at the remaining hydroxyl groups (Scheme 3.14). The complicated and broad signals of ^1H NMR spectra of the permethylated di- and tripropargyloxy-*tert*-butylcalix[4]arene (Figure 3.1) indicated that the compounds isolated from a column chromatography are mixtures of conformers (cone, partial cone and 1,3-alternate) coexisting in their dynamic equilibrium. This equilibrium proceeds quite readily as the rotation of the aryl rings through the calix[4]arene annulus cannot be prevented by the relatively small methyl group [93].

To prevent the conformational interconversion, the remaining hydroxyl groups of the di- and tripropargyloxy-*tert*-butylcalix[4]arene were alkylated with more sterically hindered groups, benzyl and propyl, using the similar procedure as the methylation. The dibenzylation and dipropylation of dipropargyloxy-*tert*-butylcalix[4]arene gave the desired products in a little lower yields than the monobenzylation and monopropylation of tripropargyloxy-*tert*-butylcalix[4]arene (Scheme 3.14). The ^1H NMR showed that the benzylated and propylated products are all in cone conformation (Figure 3.1).



R = $-CH_3$, X = -I, n = 2 } The mixture of
n = 3 } conformers
R = $-CH_2C_6H_5$, X = -Br, n = 2: 48%
n = 3: 90%
R = $-CH_2CH_2CH_3$, X = -Br, n = 2: 62%
n = 3: 82%

Scheme 3.14 The alkylation of di- and tripropargyloxy-*tert*-butylcalix[4]arene.

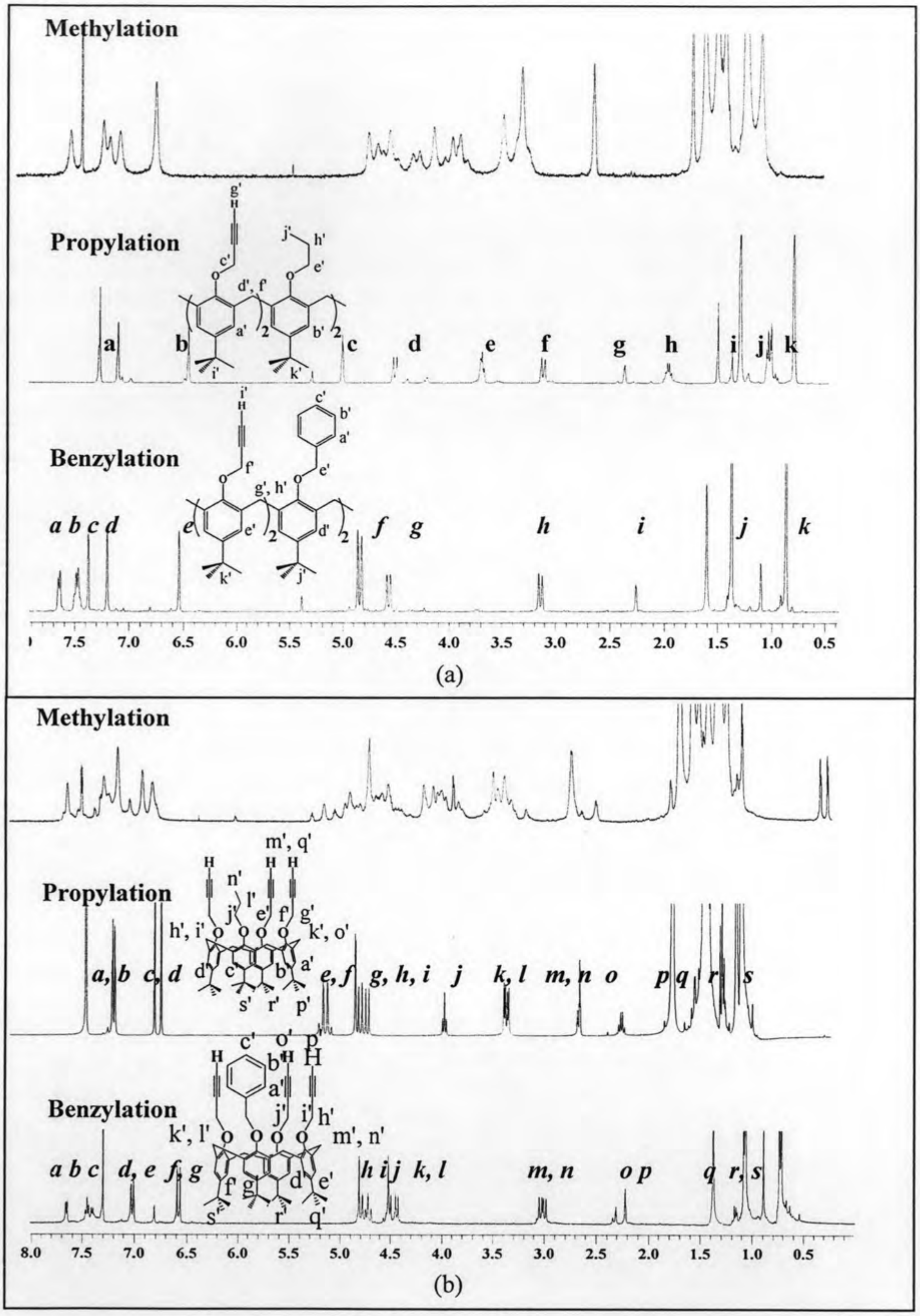
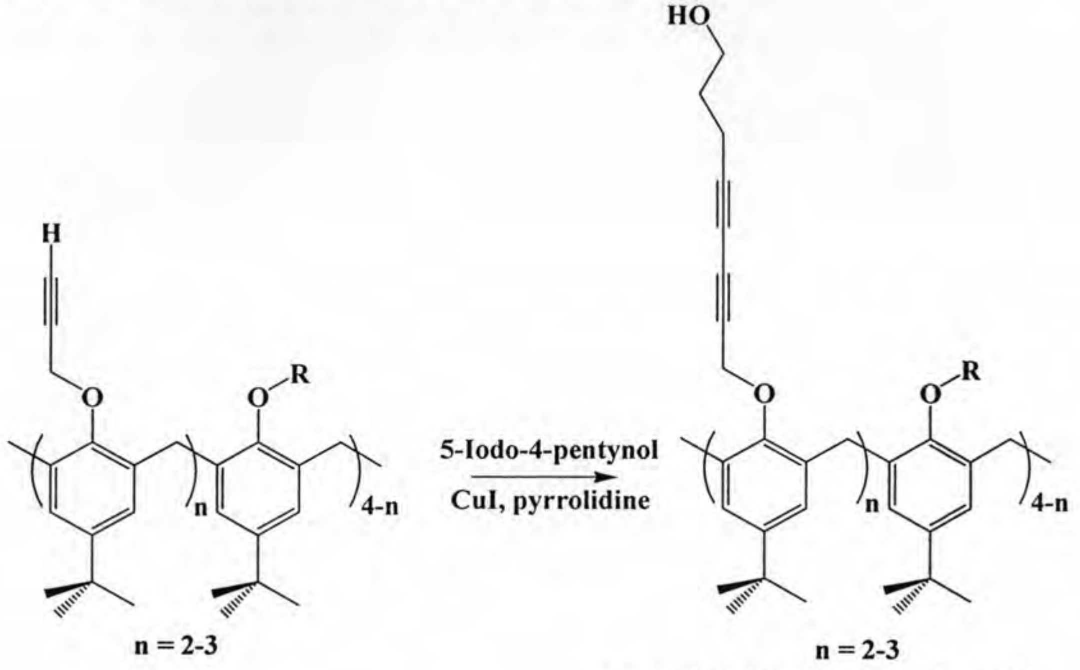


Figure 3.1 ^{1}H NMR spectra of the mixtures of conformers from methylation compared with the cone conformers from benzylation and methylation of a) di- and b) tripropargyloxycalix[4]arene.

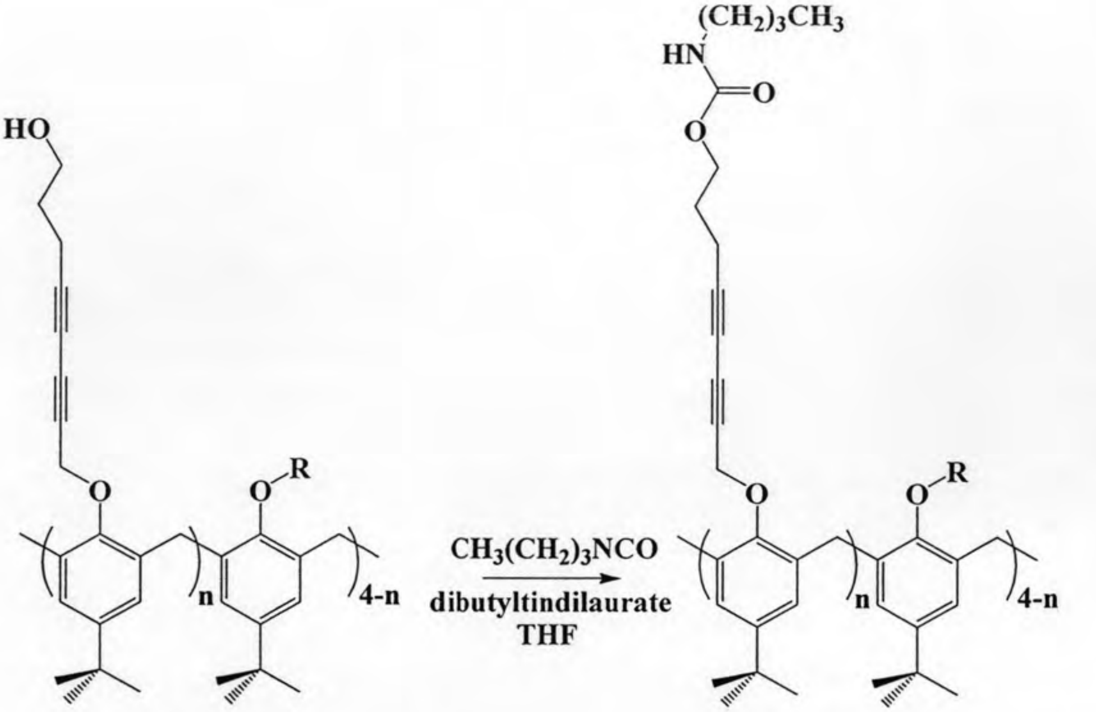
As the bulky benzyl and propyl ether groups do not allow the free rotation of aryl rings through the calix[4]arene annulus and consequently fix the di- and tripropargyloxy-*tert*-butylcalix[4]arene in the cone conformation. Therefore, the diyne synthesis was performed on these benzylated and propylated compounds. Using the modified Cadiot-Chodkiewicz cross-coupling reaction, **BnC2A, BnC3A, PrC2A** and **PrC3A** were obtained in moderate yields (Scheme 3.15).



R = $-CH_2C_6H_5$, n = 2, BnC2A: 38%
n = 3, BnC3A: 46%
R = $-CH_2CH_2CH_3$, n = 2, PrC2A: 38%
n = 3, PrC3A: 58%

Scheme 3.15 Cadiot-Chodkiewicz cross-coupling reaction of di-and tripropargyloxy-*tert*-butylcalix[4]arene protected with benzyl and propyl group: the letter Bn and Pr stands for benzyl and propyl group, respectively.

