SYNTHESIS OF SOME POLYDIACTYLENE ESTERS

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ABSTRACT

Some diacetylene ester compounds(1-13) were prepared using the well known coupling procedures. These diacetylenes monomers were polymerized by the topochenical process using UV irradiation. The resulted polymers (14-26) were found to be insoluble in all common organic solvents. The monomers were identified by IR,NMR and Mass measurements while the polymers were identified depending on their physical changes(due to insolubility) and the identification of their oligomers by Mass and NMR measurments.

Keywords*: *Polydiactylene, ester

INTRODUCTION

Usually diacetylene compourds polymerize by heat ,X-ray ,Gama ray and UV light (Lee, H.J *et al* 1995) . Some researchers succeeded in preparing polydiacetylenes containing heterocyclic ring such as purine and pyrimidine . These polymers were found to have lader like structure through the study of the,X-ray , raman spectroscopy and ^{13}C NMR magic angle (Sixi, H. and Neumann ,W 1985) ,It was found that polydiacetylenes characterized by color change due to the reaction of the end groups along the single bond of the enyne system (Huo and Russell K.C 1999) and the aggregation of the segment associated by the hydrogen bonding along the polymer chains. The conjugation of the л -electrons of the enyne system also effected by the segment which cause color change and also this conjugation along the polymer chains create an electrical conduction properties for these polymers (Dai, X. *et al* 2004) . Some researchers also studied the electrical properties of the helical structure of polydiacetylenes in solution (Lewis, C.A. and Tykwinski R.R 2006) .Poly diacetylenes were also prepared using gell method employing 10,12-patacosediynoic acid and certain gelator were used for the preparing helical fiber organogel in presence of Zn salt. This helix changes its color from blue to red according to PH changes (Pengfei, D *et al* 2009) . According to the above facts ,Polydiacetylenes found Versatile industrial and medical applications (Itoh, C. 1999 , Guk *et al* 1997 , Carpick *et al* 2004 , Yarimoga *et al* 2010) Among the medical application of polydiacetylenes are the Antimicrobial biosensors,diabetic biosensors (Wyrsta et al 2001) and diseases diagnosis (Gros *et al* 1981 , Okada *et al* 1999 , Jonas *et al* 1999, Stanish, I. and A.Singh 2001). Nano poly diacetylenes nowadays used as biosensors (Yoon *etal* 2009, Jahnke *et al* 2009) and the new studies in this field is growing dramatically and for this reason we design our work.

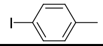
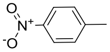
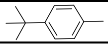
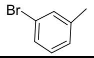
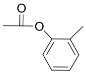
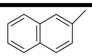
Experimental :

Melting points were measured using Galinkam HIS$_{91}$, TC$_{92}$ controller,IR spectra were measured by FT.IR,205,ATR Dimond Perkin Elmar spectrometer in Sheffield university U.K. The monomers were irradiated using UV /visible spectrophotometer, Hitachi V-2010 Double Beam operating at 245-366 nm. The molecular weights were measured by Perkin Elmer Turbo mass spectrometer, Pc-SMs Capillary column of Sheffield University.^{1}H ,^{13}CNMR were measured using Bruker AMX 400 MH$_z$. phthalyalanine was prepared according to the published procedure (Vogels, I. 1956) .The Substituted aroyl chloride (i$_1$-i$_7$) were also prepared according to the published procedure (Gilman et al 1941, Horning et al 1955, Normaa et al 1963, Takeshi, A. and S.Kikamasa 1967, Stensuud *et al* 1971, Charls, F. and F.Mary 1995, Xin-yan et al 1998) hile 2,4-Hexadiyne -1,6-diol was prepared following a new published procedure (Dafeng *et al* 2008) . N-Acetyl amino acids (i$_8$-i$_{11}$) were prepared according to the literature procedure (Kuvaeva et al 2010, Dewitt, H.D. and A.W.Ingersoll 1951, Stanley, R. and Wolf, K 1968) .2,7-Dimethyl-3,5-Ocadiyne-2,7-diol was prepared according to the well known procedure (Louis, F. and Kenneth W, 1983) .

General method for the preparation of compounds (1-6)

2,4-Hexadiyle-1,6-diol(1.32g,0.012 mol.) was dissolved in 15ml dry THF. This solution was then added to a mixture of 0.024mol substituted aroyl chloride compounds (1-6) in 20ml drytetrahydrofuran(THF) . To the final solution was added a solution of triethylamine (TEA) 3.5ml 0.025 mol in 15 ml dry THF drop-wise at zero temperature with occasional stirring for about 15min in dark place. The mixture was then refluxed for 3 hrs under nitrogen atmosphere , after cooling the solution was added to 150ml of cold distilled water . The mixture was then filtered off under dark condition . The precipitate was dissolved in 100 ml $CHCl_3$ and then washed with 300ml of saturated sodium bicarbonate solution(3 times) then with water and dried over anhydrous $MgSo_4$. Removal of the solvent under reduced pressure gave a crude product which on recrystalliztion from chloroform\ hexane (15:85%), a pure compounds were obtained Table(1)