The intramolecular hydrogen-bonding side group associated with diacetylene backbone can bind diyne units together leading to topological polymerization [94]. The hydrogen bonding between C=O and N-H groups of carbamate (urethane) substituents was studied to attribute the organization of diacetylene packing. The final desired products (**BnC2A**, **BnC3A**, **PrC2A** and **PrC3A**) were successfully obtained by reaction of various isocyanates with *tert*-butylcalix[4]arene derivative containing hydroxyl groups (Scheme 3.16).



n = 2 and 3
R = $-CH_2C_6H_5$ (Bn) and $-C_3H_7$ (Pr)

BnC2BU = 70% PrC2BU = 55%

BnC3BU = 47% PrC3BU = 32%

Scheme 3.16 Carbamate formation of **BnC2A**, **BnC3A**, **PrC2A** and **PrC3A** with butylisocyanate.

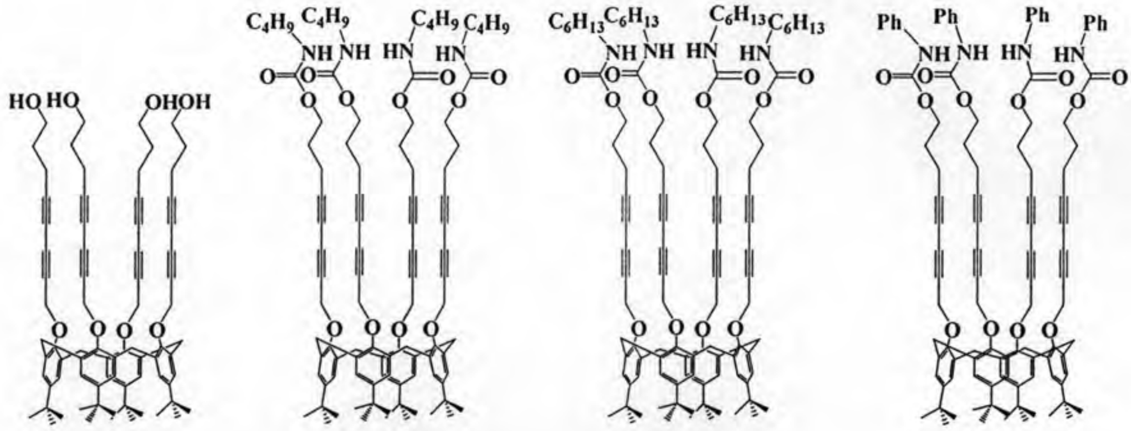
3.2 Solid-state photopolymerization study

3.2.1 Color change upon UV-irradiation of *tert*-butylcalix[4]arene containing multiple diyne units

Preliminary screening for solid-state topological polymerizability of diacetylene monomers was generally performed by UV-irradiation and observation of their color change. Typically, the change of monomer to highly colored material signify the topological 1,4-addition polymerization of the diyne units to form the conjugated ene-yne polymer backbone [95]. In this thesis work, the synthesized compounds having multiple diyne units mounted on the *tert*-butylcalix[4]arene platform were preliminarily studied for their color change upon the irradiation of UV light.

- **Effect of the carbamate head group**

The polycrystalline solids of *tert*-butylcalix[4]arene derivatives containing four diyne units with hydroxyl and carbamate head groups (Figure 3.2) were irradiated with UV light (TUV 15W/G15 T18 lamp; Philips, Holland). After irradiation, the white color of **C4BU** and **C4HU** turned into intense red color within 5 min (Table 3.1) while the white color of **C4A** solid remained virtually the same even after relatively long exposure to UV-irradiation (30 min). Moreover, **C4PU** turned into yellow color. The intense color change of a diacetylene solid after UV-irradiation signifies the formation of extensive ene-yne conjugation resulted from the topological 1,4-addition polymerization of the diyne units. Dissolution of the irradiated **C4BU** and **C4HU** in chloroform gave solutions of **C4BU** and **C4HU** (confirmed by TLC and NMR) and insoluble red powders. No significant insoluble solid observed in the dissolution of irradiated **C4A** in chloroform and the soluble materials were identified as the starting **C4A**. The red insoluble solids obtained from the irradiation of **C4BU** and **C4HU** are thus likely to be polydiacetylene of the corresponding monomers which will be denoted in the later discussion as **PC4BU** and **PC4HU**, respectively.



C4A **C4BU** **C4HU** **C4PU**

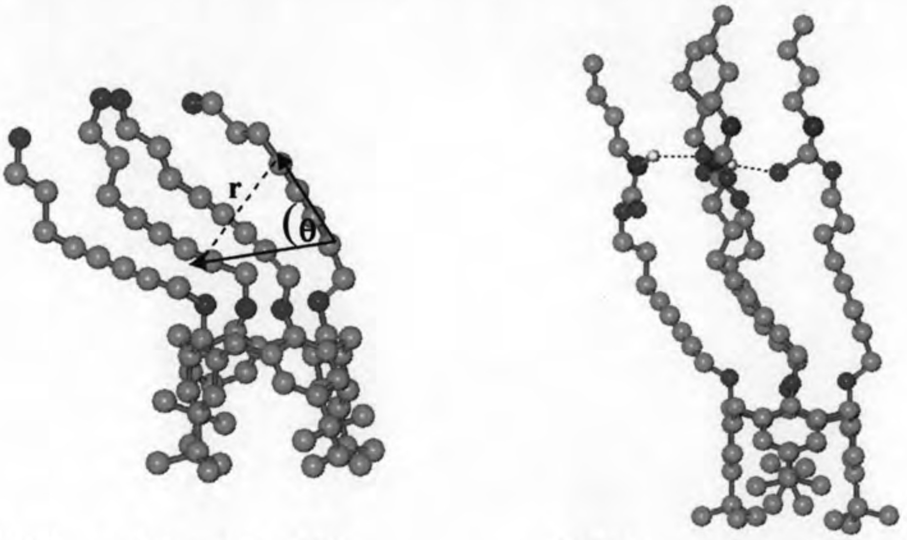
Figure 3.2 The structures of *tert*-butylcalix[4]arene derivatives containing four diyne units with hydroxyl and carbamate head groups used in solid-state photopolymerization study.

Table 3.1 Color change of *tert*-butylcalix[4]arene derivatives containing four diyne units upon exposure to UV-irradiation for 30 min.

Compound	Color			
	Before irradiation		After irradiation	
C4A	white		white	
C4BU	white		red	
C4HU	white		red	
C4PU	light yellow		yellow	

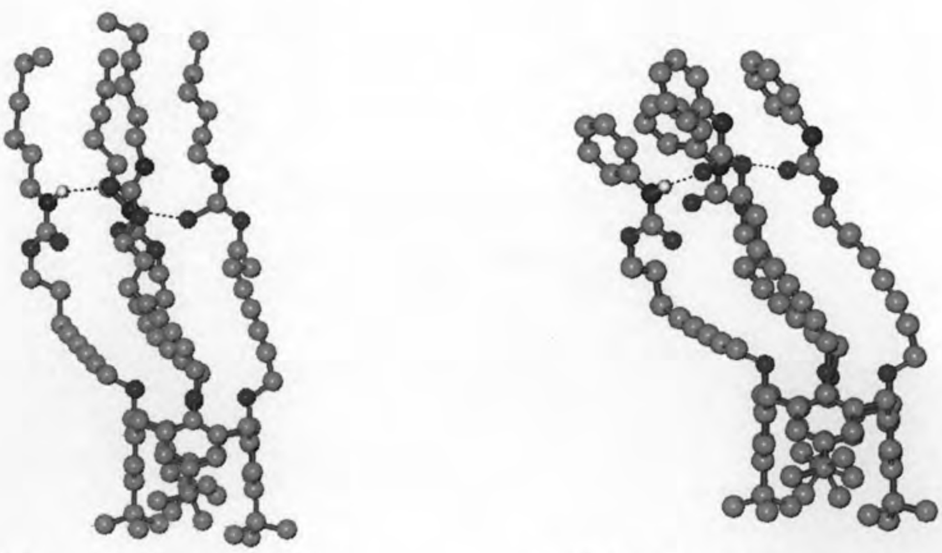
The results clearly demonstrated that **C4BU** and **C4HU** were readily polymerized by UV-irradiation while **C4A** were not and **C4PU** were but most likely to obtain short conjugated polymer. Two packing parameters, the distance between the first carbon and the last carbon of neighboring diacetylene (r ~ 4 Å) and the inclination angle between the diacetylene and stacking axis of diacetylene ($\theta \sim 45°$), are required for topological polymerization of diacetylene monomers [8]. The hydrogen bonding between the head groups plays important role in controlling these packing parameters [5]. From optimization by MM+ force field followed by the AM1 method, the distance between the first carbon and the last diynic carbons and the inclination angle between the diacetylene and stacking axis of diacetylene were estimated.

These parameters for **C4A**, **C4BU**, **C4HU** and **C4PU** were summarized (Figure 3.3). The distance between the first carbon and the last diynic carbons was not significantly different for all compounds because the arrangement of diyne units is determined by the hydrogen bonding between carbamate groups and Van der Waals interaction of four diyne units. Another parameter of **C4BU** and **C4HU**, the inclination angles between the diacetylene and stacking axis of diacetylene, were found to be quite different from **C4A** and **C4PU**. In **C4BU** and **C4HU**, the strong hydrogen bonding between the *N*-alkyl carbamate groups allowed the required packing direction of the diyne units resulting in the suitable angle between the diacetylene and stacking axis of diacetylene. The increase of inclination angle (θ) of **C4A** is due to the lack of carbamate groups controlling the favor direction of diyne units. In addition, the distance between reacting carbons (r) and the increase of inclination angle (θ) of **C4PU** were not significantly different with others probably due to the bulky phenyl groups on the carbamate head group precluding the extensive close packing in either inter- or intramolecular distances between the active carbon atoms in the diyne units.to undergo further inter 1,4 topological addition.



C4A (r = 4.4 Å and θ = 61°)

C4BU (r = 4.0 Å and θ = 56°)



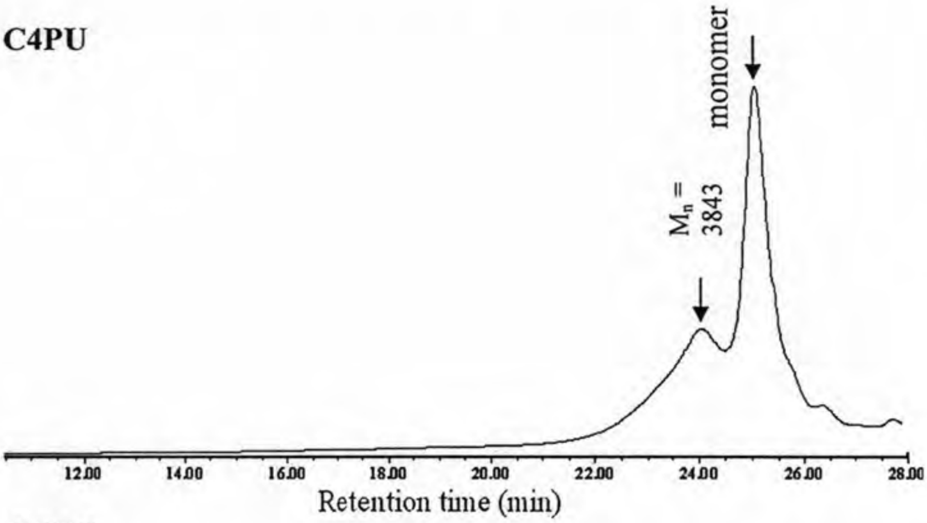
C4HU (r = 4.0 Å and θ = 55°)

C4PU (r = 4.1 Å and θ = 58°)

Figure 3.3 AM1-optimized structures of **C4A**, **C4BU**, **C4HU** and **C4PU**. All hydrogen atoms were omitted for clarity.

The appearance of yellow color from **C4PU** upon exposure to UV light signified its partial polymerization to give short conjugated polydiacetylene. The gel permeation chromatography (GPC) of the solution of irradiated **C4PU** (6 hr) in tetrahydrofuran showed two peaks resulting the monomer and a new peak at the number average molecular weight of 3.8 kDa (M_w/M_n = 1.02 and repeating unit = 3) against polystyrene standards using a universal calibration (Figure 3.4). After **C4HU** was irradiated for the same period, the GPC result of crude showed four peaks resulting the monomer and three new peaks at the number average molecular weight of 7.39×10^2 kDa (M_w/M_n = 1.02 and repeating unit = 451), 1.58×10^2 kDa (M_w/M_n = 1.03 and repeating unit = 97) and 1.01×10^2 kDa (M_w/M_n = 1.15 repeating unit = 62). **C4HU** gave the higher molecular weight than **C4PU**. It thus indicated that the ability of polymerization in **C4HU** is greater than that in **C4PU** corresponding to the appearance of yellow color and the structure optimization data of **C4PU**.

a) Crude **C4PU**



b) Crude **C4HU**

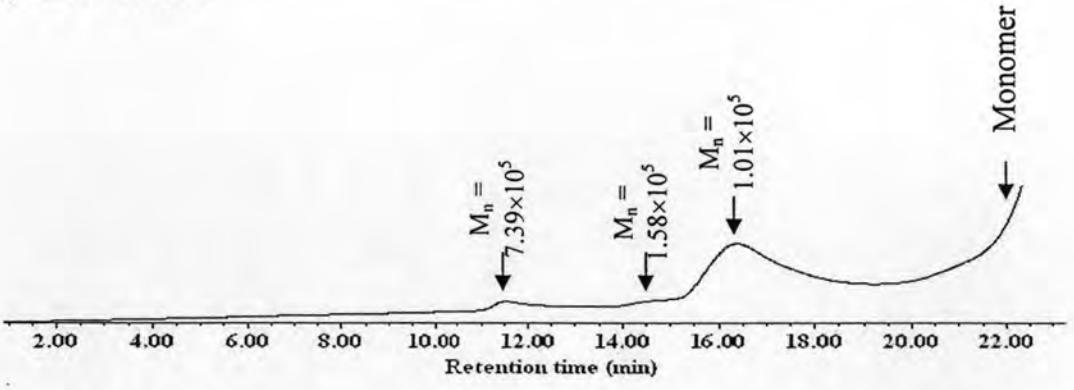
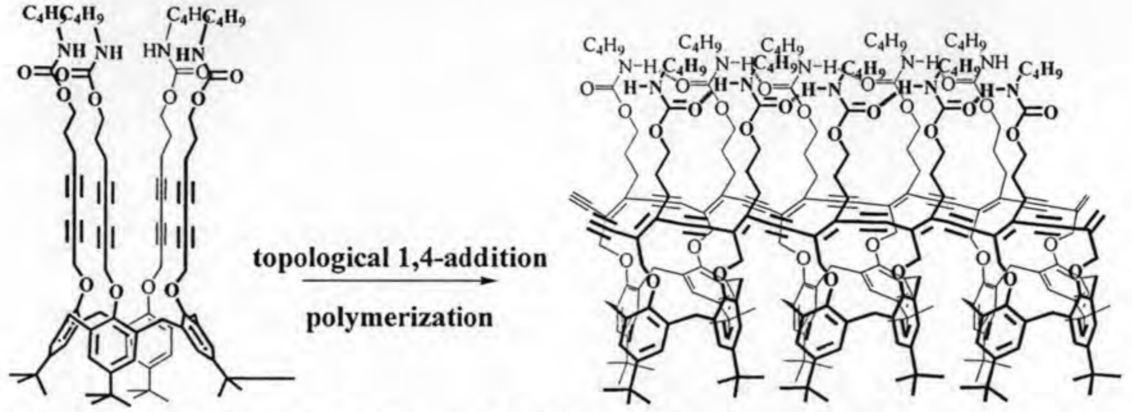


Figure 3.4 GPC chromatogram of a) crude **C4HU** and b) crude **C4PU** powder after UV-irradiation (6 hr) using tetrahydrofuran as an eluent.

Due to the rigidity of the pre-organized *tert*-butylcalix[4]arene platform, the topological 1,4-addition polymerization of the four diyne units of **C4BU** is most likely to proceed through a parallel intramolecular 1,4-addition (Scheme 3.17). The observation of the polydiacetylene from **C4BU** thus provided us the first evidence of the intramolecular 1,4-addition of diynes. The resulting polydiacetylene also possesses intriguing molecular architecture containing a parallel conjugated ene-yne backbone with *tert*-butylcalix[4]arene as hollow side chains.



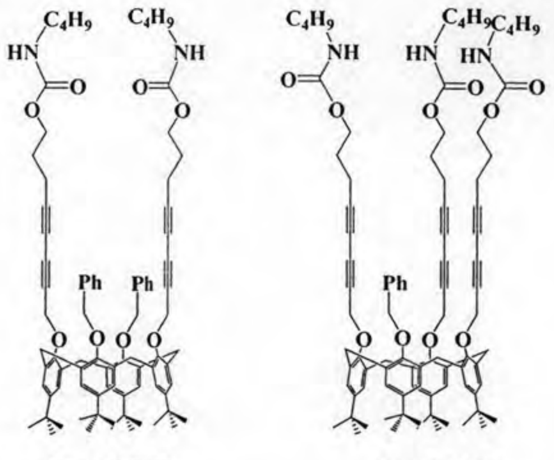
Scheme 3.17 Proposed topological 1,4-addition polymerization of four diyne units in **C4BU**

- **Effect of the number of diyne units**

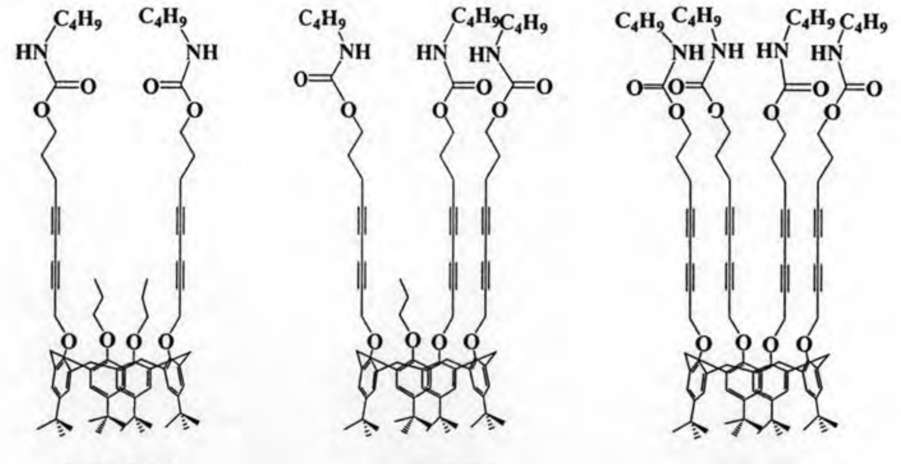
To determine if C_4 symmetry of the *tert*-butylcalix[4]arene derivatives containing multiple diyne units is required for the monomers to undergo the topological polymerization, the *tert*-butylcalix[4]arene containing two and three diyne units were also synthesized and studied.

Initially, the remaining phenoxyl groups of the *tert*-butylcalix[4]arene containing two and three diyne units were protected with benzyl group. Irradiation **BnC2BU** and **BnC3BU** solid powder by UV light for 30 min showed that no color change for **BnC2BU** and the color change from white to orange for **BnC3BU** (Table 3.2). The low photoreactivity of **BnC2BU** and **BnC3BU** comparing to **C4BU** may be attributed to either the relatively bulky benzyl protecting group or the lower symmetry preventing the suitable packing of diyne units for topological polymerization or imply "less" number of monomers within each polymer chain. To rule out the first possibility, the protecting group was changed to propyl group which is the smallest group being able to lock *tert*-butylcalix[4]arene platform in the cone conformation.

tert-Butylcalix[4]arene derivatives containing butylcarbamate-substituted two, three and four diyne units and protecting propyl groups (Figure 3.5) were also irradiated by UV light for 30 min in a solid state. The result showed that the **PrC2BU** did not change its color while the color of **PrC3BU** changed from white to orange upon exposure to UV light (Table 3.2). It showed that calix[4]arene derivatives containing propyl groups give the same result as benzyl groups so propyl and benzyl group has no significantly different effect on unfavorable packing of diyne units.



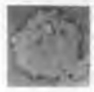
BnC2BU **BnC3BU**



PrC2BU **PrC3BU** **C4BU**

Figure 3.5 The structures of *tert*-butylcalix[4]arene derivatives containing butylcarbamate-substituted multiple diyne units for photopolymerization study.

Table 3.2 Color change of *tert*-butylcalix[4]arene derivatives containing butylcarbamate-substituted multiple diyne units upon exposure to UV-irradiation for 30 min.

Compound	Color	
	Before irradiation	After irradiation
BnC2BU	white 	white 
BnC3BU	white 	orange 
PrC2BU	white 	white 
PrC3BU	white 	orange 
C4BU	white 	red 

By this color change of *tert*-butylcalix[4]arene derivatives, the difference in topological polymerizability of *tert*-butylcalix[4]arene containing different number of diyne units maybe explained by the molecular packing in the solid state of the monomers. For **C4BU** to be effectively topologically polymerized, the calix[4]arene cones must arrange themselves in the same direction that allows diyne units align side by side (Figure 3.6).