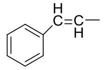
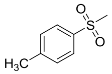
Table (1) : Physical properties of compounds 1-6

Comp. No.	Aromatic	Color	Yield (%)	M.P (°C)	Molecular weight		
					Mol Form	Calc	Meas
1		**White**	**70**	**148-150**	$C_{20}H_{12}I_2O_4$	**570.04**	**570**
2		**Pale yellow**	**62**	**137-139**	$C_{20}H_{12}N_2O_8$	**408.24**	**408**
3		**Pale yellow**	**50**	**75-77**	$C_{28}H_{30}O_4$	**430.24**	**430**
4		**Pale yellow**	**74**	**140-142**	$C_{20}H_{12}Br_2O_4$	**476.048**	**476**
5		**Yellow**	**53**	**177-179**	$C_{24}H_{18}O_8$	**434.24**	**435**
6		**Pale gray**	**95**	**131-133**	$C_{24}H_{18}O_8$	**418.36**	**418**

Synthesis of 2,7-Dimethyl-3,5-Octadiyne -2,7-Bis cinnmate or para toluenesulfonate (7,8)

2,7-Dimethyl-3,5-octadyne-2,7-diol (2.09,0.012 mol) dissolved in 10ml dry THF was added to a mixture of cinnamoyl chloride (0.024 mol.) or para toluene sulfonyl chloride in 20 ml of dry THF. To the final mixture was added drop-wise a mixture made of (2.55g,0.025 mol.) TEA in 10ml or dry THF. Working up following the general procedure affords the final product. The product was purified by recrystallization from ethylacetae petroleum ether mixture 20:80 respectively . The physical properties are indicated in Table(2).

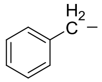
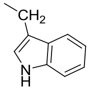
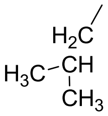
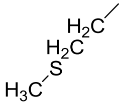
Table (2) : Physical properties of compounds 7,8

Comp. No.	R	Color	Yield (%)	M.P (°C)	Molecular weight		
					Mol Form	Calc.	Meas.
7		**Pale yellow**	**55.0**	**124-125**	$C_{28}H_{26}O_4$	**426**	**424**
8		**White**	**61.0**	**93-95**	$C_{24}H_{26}O_6S_2$	**474.4**	**475**

Synthesis of 2,7-Dimethl-3,5-Octadiyne-2,7-Bis(N-acetyl) amino acid esters (9.12)

Aminoacidesters(0.005mol.)in a solution of dry(THF),(30ml),4-N,N-dimethylaminopyridine (DMAP),(0.005mol.) and dicyclohexyl carbodiimide (DCC) (1.14g,0.0005 mol.) were mixed together at r.t. To the final mixture a solution of 2,7-dimethyl-3,5-Octalyne-2,7-diol in 20 ml of dry THF was added drop-wise. The mixture was stirred in dark place for 24 h. The solvent was evaporated under reduced pressure. The crude product was dissolved in DCM(50 ml) then it was filtered off and washed with 5% acetic acid three times. The organic layer was dried on anhydrous $NaSo_4$. The final product was purified by silicagel clumn chromatography (Table 3).

Table (3) : Physical properties of compounds 9-12

Comp. No.	R	Color	Yield (%)	M.P (°C)	Molecular weight			ES	
					Mol Form	Calc	Meas	Solvent Mixture	Ratio
9		Pink	57	61-63	$C_{32}H_{36}N_2O_6$	544.7	544.30	THF	Only
10		Pale brown	61	98-100	$C_{36}H_{38}N_4O_6$	622.76	624.4	Ethyl acetate Petroleum Ether	5:1
11		White	40	49-51	$C_{26}H_{40}N_2O_6$	476.66	478.4	Ethyl acetate Petroleum Ether	1:1
12		Pale yellow	44	56-58	$C_{24}H_{36}N_2O_6S_2$	512.5	518.2	Ethyl acetate Petroleum Ether	2:1

Synthesis of 2,7-Dimethyl-3,5-octodiyne-2,7-7 Bis Phthalyl alanine ester (13)

Phthalyl alanine (A_{18}) (1.19,0.005 mol) in 30ml THF ,0.61g,0.005 mol of DMAP and(1-14g,0.0055 mol) of DCC were mixed together at r.t in dark place. Working up as above. The product was purified by silica gel column using ethyl acetate as the mobile phase. A pure compound of the diyne (1.2g) was obtained, mp. 68-70 C^0. The molecule weight was 568g/mol. The calculated one was 568.62. The yield of the comp was 84%.