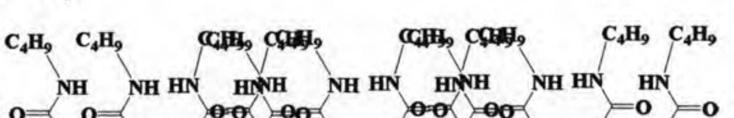
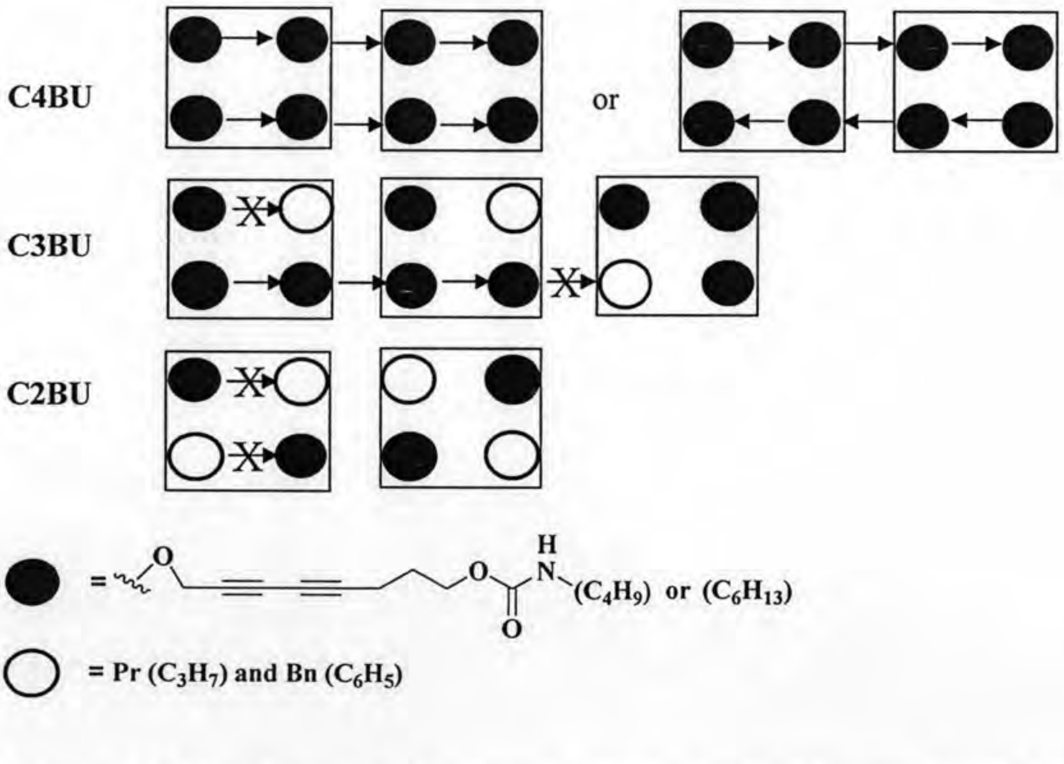


Figure 3.6 Side view of the proposed molecular packing patterns in a cone conformation of *tert*-butylcalix[4]arene derivatives.

This arrangement can be continued for at least in each row of **C4BU** molecules attributed to inter- and intramolecular hydrogen bonding among the carbamate groups (Scheme 3.18). For **PrC3BU** and **BnC3BU**, the same molecular arrangement is subjected to some defect possibilities because of one missing diyne unit per each monomeric molecule. The topological polymerization of **C3BU** thus cannot proceed very far. This result was confirmed by GPC chromatography. GPC chromatogram of crude **BnC3BU** after UV-irradiation for 3 hr until the color change was induced from white to dark orange shows the remaining peak of monomer and the new peak at the number average molecular weight of 3.99 kDa (M_w/M_n = 1.07) calculated as only three repeating units (Figure 3.7).

With two diynes units missing, **C2BU** is not possible to have any continuous alignment of the diyne units beyond two consecutive units and thus the topological polymerization is totally forbidden (Scheme 3.18). This packing analysis confirms that the topological polymerization of **C4BU** operates through the parallel or antiparallel 1,4-addition involving both inter- and intramolecular reactions.



Scheme 3.18 Top views of the proposed molecular packing patterns in solid state of **C4BU**, **C3BU** and **C2BU**. The arrow indicates the direction of topological polymerization and X indicates the mismatched pair of the substituents to undergo the topological polymerization.

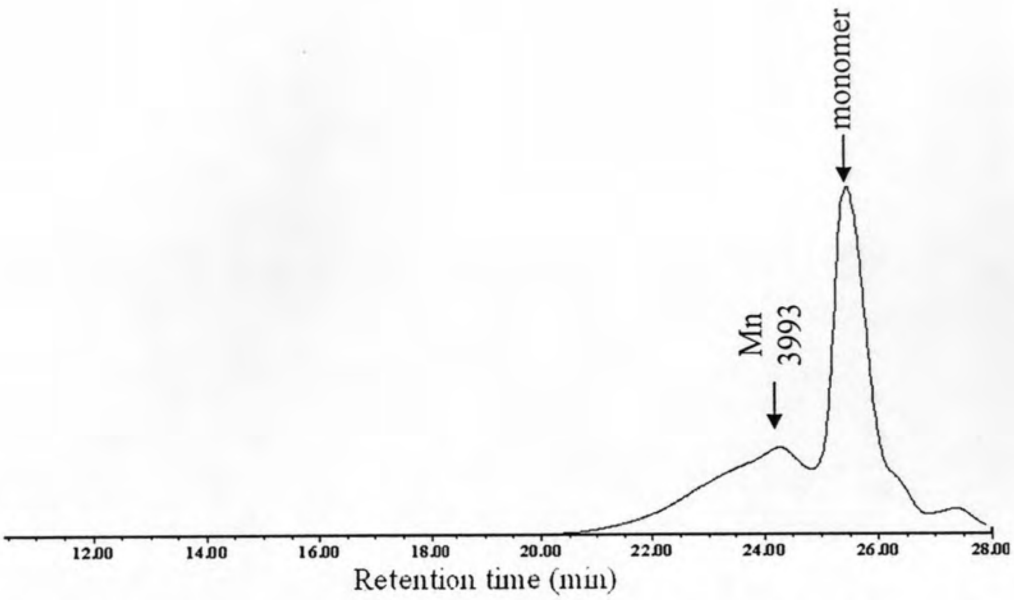
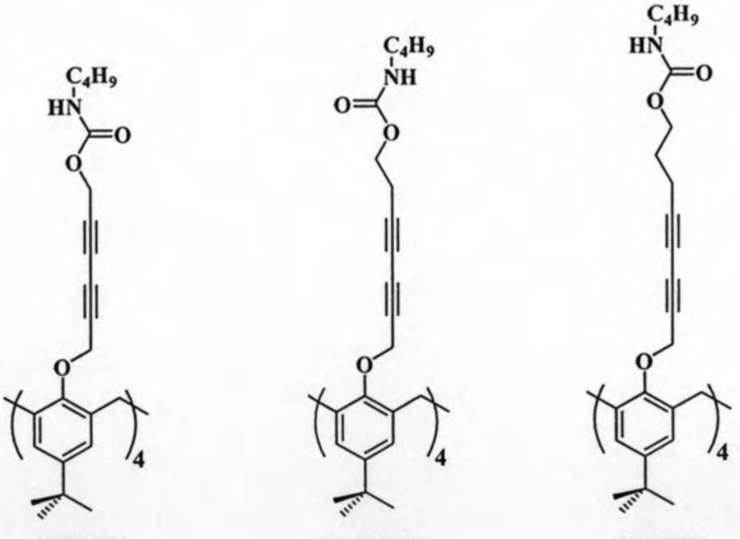


Figure 3.7 GPC chromatogram of crude **BnC3BU** powder after UV-irradiation (3 hr) using tetrahydrofuran as an eluent.

- **Effect of the length of alkyl chain between the diyne and carbamate group**



C4BU' **C4BU''** **C4BU**

Figure 3.8 The structures of *tert*-butylcalix[4]arene derivatives containing four butylcarbamate-substituted diyne units varying alkyl chain length.

To investigate the effect of the alkyl chain length between diyne unit and carbamate group on topological polymerization, **C4BU′** and **C4BU″** (Figure 3.8) containing one and two methylene linker between the diyne unit and carbamate group were also synthesized and studied in a comparison to **C4BU**. Upon exposure to UV light, no color change was observed for **C4BU′** even after 30 min of irradiation, whereas the color of **C4BU″** changed immediately form white to orange (Table 3.3). Like **C4BU** described previously, the color change of **C4BU″** signifies the formation of the ene-yne conjugation of the corresponding polydiacetylene. The inability to polymerize of **C4BU′** indicates that the length of alkyl chain between the diyne and carbamate group has a pronounce effect on the solid-state packing of the diyne units.

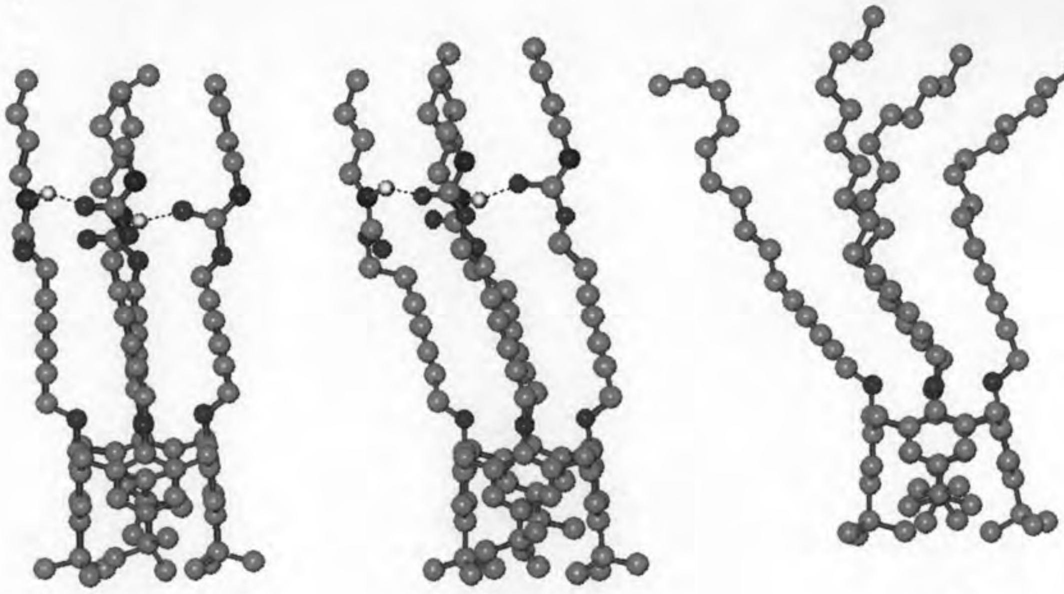
Table 3.3 Color change of *tert*-butylcalix[4]arene derivatives containing four butylcarbamate-substituted diyne units upon exposure to UV-irradiation for 30 min.

Compound	Color	
	Before irradiation	After irradiation
C4BU′	yellow 	yellow 
C4BU″	white 	orange 
C4BU	white 	red 

The topological polymerization reactivity of the diacetylene is known to be governed by two packing parameters,*i.e.* the stacking axis of approximately 45° and the distance between the neighboring reacting carbon atoms of about 4 Å [8]. The structure of **C4BU′**, optimized by MM+ force field followed by AM1 method, gave the distance between the reacting carbons of the diacetylene units of 4.6 Å and inclination angle of 65° which is much more different than 45° and cannot thus proceed the topological polymerization (Figure 3.9). On the other hand the optimized structure of **C4BU″** showed the inclination angles of 59° which closed to that of **C4BU** (56°) possible to allow topological polymerization.

- **Effect of the simple diyne hydrocarbon chain with 15 carbons without carbamate group**

C4PD was irradiated by UV light for 30 min. It was found that the color change of **C4PD** was not observed. It indicates that hydrogen bonding plays important role for topological polymerization. The structure of **C4PD** was optimized by MM+ force field followed by the AM1 method. The distance between reacting carbons of 5.0 Å and the inclination angle of 63° from structure optimization confirms the unfavorable topological polymerization due to the lack of hydrogen bonding from alkyl chain.



C4BU′ (r = 4.6 Å and θ = 65°)

C4BU″ (r = 4.1 Å and θ = 59°)

C4PD (r = 5.0 Å and θ = 63°)

Figure 3.9 AM1-optimized structures of **C4BU′**, **C4BU″** and **C4PD**.

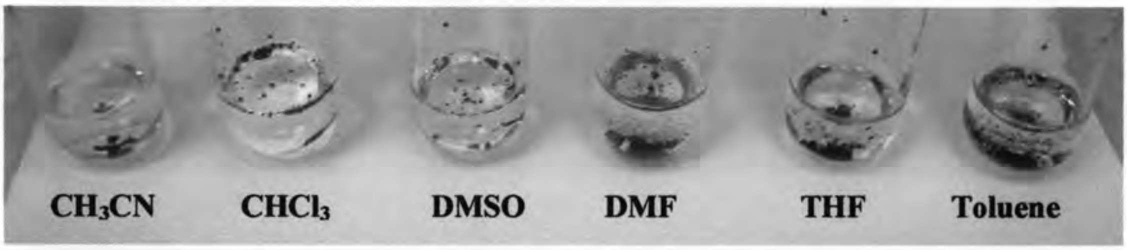
3.2.2 Gamma irradiation, product purification and product characterization

Due to its low penetration power, UV-irradiation is known to give only surface reaction on solid. To obtain higher yields of **PC4BU**, **PC4HU** and **PC4BU″**, the polymerization was conducted by exposing **C4BU**, **C4HU** and **C4BU″** to 60 Mrad of γ-radiation from ^{60}Co. The resulting deep red polymerized solid was dissolved in 30 mL tetrahydrofuran with an assistance of ultrasonication. The red solution was filtered through a 0.45 μm cellulose acetate filter, concentrated under vacuum until a little amount of tetrahydrofuran remained (~2 mL) in a crude product, dropped into methanol and stirred for 2 hr at room temperature to give red precipitate. The precipitate was collected by filtration and dried under vacuum to afford purified polydiacetylene that allow more definitive characterization

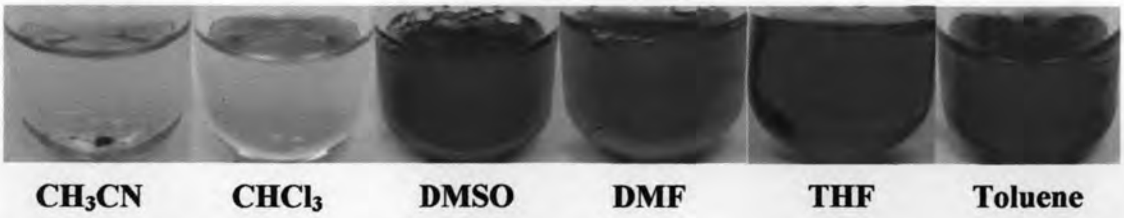
- **Solubility**

The solubility of polymer was investigated by dissolving **PC4BU** (0.50 mg) in 1.00 mL of various organic solvents. The polymer appeared to be insoluble in all solvents (Figure 3.10a). However, after sonication at room temperature for 20 min, the polymer was completely dissolved in *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) to give clear red solutions (Figure 3.10b). The polymer was insoluble in acetonitrile but partially soluble in chloroform after sonication. The polymer appeared to be soluble in dimethylsulfoxide (DMSO) and toluene after sonication. It was however precipitated as swollen gel when left in a freezer for 48 hr (Figure 3.10c). The results indicate that **PC4BU** is soluble in DMF and THF but swell in DMSO and toluene and insoluble in acetonitrile and chloroform.

a) Before sonication



b) After sonication



c) After sonication and left in a freezer for 24 hr

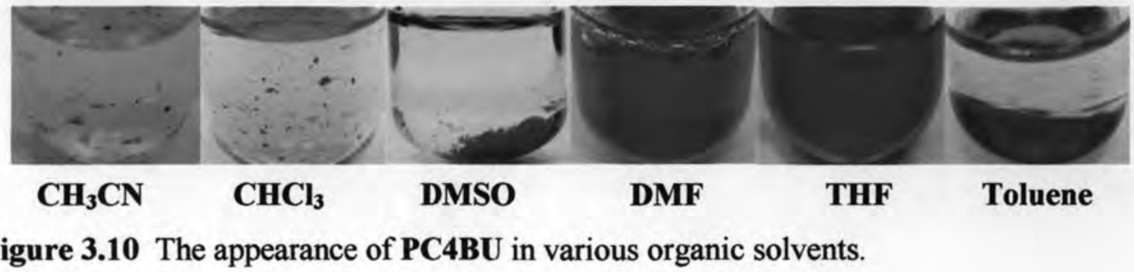


Figure 3.10 The appearance of **PC4BU** in various organic solvents.

PC4BU solution in THF and DMF (0.3% w/w) was stable upon standing in refrigerator for several months without noticeable precipitation (Table 3.4). At the same concentration, the THF solution of **PC4BU″** was also stable upon standing in refrigerator but not its DMF solution. **PC4HU** in tetrahydrofuran and *N,N*-dimethylformamide was however precipitated when they were left in a refrigerator for two months.

Table 3.4 Solubilization of **PC4BU**, **PC4BU″** and **PC4HU** in tetrahydrofuran and *N,N*-dimethylformamide and the stability of the resulting solution upon refrigeration.

Solvent	Appearance		
	Before sonication	After sonication	After 2 month in refrigerator
PC4BU			
Tetrahydrofuran			
N,N-Dimethylformamide			
PC4BU″			
Tetrahydrofuran			
N,N-Dimethylformamide			
PC4HU			
Tetrahydrofuran			
N,N-Dimethylformamide			

- **UV-Vis spectroscopy**

The formation of ene-yne conjugation of polydiacetylene was confirmed by UV/Vis spectroscopy. The spectra of monomers in tetrahydrofuran, **C4BU**, **C4HU** and **C4BU″**, showed no visible absorption while those of the corresponding polymers, **PC4BU**, **PC4BU″** and **PC4HU**, contained broad absorption bands in the visible range

(Figure 3.11) characteristic to the polydiacetylene [96]. **PC4BU** and **PC4BU″** have the first absorption maximum around 445 nm while that of **PC4HU** appeared at longer wavelength 489 nm. All spectra also have an absorption shoulder at the wavelength longer than 500 nm. The shoulder may signify that the purified polymer still contains polydiacetylene with different conjugation lengths.

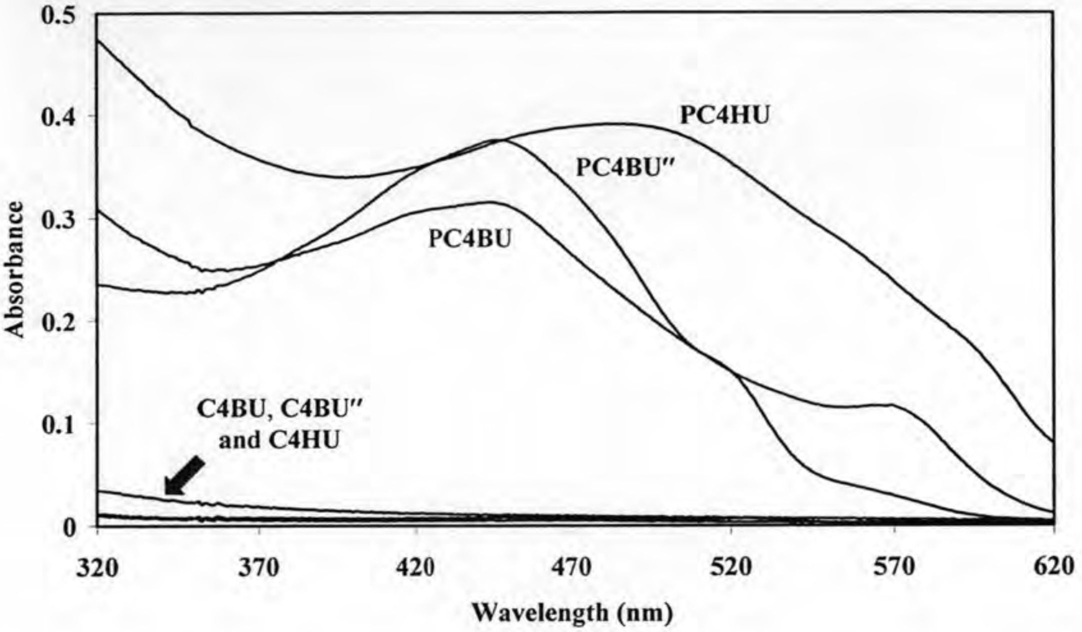


Figure 3.11 UV/vis spectra of **PC4BU**, **PC4BU″** and **PC4HU** and their corresponding monomers in tetrahydrofuran. All of the monomers showed no absorption band in the visible region.

- Polymerization yields

Due to its low penetration power, UV-irradiation is known to give only surface reaction on solid. To obtain higher yields of polymerization the polymerization was conducted by γ-radiation. The resulting deep red polymerized solid was dissolved in THF with an assistance of ultrasonication. The red solution was filtered through a 0.45 μm cellulose acetate filter and concentrated under reduced pressure. The concentrated crude was dropped into methanol at room temperature to give red insoluble precipitate. The precipitate was collected by filtration and dried under vacuum to afford pure red polydiacetylene.

The yields of purified polydiacetylenes obtained from UV and gamma irradiation (60 Mrad) were determined and compiled in Table 3.5 for comparison. As anticipated, gamma irradiation gave significantly higher yields of polydiacetylene than UV-irradiation did. It indicated that gamma ray showed radiation penetrating more deeply into monomers than UV-irradiation.

Table 3.5 Yields of the polydiacetylenes from UV and gamma irradiation.

Compound	% yield	
	UV irradiation[a]	Gamma irradiation[b]
PC4BU	31	74
PC4HU	52	71
PC4BU″	44	91

[a] UV exposure for 30 min

[b] Gamma exposure of 60 Mrad

- **Product purification and polymer characterization**

The good solubility of **PC4BU, PC4HU** and **PC4BU″** in THF indicates that the polymers are not crosslinked and the molecular weight determination by gel permeation chromatography (GPC) is viable. The GPC chromatogram showed that the corresponding red materials obtained from gamma irradiation of **C4BU** contained both monomer and polymer. The polymers were purified by precipitation in methanol from their tetrahydrofuran (THF) solutions. The precipitated **PC4BU** showed no monomer peak compared to pure monomer in GPC chromatogram (Figure 3.12). The result confirms that the precipitation is an effective method for purification of the polymer.