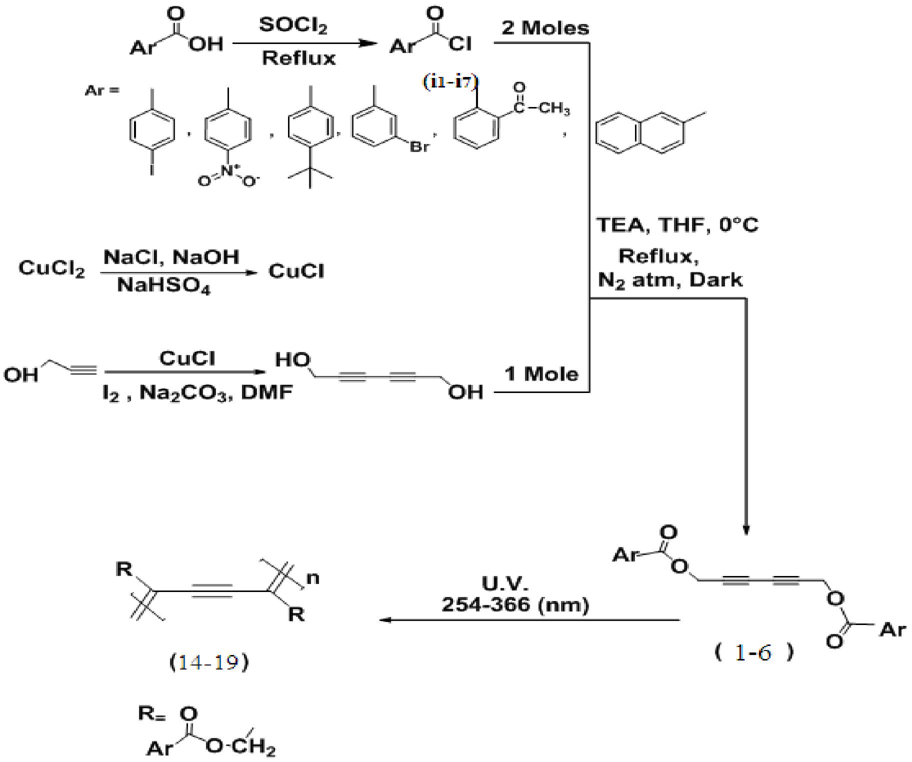
Synthesis of streo regular diacetylene polymers by radical polymerization

General method

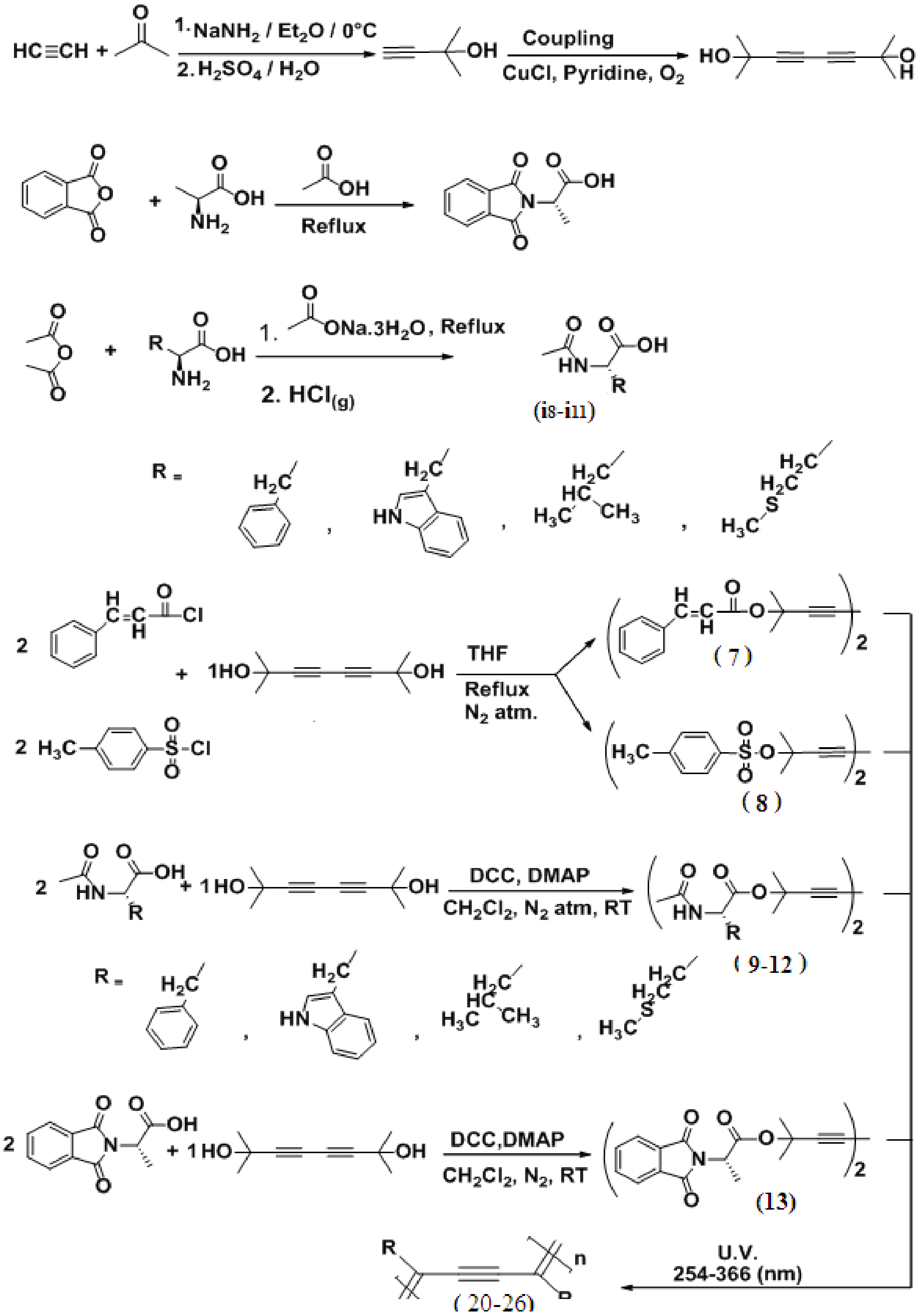
Diacetylene compound (0.01 mol) was irradiated by UV light source operating on wave length (254-366 nm) for 5 h . The irradiation was stopped each one hour. After irradiation the compound was washed with chloroform, filtered . The physical properties of the polymers were indicated in Table(4).