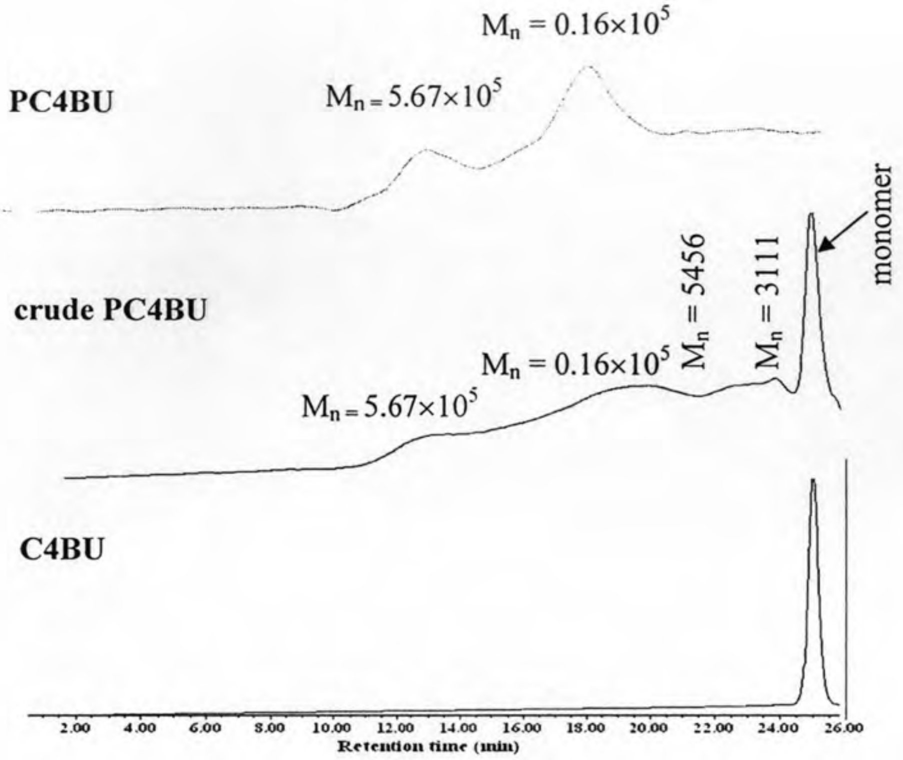


Figure 3.12 GPC traces of **PC4BU**, crude **PC4BU** and **C4BU** using tetrahydrofuran as eluent.

- **Gel permeation chromatography**

The molecular weights of **PC4BU, PC4HU** and **PC4BU″** after purification were determined by GPC using THF as an eluent calibrated against polystyrene standards. The GPC results showed the presence of new peaks at a number average molecular weight of 5.67×10^5 Da ($M_w/M_n = 1.60$) and 0.16×10^5 Da ($M_w/M_n = 1.39$) for **PC4BU**, 50.07×10^5 Da ($M_w/M_n = 1.61$) and 0.22×10^5 Da ($M_w/M_n = 2.17$) for **PC4BU″** and 12.62×10^5 Da ($M_w/M_n = 1.07$), 1.68×10^5 Da ($M_w/M_n = 1.20$) and 0.14×10^5 Da ($M_w/M_n = 1.29$) for **PC4HU** (Table 3.6). The repeating units of polymer were calculated showing 371 and 10 for **PC4BU**, 3406 and 15 for **PC4BU″** and 770, 103 and 9 for **PC4HU**.

Table 3.6 Yield and GPC results of **PC4BU**, **PC4HU** and **PC4BU″** after γ irradiation (60 Mrad).

Compound	$M_w \times 10^5$ (Daltons)	$M_n \times 10^5$ (Daltons)	PDI	Repeating units
PC4BU	9.06, 0.22	5.67, 0.16	1.60, 1.39	371, 10
PC4BU″	80.62, 0.48	50.07, 0.22	1.61, 2.17	3406, 15
PC4HU	13.57, 2.02, 0.18	12.62, 1.68, 0.14	1.07, 1.20, 1.29	770, 103, 9

- **Raman and IR spectroscopy**

Raman scattering spectroscopy has been one of the most effective techniques to unambiguously characterize the ene-yne conjugation of polydiacetylenes especially for the insoluble polymers [94]. The spectrum of **C4BU** has a single peak at 2243 cm^{-1} associated with the C≡C internal diyne stretching (Figure 3.13). The C≡C stretching peak shifts to lower energy at 2099 cm^{-1} in the spectrum of **PC4BU** and a new C=C stretching peak appears at 1482 cm^{-1} confirming the presence of ene-yne conjugation in the red **PC4BU** powder. Similar results were also observed upon the conversion of **C4HU** to **PC4HU** (Figure 3.13). Moreover, the relative intensity of the broad band of C-H stretching at 2917 cm^{-1} in the spectra of the monomers reduced considerably upon their conversion to the corresponding polydiacetylenes. There are two possibilities causing the reduction of this signal: 1) the more Raman active of the conjugated ene-yne backbone comparing to the diyne unit in the monomer due to its higher symmetry, 2) the more restricted symmetrical stretching of the methylene group due to the tighter packing between the alkyl chains upon the polymerization.

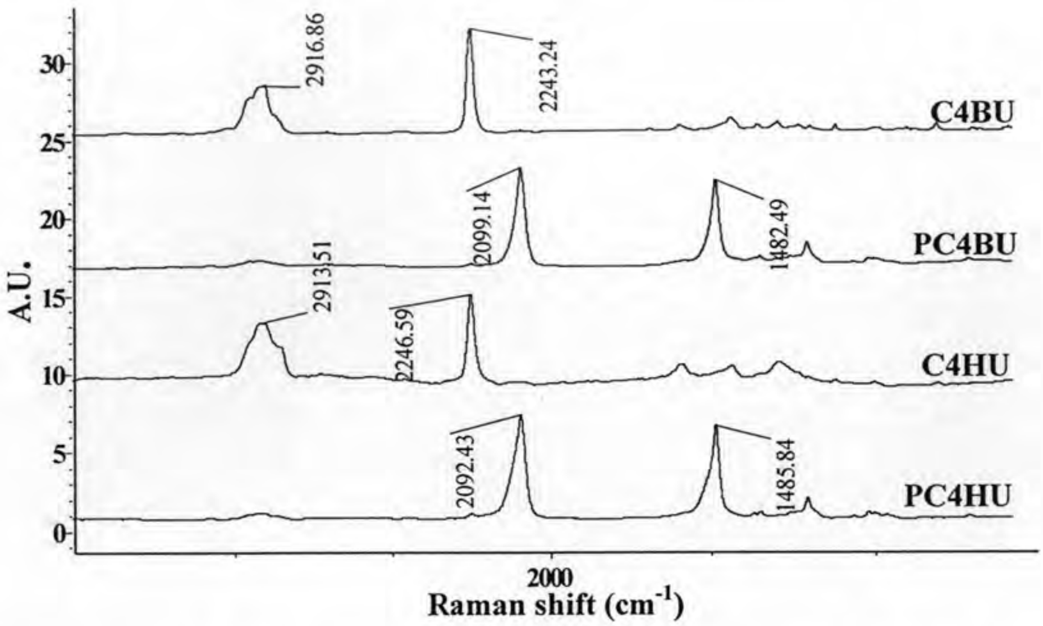


Figure 3.13 FT-Raman spectra of **C4BU**, **PC4BU**, **C4HU** and **PC4HU** (KBr pellet).

To study the change of hydrogen bond between the diacetylene monomer and polymer, FT-IR spectroscopic analysis was performed for monomers (**C4BU**, **C4BU″** and **C4HU**) comparing to polymers (**PC4BU**, **PC4BU″** and **PC4HU** after UV-irradiation, respectively). Polymers and monomers were determined at the peak of N-H (~3300 cm^{-1}) and C=O (~1700 cm^{-1}) (Figure 3.14). The N-H stretching band of monomers (**C4BU**, **C4BU″** and **C4HU**) at 3300 cm^{-1} became broader and extended into higher energy range upon polymerization into polymers (**PC4BU**, **PC4BU″** and **PC4HU**), indicated that monomer showed relatively stronger hydrogen bonding of C=O and H-N than polymer. According to hydrogen bonding diminution in polymer, it revealed that the conformation of polymer showed the changeable orientation and therefore it cannot promote the hydrogen bonding along the backbone.

The C=O stretching peak which is due to hydrogen bond among carbamate groups in polymer, is also very important in analyzing the orientation of the backbone because the vibrational direction of carbonyl bonds occur along the backbone. At C=O position, the peak of polymers (**PC4BU**, **PC4BU″** and **PC4HU**) definitely became broader than monomer (**C4BU**, **C4BU″** and **C4HU**) especially in **C4HU** and **PC4HU** and their positions also shifted to higher energy range upon polymerization into polymers. It implied that monomer showed relatively stronger hydrogen bonding of C=O and H-N than polymer.

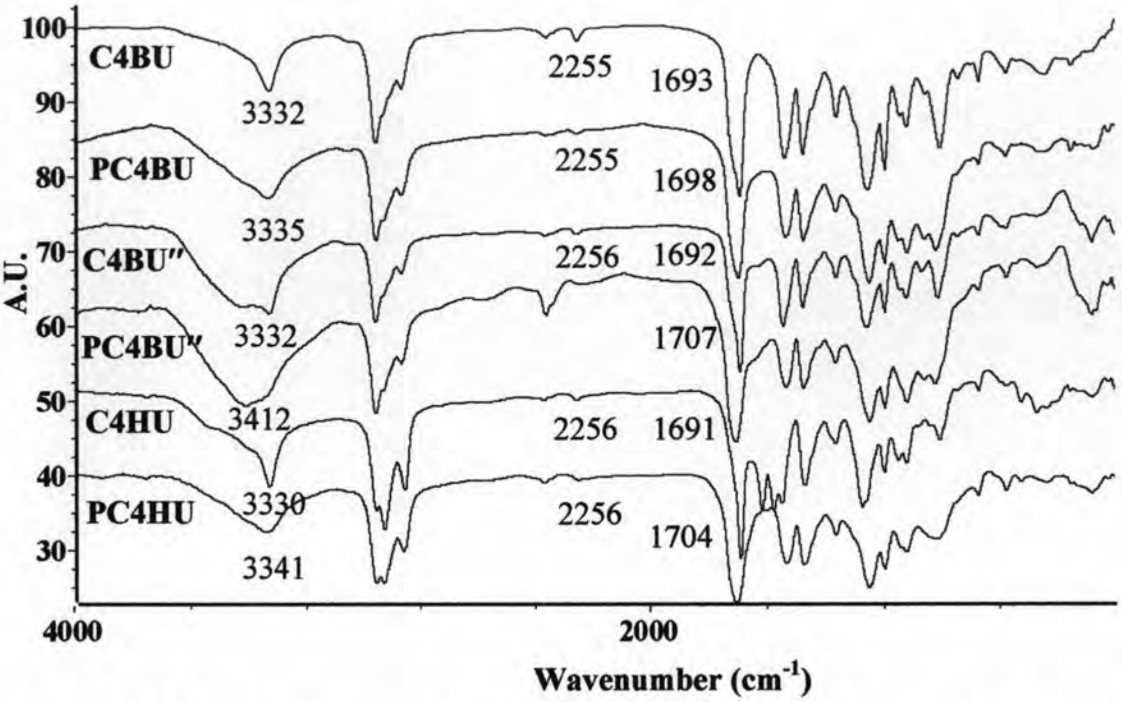


Figure 3.14 FT-IR spectra of **C4BU**, **PC4BU**, **C4BU''**, **PC4BU''**, **C4HU** and **PC4HU** (KBr pellet).

3.3 Nanostructure and thermal properties of the molecular assembly of the polydiacetylenes containing *tert*-butylcalix[4]arene

3.3.1 Nanostructures of molecular self assembly of PC4BU and PC4HU

- **Dynamic light scattering spectroscopy (DLS)**

PC4BU and **PC4HU** was not only well dispersed in THF, they could also disperse in water but not in hexane (Figure 3.15). As the structure of both **PC4BU** and **PC4HU** were mainly hydrophobic, it would be interesting to know structures of the molecular assembly of these polymers dispersed in water but not in hexane.

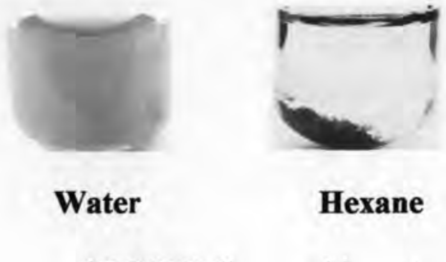


Figure 3.15 The appearance of **PC4BU** dispersed in water and hexane.