Table (4) : Physical properties of polymers 14-26

Polymer No	Radiation Time (h)	Conversion (%)	Color	M.P (°C)
14	40	82	Yellow	216-217
15	40	60	Deep yellow	203-205
16	45	57	Deep yellow	140-142
17	30	80	Deep yellow	210-211
18	25	63	Violet	245-247
19	40	86	Deep gray	199-201
20	30	72	Deep yellow	164-165
21	25	85	Deep gray	138-140
22	20	74	Yellow	170-173
23	25	78	Deep yellow	207-210
24	45	61	Pale yellow	110-112
25	45	59	Yellow	117-120
26	40	76	Pale yellow	161-163


SOCl2
Reflux
(i1-i7)
2 Moles
Ar =
TEA, THF, 0°C
Reflux,
N2 atm, Dark
CuCl2
NaCl, NaOH
NaHSO4
CuCl
CuCl
I2 , Na2CO3, DMF
1 Mole
U.V.
254-366 (nm)
(14-19)
(1-6)
R=

Scheme (1)


HC≡CH +
1. NaNH2 / Et2O / 0°C
2. H2SO4 / H2O
OH
Coupling
CuCl, Pyridine, O2
HO
OH
Reflux
N
1. ONa.3H2O, Reflux
2. HCl(g)
R
NH2
HN
(i8-i11)
R =
H2C
HN
HC
H3C
CH3
S
Cl
THF
Reflux
N2 atm.
1HO
(7)
(8)
DCC, DMAP
CH2Cl2, N2 atm, RT
(9-12)
DCC,DMAP
CH2Cl2, N2, RT
(13)
U.V.
254-366 (nm)
n
(20-26)

Scheme 2

RESULTS AND DISCUSSION

Substituted aroyl chlorides were synthesized by addition of thionyl chloride to corresponding carboxylic acid. The physical properties were in an agreement with the published one .The ^{1}HNMR of these compounds indicate the absence of the signal 10.3ppm belongs to carboxylic protons. The 2,4-Hexadiyle-1,6-diol compound was prepared according to new coupling procedure as mentioned in the experimental part (Dafeng *et al* 2008). The IR spectrum of this compound shows absorption band at 3302 Cm^{-1} related to the OH group while the -C≡C- appeared at 1200 Cm^{-1} , Other absorption bands are shown it Table(5). The NMR spectrum shows singlet signal at 3.6ppm related to OH and of 4.28 ppm belongs to -CH2- appeared as singlet signal .Table (6).The melting point was found identical with published one (Reppe, W. and E. Keyssner 1987).

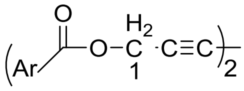
2,4-Hexadiylne-1,6-Bis substituted aryl or ß – naphthyl ester (1-6)

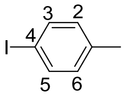
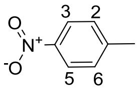
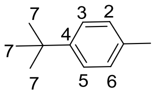
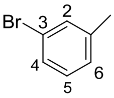
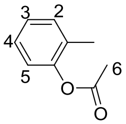
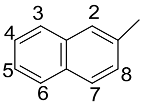
The above compounds were prepared according to the procedure mentioned in the experimental part from Aroyl chloride and 2,4-Hexadiyne-1,6-diol. Scheme (1). The compounds were identified by a combination of Mass, IR and NMR measurements. The IR spectra indicate the presence of absorption bands between 2150-2188 Cm^{-1} belongs to -C≡C- and at (1718-1732 Cm^{-1}) for -C=O of ester group ,Other bands are shown in Table(5). The ^{1}HNMR spectra showed the following signals: 4.97-5.07 ppm belongs to -CH$_2$- as singlet signal and the aromatic protons indicated in Table(6). ^{13}CNMR showed signals at 52.58-5.35 ppm related to C$_3$ and signals at 163.49-165.8 ppm related C$_4$. The detail is indicated in Table(7).

Table (5) : IR data of compound 1-6 and the1,6- diol compound

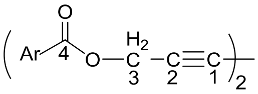
Comp. No.	IR, ʋ (cm^{-1})						
	O—H (Str.)	C—H (Str.)		C≡C (Str.)	C=O (Str.)	C=C , C⋯C (Str.)	C—O (Str.)
		Aromatic	Aliphatic				
1,6 Diol	**3302**	**---**	**2929**	**2120**	**---**	**---**	**1034**
1	**---**	**3074**	**2930**	**2164**	**1721**	**1584,1572**	**1006**
2	**---**	**3112**	**2870**	**2154**	**1732**	**1608,1595**	**1090**
3	**---**	**3065**	**2962**	**2150**	**1723**	**1608,1570**	**1091**
4	**---**	**3096**	**2932**	**2188**	**1731**	**1614,1591**	**1106**
5	**---**	**3080**	**2942**	**2173**	**1718**	**1607,1579**	**1074**
6	**---**	**3060**	**2935**	**2160**	**1726**	**1628,1597**	***1086***

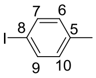
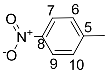
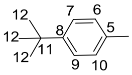
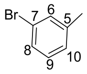
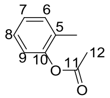
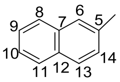
Table (6): ^{1}HNMR data of compounds 1-6 and 1,6 Diol



Comp. No.	Ar	^{1}H-NMR, δ(ppm) CHCl$_3$
1,6 Diol	**H**	**3.6(s,1H) C_1-OH, 4.28(s,2H) C_1-H**
1		**5.0(s,2H) C_1-H, 7.79 (d,2H) C $_{2,6}$-H, 7.92 (d,2H) $C_{3,5}$-H**
2		**5.06(s,2H) C_1-H, 8.25 (d,2H) C $_{2,6}$-H ,8.32 (d,2H) $C_{3,5}$-H**
3		**1.35(s,9H) C_7-H , 5.0(s,2H) C_1-H ,7.48 (d,2H) $C_{3,5}$-H, 7.99(d,2H) C $_{2,6}$-H**
4		**5.01(s,2H) C_1-H, 7.36(t,1H) C_5-H,7.73 (d,1H)C_4-H, 7.99(d,1H) C_6-H, 8.22(s,1H) C_2-H**
5		**2.4(s,3H) C_6-H,4.97(s,2H) C_1-H,7.15 (t,1H) C_4-H ,7.35 (t,1H) C_3-H, 7.62(d,1H) C_5-H, 8.09 (d,1H)C_2-H**
6		***5.07(s,2H) C_1-H, 7.53 (t,2H) $C_{4,5}$-H, 7.67 (d,3H) $C_{3,6,7}$-H, 7.99(d,1H) C_8-H, 8.63(s,1H) C_2-H***

Table(7):^{13}CNMR data of compounds 1-6



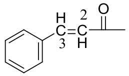
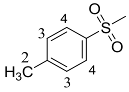
Comp. No.	Ar	^{13} C-NMR, δ(ppm) CHCl$_3$
1		**52.96 C_3, 70.67C_1, 73.59 C_2, 101.49 C_5, 128.62 C_8, 131.73 $C_{6,10}$,138.40 $C_{7,9}$, 165.18 C_4**
2		**53.52 C_3 ,70.95 C_1,73.32 C_2,123.68 $C_{7,9}$,131.01 C $_{6,10}$, 134.45 C_5 ,150.85 C_8 , 163.79 C_4**
3		**31.09 C_{12}, 35.15 C_{11} , 52.58 C_3 ,70.46 C_1 ,73.84 C_2 ,125.67 $C_{7,9}$,126.39 C_5 , 130.14 $C_{6,10}$, 157.20 C_8 , 165.65 C_4**
4		**53.10 C_3 ,70.75 C_1 ,73.52 C_2 ,122.58 C_7 ,128.43 C_{10} ,130.07 C_9 ,131.06 C_6 ,132.82 C_5 ,136.44 C_8 ,164.33 C_4**
5		**21.02 C_{12}, 52.94 C_3, 70.78 C_1, 73.51 C_2, 122.31 C_5, 123.97 C_9, 126.15 C_7,132.06 C_6,134.47 C_8,150.83 C_{10},163.49 C_4,169.73C_{11}**
6		***52.93 C_3, 70.72 C_1, 73.98 C_2, 125.19 C_{14},126.12 C_9, 126.80 C_{11}, 127.81 C_5, 128.32 C_{13}, 128,56 C_{10}, 129.46 C_8, 131.59 C_6, 132.42 C_7, 135.72 C_{12}, 165.80 C_4***

2,7-Dimethyl-3,5-Ocadiyne-2,7-Bis Cinnamate and para toluene sulfonate(7,8)

The above two compounds were identified by the combination of Mass,IR and NMR methods. IR spectrum of comp (7) showed absorption band of 2160 Cm^{-1} for -C≡C- and 1764 Cm^{-1} belongs to C=O ester and 1147,1170 Cm^{-1} for SO_2 symmetric and non symmetric stretch.^{1}HNMR showed the following signals: 2.2 ppm for C_1 ,7.5,7.6 ppm for aromatic protons ppm .

compound (8) showed the following signals: 1.54 for $C_{1,}$ 7.43,7.94 ppm for aromatic protons, Other signals are indicated in Table(8). ^{13}CNMR showed signal of 160.6 ppm for C=O of comp (7) and other resonated signal at 21.8 ppm belongs to C_{11} of compound (8).