Dynamic light scattering (DLS) spectroscopy was used for measuring the average particle size and size distribution of **PC4BU** dispersed in water. **PC4BU** and **PC4HU** showed ranges of particle size with the average mean diameter of 192 and 188 nm, respectively (Figure 3.16). The DLS spectra of polymer showed several peaks, it implies that polymer formed in various particle sizes.

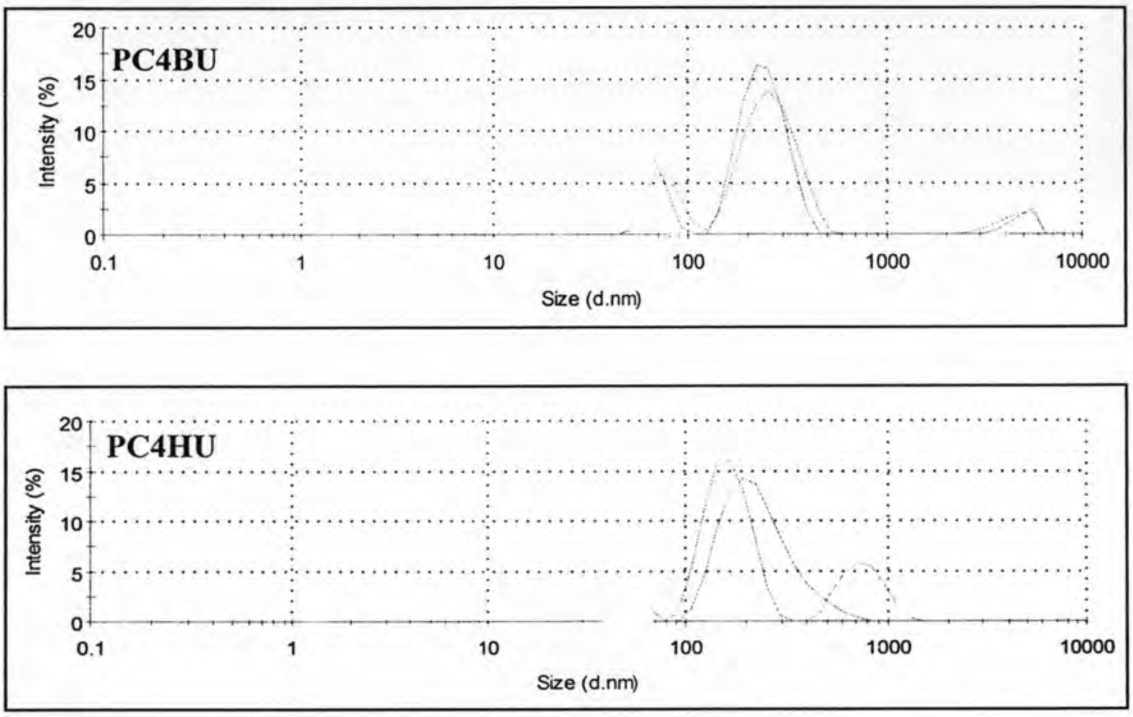
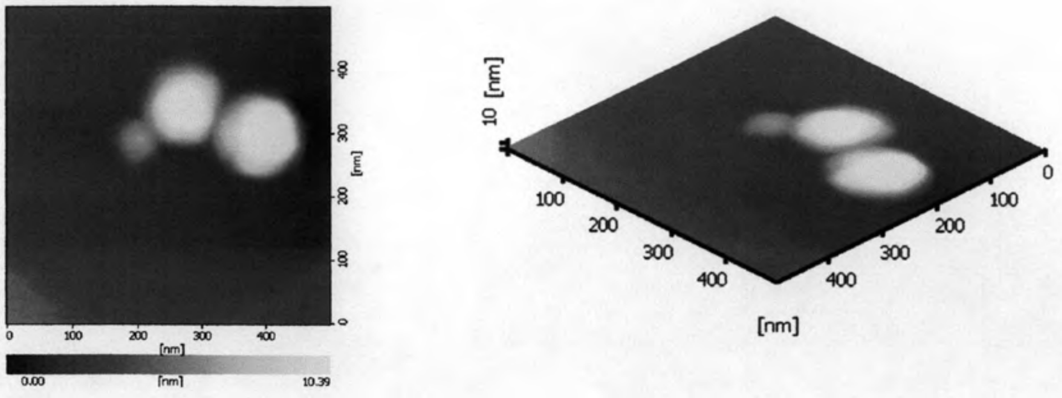


Figure 3.16 Dynamic light scattering (DLS) spectroscopy of **PC4BU** and **PC4HU**

- **Atomic force and transmission electron microscopy (AFM and TEM)**

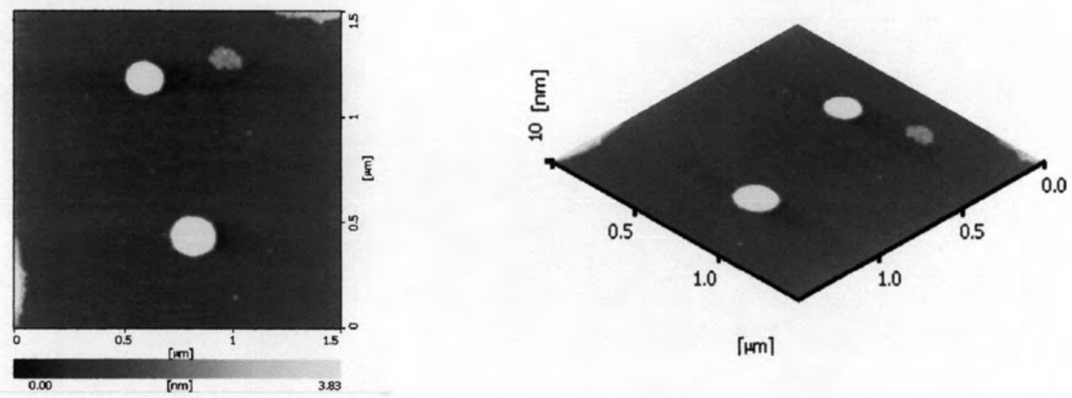
To realize the shape and confirm the size of assembly, the atomic force microscopy and transmission electron microscopy (AFM and TEM) were performed on the dry samples of the **PC4BU** and **PC4HU** disperse. The AFM and TEM images revealed that the assemblies were round with average diameter of 150 nm (Figure 3.17). The AFM 3D image also showed that the assembly was relatively flat, therefore, it indicated that the particles collapsed when water was evaporated.

PC4BU (AFM)



1D structure 3D structure

PC4HU (AFM)



1D structure 3D structure

PC4BU (TEM)

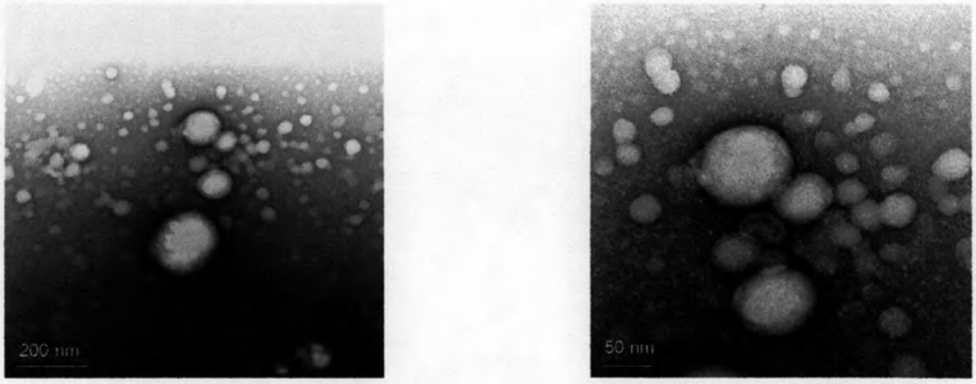


Figure 3.17 AFM images of **PC4BU** and **PC4HU** deposited upon mica slide and TEM image of **PC4BU** deposited on Formvar film coated copper grids (200 mesh), and stained with 2% uranyl acetate solution.

According to the corresponding evidences of dispersion in water and hexane, atomic force microscopy (AFM) and transmission electron microscopy (TEM) images, it implied that **PC4BU** most likely to arrange itself as an amphiphilic structure having hydrophobic and hydrophilic properties (Figure 3.18). The self assembly of polymers was proposed that the polymers with various chain lengths formed micelle which the hydrophilic head, carbamate group, turned to the outside contact with water surface and the hydrophobic tail, *tert*-butylcalix[4]arene, turned to the micelle center and led to the disk shape in water. From the stacking of many disks, the self assembly probably led to the nanodisk corresponding to the nanocircle in AFM image.

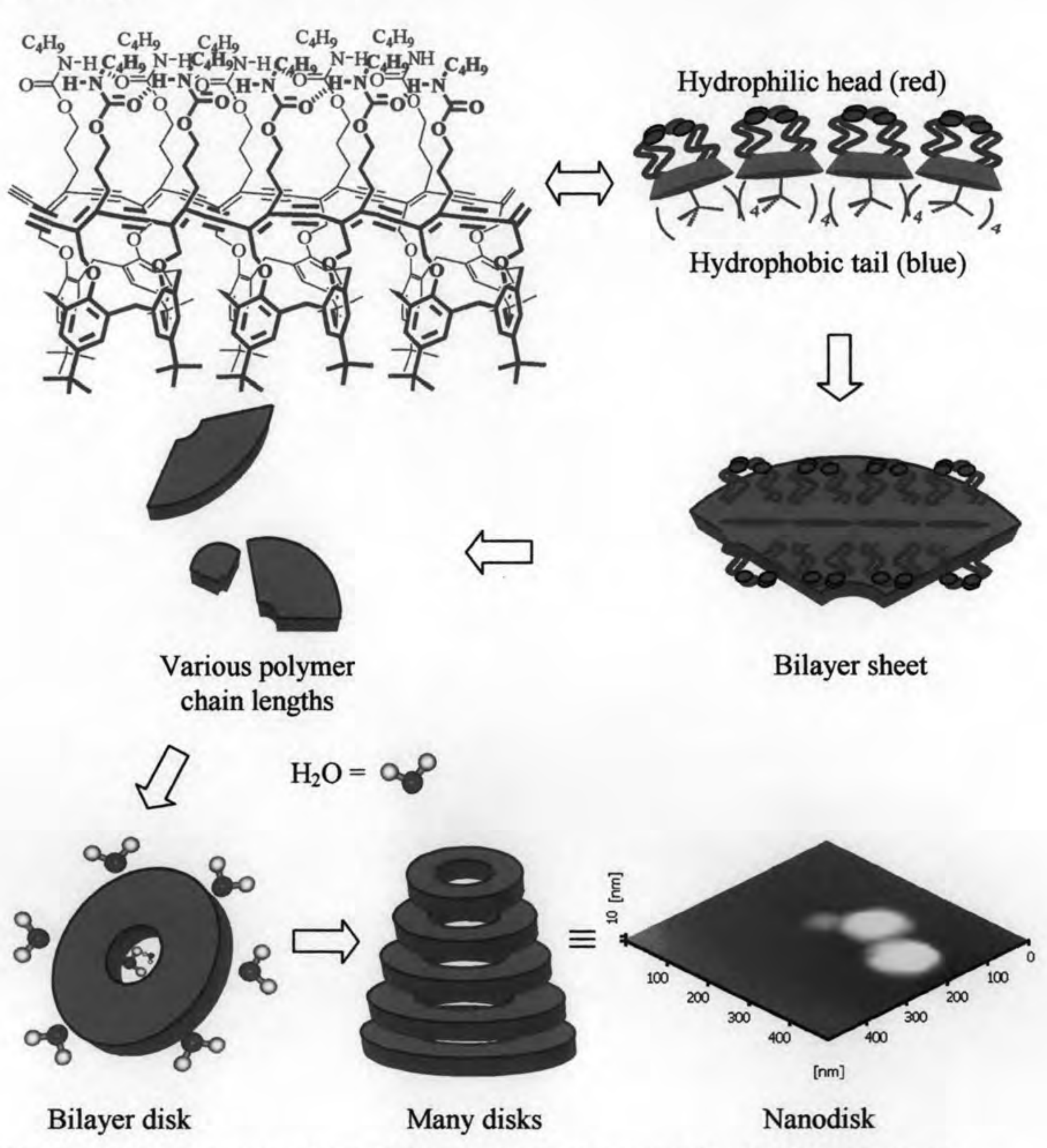


Figure 3.18 The representative of the proposed self assembly of **PC4BU** in water.