Table (8) :^{1}HNMR data of compounds 7,8

Comp. No.	**R**	**^{1}H NMR, δ(ppm) $CHCl_3$**
7		**2.2 (s,6H) C_1-H, 6.55 (d,1H) C_2-H, 7.54 (m,5H) Ar-H, 7.88 (d,1H) C_3-H,**
8		***1.54 (s,6H) C_1-H, 2.51 (s,3H) C_2-H, 7.43 (d,2H) C_3-H, 7.94 (d,2H) C_4-H***

N-Acetyl amino acids (i_8-i_{11})

These compounds were checked by IR,^{1}HNMR and were found in agreement with the published one.

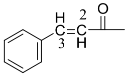
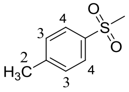
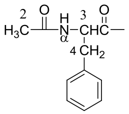
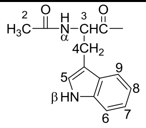
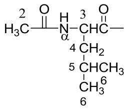
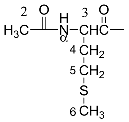
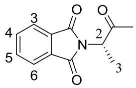
2,7-Dimethyl-3,5-Octadiyne-2,7-Bis(N-acetyl amino acid esters) (7-13)

The above compounds (scheme 2) were prepared from the reaction of N-Acetyl amino acids **(i_8-i_{11})** with Octadiyne-2,7-Diol as mentioned in the experimental part of this work. These compounds were identified by combination of Mass, IR and NMR methods. The IR showed absorption bands at 2150-2164 Cm^{-1} for -C≡C- and at 1694-1704 Cm^{-1} for C=O ester and 1639-1659 Cm^{-1} for C=O amide group while the other bands can be shown in Table (9). ^{1}HNMR spectra showed the following resonating signals: 1.52-2.12 ppm for C_1 and of 1.83-2.04 ppm for C_2 for all compounds. Other signals can be shown in Table (10). ^{13}CNMR gave the following signals: 21.5-24.1ppm for C_8 and 166.97-174.9 ppm for C5 of the above compounds. The detail signals are indicated in Table (11).

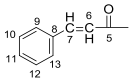
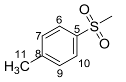
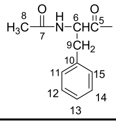
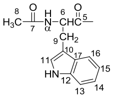
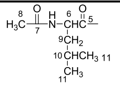
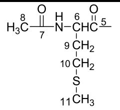
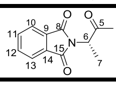
Table(9) : IR spectral data of compounds 7-13

Comp. No.	IR, υ (cm^{-1})								
	$N-H$ **(Str.)**	$C-H$ **(Str.)**		$C\equiv C$ **(Str.)**	$C=O$ **(Str.)**		**Aromatic** $C=C$, $C\cdots C$	$N-H$ **Ben.)(**	**Others (Str.)**
		Aromatic	**Aliphatic**		**Ester**	**Amide**			
7	---	3028	2983	2160	1764	---	1600 1578	---	1631, $C=C$
8	---	3111	2982	2159	---	---	1592 1538	---	1147،1170 O=S=O
9	3302	3031	2933	2162	1704	1643	1608 1586	1530	---
10	3283	3063	2928	2164	1697	1644	1599 1559	1536	1634, $C=C$
11	3276	---	2958	2156	1694	1659	---	1528	---
12	3272	---	2928	2164	1701	1639	---	1532	---
13	---	3020	2930	2120	1713	---	1646 1598	---	*Imide,* $C=O$ *1780،1745*

Table(10) : ^{1}HNMR spectral data of compound 7-13

Comp. No.	R	^{1}H NMR, δ(ppm) $CHCl_3$
7		**2.2 (s,6H) C_1-H, 6.55 (d,1H) C_2-H, 7.54 (m,5H) Ar-H, 7.88 (d,1H) C_3-H,**
8		**1.54 (s,6H) C_1-H, 2.51 (s,3H) C_2-H, 7.43 (d,2H) C_3-H, 7.94 (d,2H) C_4-H**
9		**1.52 (s,6H) C_1-H, 1.83 (s,3H) C_2-H, 2.98(d,2H) C_4-H, 4.35(t,1H) C_3-H, 7.34 (m,5H) Ar-H, 8.82 (s,1H)Nα-H**
10		**1.54 (s,6H) C_1-H, 1.93 (s,3H) C_2-H, 3.24(d,1H) C_4-H, 4.22 (t,1H) C_3-H, 7.20 (t,2H) $C_{7,8}$-H, 7.26 (s,1H) C_5-H, 7.37 (d,1H) C_6-H, 7. 60 (d,1H) C_9-H, 8.53(s,1H)Nα-H, 10.43(s,1H)$N_β$-H**
11		**0.97 (d,6H) C_6-H,1.25 (m,1H) C_5-H, 2.0(s,3H) C_2-H, 2.03(t,2H) C_4-H,2.12(s,6H) C_1-H ,4.22 (t,1H) C_3-H, 8.52(s,1H) Nα-H**
12		**1.52 (s,6H) C_1-H, 2.04(s,3H) C_2-H, 2.12(s,3H) C_6-H, 2.15 (q,2H) C_4-H,2.54 (t,2H) C_5-H,4.15 (t,1H) C_3-H, 8.54 (s,1H)Nα-H**
13		***1.53 (s,6H) C_1-H, 1.64(d,3H) C_3-H, 5.2-5.6(q,1H) C_2-H, 7.83-7.89 (m,4H) Ar-H***

Table(11) : ^{13}CNMR spectral data of compound 7-13

Comp. No.	R	^{13}C NMR, δ(ppm) $CHCl_3$
7		**30.94 C_4,76.73 C_3,77.05 C_1,77.37 C_2,116.76 C_{11},128.60 $C_{9,13}$, 129.09 $C_{10,12}$, 131.30 C_8, 133.74 C_7,148.67C_6 162.50 C_5**
8		**21.8 C_{11}, 31.04 C_4, 65.59 C_3, 66.34 C_1, 83.94 C_2, 127.06 $C_{6,10}$, 130.23 $C_{7,9}$,141.71 C_8, 146.79 C_5,**
9		**21.5 C_8, 29.6 C_4, 35.5 C_9, 53.4 C_6, 64.0 C_3,67.79 C_1, 83.3 C_2, 126.0 C_{13}, 126.9 $C_{11,15}$, 127.9 $C_{12,14}$, 134.91C_{10}, 174.90 C_5, 175.41 C_7**
10		**24.18 C_8,29.33 C_4,30.03 C_9,58.92 C_6, 64.30 C_3,67.17 C_1, 83.21C_2, 108.81 C_{10}, 110.47 C_{13}, 117.47 C_{16}, 118.47 C_{15} 121.17 C $_{14}$, 122.38 C_{11}, 127.78 C_{17}, 135.46 C_{12}, 166.97 C_5 ,170.32 C_7**
11		**22.82 C_{11}, 23.48 C_8, 24.81 C_{10}, 27.90 C_4, 40.54 C_9, 50.52 C_6, 67.14 C_3, 67.63 C_1,85.45 C_2, 169.30 C_5, 172.62 C_7**
12		**14.52 C_{11}, 21.73 C_8, 23.82 C_4, 29.13 C_{10}, 31.74 C_9, 53.82 C_6 64.25 C_3, , 68.41 C_1, 84.38 C_2, 169.55 C_5, 170.72 C_7**
13		***14.32 C_7, 27.65 C_4, 54.89 C_6, 64.37 C_3, 67.94 C_1, 83.83 C_2, 122.46 $C_{10,13}$, 130.13 $C_{9,14}$, 133.16 $C_{11,12}$,166.30 $C_{8,15}$, 168.46 C_5***

2,7-Dimethyl-3,5-Octadiyne-2,7-Bis (phthalyl alinine ester) (13)

This compound was confirmed by Mass, IR and NMR methods. IR spectrum showed absorption band at 2120 Cm^{-1} for C≡C and 1780,1745 Cm^{-1} for C=O phthalimide and 1713 for C=O ester ,see Table (9). ^{1}HNMR showed the following signals: 1.53 ppm for C_1 as singlet signal ,1.64 ppm for C_3 (doublet) and 5.2-5.6 ppm belongs to C_2 as quartet, see Table (10). ^{13}CNMR showed the following resonating signals : 14.32 ppm , 27.65 ppm for C_4 and 168.46 ppm for C_5 , Other resonating signal could be seen in Table (11).

Poly 2,4-Hexadiyn -1,6-Bis Substituted Aryl and ß -Naphthyl ester (14-19)

The above polydiacetylen compounds (scheme 1) were insoluble in all common solvents. The structure of these polymers was confirmed according to IR spectra Table (12) which indicate the absence of -C≡C- stretching due to the symmetry of the enyne system (Qasim, A.A. 2011) and the Mass study of the olegomers formed during the progress of the reaction in early stages. These olegomers were soluble and their molecular weights were measured Table (13). ^{1}HNMR spectra revealed that the protons of the repeating units are in agreements with protons of the monomers chemical shifts with very small difference due the new polymer structure.