3.3.2 Thermochromic study

The color of polymer solutions (**PC4BU** and **PC4BU″**) in *N,N*-dimethylformamide changed from red to yellow when temperature was raised from 30 to 130 °C (Figure 3.19) with their maximum absorption undergoes gradual shifts from 510 to 420 nm. A single isobestic point of **PC4BU** and **PC4BU″** at 450 and 435 nm, respectively was observed upon heating implying that the quantitative conversion between two conformers (red and yellow) of the polymer (Figure 3.20). **PC4HU** was not conducted in thermochromisn study because of its low solubility in *N,N*-dimethylformamide.

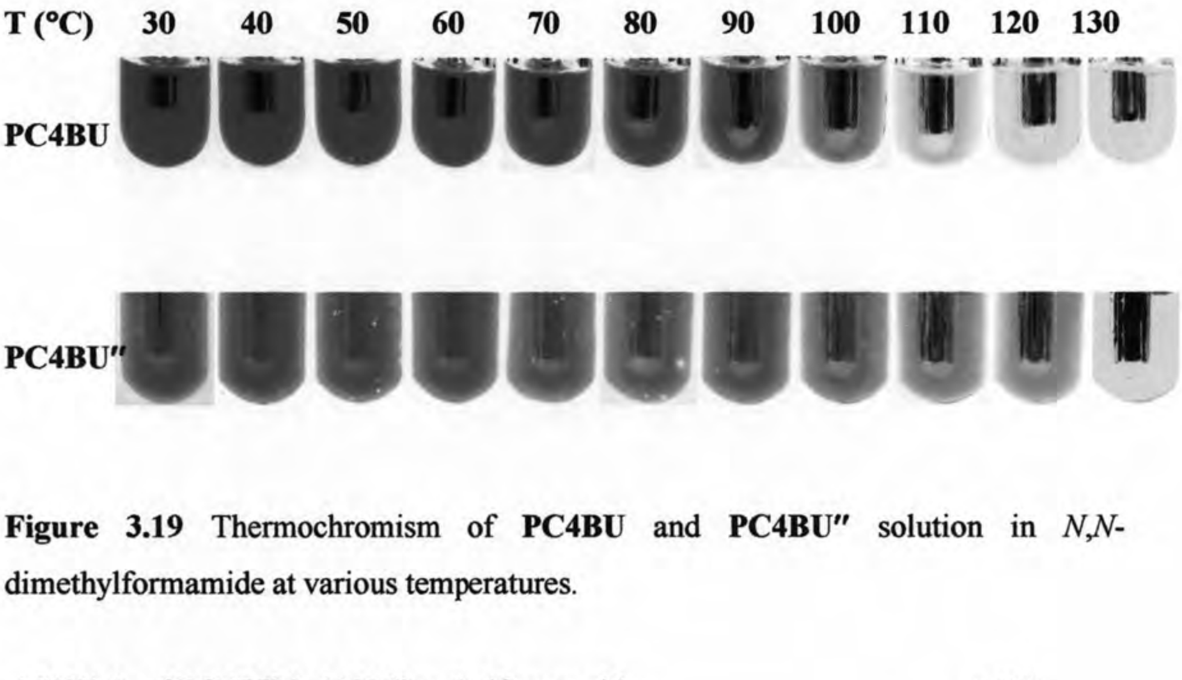
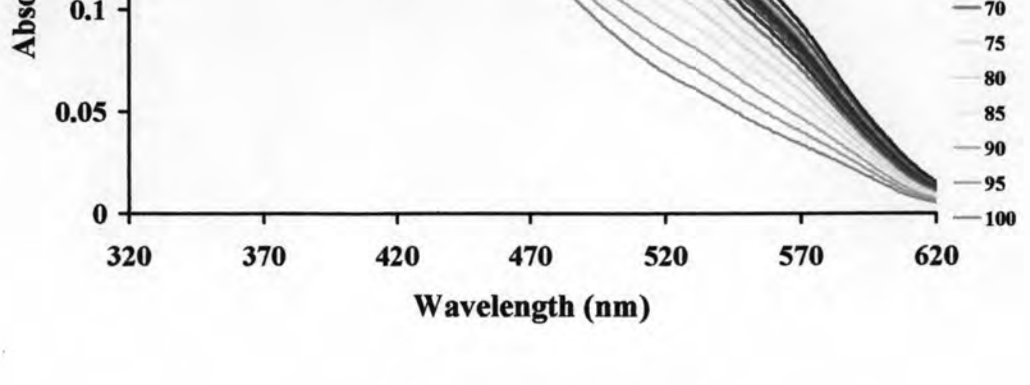
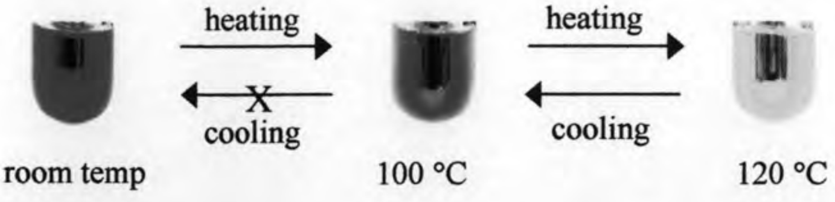


Figure 3.19 Thermochromism of **PC4BU** and **PC4BU″** solution in *N,N*-dimethylformamide at various temperatures.

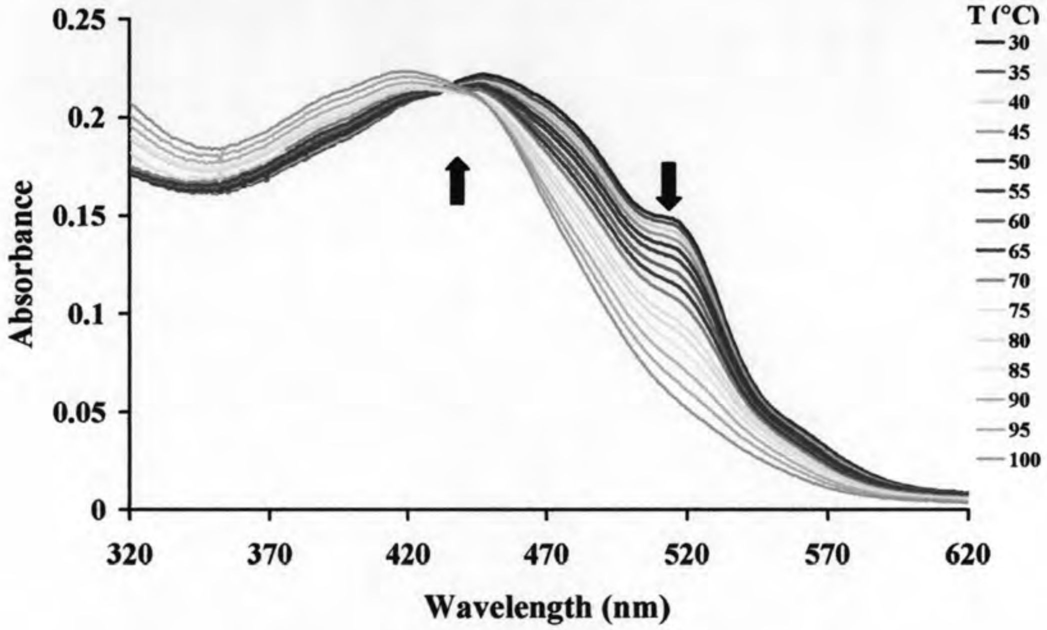
a) UV/vis of **PC4BU** in *N,N*-dimethylformamide



The reversibility of color change of **PC4BU** in *N,N*-dimethylformamide



b) UV/vis of **PC4BU″** in *N,N*-dimethylformamide



The reversibility of color change of **PC4BU″** in *N,N*-dimethylformamide

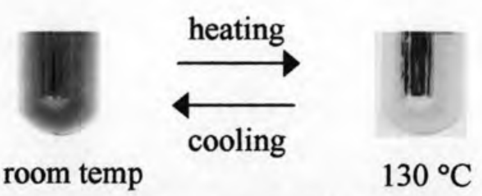


Figure 3.18 Visible absorption spectra and the reversiblity of color change of a) **PC4BU** and b) **PC4BU″** in *N,N*-dimethylformamide at various temperatures.

The color of polymers from red to yellow and orange to yellow for **PC4BU** and **PC4BU″**, respectively indicated the increases of the energy gap between the ground and excited states, presumably the HOMO and LUMO gap of the π-conjugated backbone. The increase in the energy gap of polymer is generally interpreted as the reduction of the conjugation length due to the twisting of the single bonds between the double and triple bonds. Another theory proposed for explanation of the increase of the energy gap is the relief of mechanical strain in the conjugated backbone [97].

It was noticeable that the thermochromic change of **PC4BU** exhibited reversible when it was heated up to the range of 100 °C as orange color, the complete recovery was obtained that it showed red color when it was cooled down to room temperature. Whereas the less recovery was obtained when it was heated above 100 °C as yellow color and cooled down to room temperature, the presence of orange color was observed. On the other hand, the yellow form of **PC4BU″** upon heating to 130 °C was totally reversible.

As a result, upon heating to 100 °C, the reversibility of orange color of **PC4BU** indicated that the orange form is just the thermodynamically unstable transition state of the red form which can be observed at higher temperature due to the increase of the entropic term (TΔS). In contrast, the yellow form appeared to lack the reversibility evidenced by the absorption spectra at the temperature above 100 °C. The irreversibility of the yellow color was described that the yellow form is the most thermodynamically stable form among the orange and red forms probably due to the gain in entropy (positive ΔS) and relieve of the backbone strain (negative ΔH) [98] to overcome for some lost of the hydrogen bonding. Most of the hydrogen bonds probably recover but not to the same orientation as those in the red form upon cooling.

The reversibility of yellow form of **PC4BU″** was however present upon heating to 130 °C, it confirmed that the yellow form is the thermodynamically unstable transition state of the orange form due to the same explanation as the orange form of **PC4BU**. Hence the most of the hydrogen bonds was supposed to totally recover to the same orientation as those in orange form.