Table 12: IR spectral data of compounds 14-19

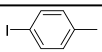
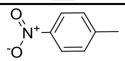
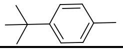
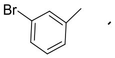
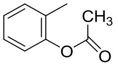
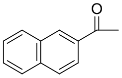
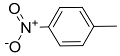
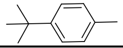
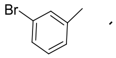
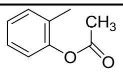
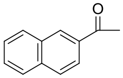
Polymer No.	**R**	IR, υ (cm^{-1})				
		C—H (Str.)		C=O (Str.)	C=C , C≡C (Str.)	C−O (Str.)
		Aromatic	Aliphatic	Ester	Aromatic	
14		**3055**	**2930**	**1722**	**1584,1572**	**1007**
15		**3111**	**2833**	**1733**	**1608,1595**	**1092**
16		**3092**	**2965**	**1719**	**1608,1570**	**1094**
17		**3096**	**2931**	**1729**	**1614,1591**	**1105**
18		**3072**	**2940**	**1752,1717**	**1593,1579**	**1072**
19		**3060**	**2935**	**1709**	**1628,1597**	***1086***

Table 13: Mwts of some Oligomers of compounds 14-19

Oligomer No.	**R**	**Radiation time (h)**	**Monomer Mwt. g/mol)(**	**Oligomer Mwt. g/mol)(**	**Repeating Unit (n)**
14		**10**	**570**	**6592**	**12**
15		**10**	**408**	**5187**	**13**
16		**10**	**430**	**3682**	**9**
17		**10**	**476**	**7763**	**16**
18		**10**	**435**	**7379**	**17**
19		**10**	**418**	**4078**	***10***

Poly2,7-Dimethyl-3,5-Octadiyne-2,7-Bis Cinnamate and para toluene sulfonate (20,21)

The above polymers were also prepared by topochemical polymerization using U.V light as it was mentioned in the experimental part. The polymers were insoluble in all common solvents . The IR spectral date are indicated in Table (14).

Table 14: IR spectral data of compounds 20,21

Polymer No.	IR, υ (cm^{-1}) C–H (Str.)		C=O (Str.)	C=C , C≡C (Str.)		Others (Str.)
	Aromatic	Aliphatic	Ester	Aromatic	Aliphatic	
20	**3061**	**2983**	**1765**	**1600-1577**	**1631**	**(C-O)1067**
21	**3083**	**2984**	**---**	**1592-1539**	**---**	***(O=S=O)1170-1147***

Poly2,7-Dimethyl-3,5-Octadiyne-2,7-Bis (N-acetyl amino acid esters and phthaly alanine esters) (22-26)

These polymers were also insoluble in all common solvents. Their structures were confirmed according to color change after irradiation and their IR spectral data as shown in Table (15).

The IR spectra revealed the presence of the following absorption bands : 3272-3306 Cm^{-1} for N-H,1686-1712 Cm^{-1} for C=O ester,1640-1660 Cm^{-1} for C=O amide and C=C of the enyne system. It is worth noting here that these polymers could be confirmed by ^{13}CNMR magic angle measurements but this technique was not available in Sheffield University so the structure elucidation was depend on color change, melting point after monomer removal and the measurement of some oligomer molecular weights formed in early stages of irradiation .

Table 15: IR spectral data of compounds 22-26

Polymer No.	IR, υ (cm^{-1}) N–H (Str.)	C–H (Str.)		C=O (Str.)		C=C , C≡C (Str.)		N–H (Ben.)
		Aromatic	Aliphatic	Ester	Amide	Aromatic	Aliphatic	
22	**3306**	**3030**	**2932**	**1686**	**1645**	**1590** **1574**	**---**	**1524**
23	**3278**	**3012**	**2930**	**1697**	**1655**	**1593** **1568**	**1633**	**1536**
24	**3272**	**3059**	**2954**	**1707**	**1660**	**---**	**---**	**1525**
25	**3288**	**---**	**2928**	**1704**	**1640**	**---**	**---**	**1531**
26	**---**	**3028**	**2932**	**1712**	**1780,1750** **(Imide)**	**1609** **1598**	**---**	***(C-O)1073***

CONCLUSIONS

In our present work we use UV light as an easy and clean tool for the radical polymerization of the monomers in their solid state(solvent free).The synthesized new polymers are characterized by long conjugated system. According to this conjugation they might be used in photo cells. An arrangement for collaboration with Sheffield university to this study has been performed . Due to the luck of solubility in common organic solvents we decided to used these polymers in other purposes such as optical applications. We began here in our Education college this type of work and is in progress as a type of collaboration with physics Department.

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تحضير بعض البولي استرات الثنائية الاستلين

الملخص

تم تحضير بعض الاسترات الثنائية الاستلين وهي المركبات(1-13) باستعمال طرق الاقتران المعروفة.تم بلمرة هذه المونومرات باستعمال البلمرة بالحالة الصلبة و باستخدام الاشعة فوق البنفسجية.لقد وجد بان البوليمرات الناتجة وهي المركبات (14-26)لاتذوب بامذيبات العضوية المعروفة. تم تشخيص المونومرات بالطرق الطيفية وهي الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي وطيف الكتلة. بينما البوليمرات اعتمد في تشخيصها على التغيرات الفيزيائية بسب عدم قابليتها للاذابة بالمذيبات العضوية وكذلك اعتمادا على تشخيص بعض اوليكومراتها بالطرق الطيفية المتمثلة بطيف الكتلة والرنين النووي المغناطيسي.