AL-Qadisiya Journal For Science Vol .17 No.1 Year 2012
hizoom mola AL-Mayiah ISSN-1997-4290

Plasticization of new polymers derivatives from poly (vinyl alcohol)

Hizoom Mola Al-mayiah
Department of chemistry, college of science
university of Baghdad, Jadiriya, Baghdad, Iraq

Abstract :-

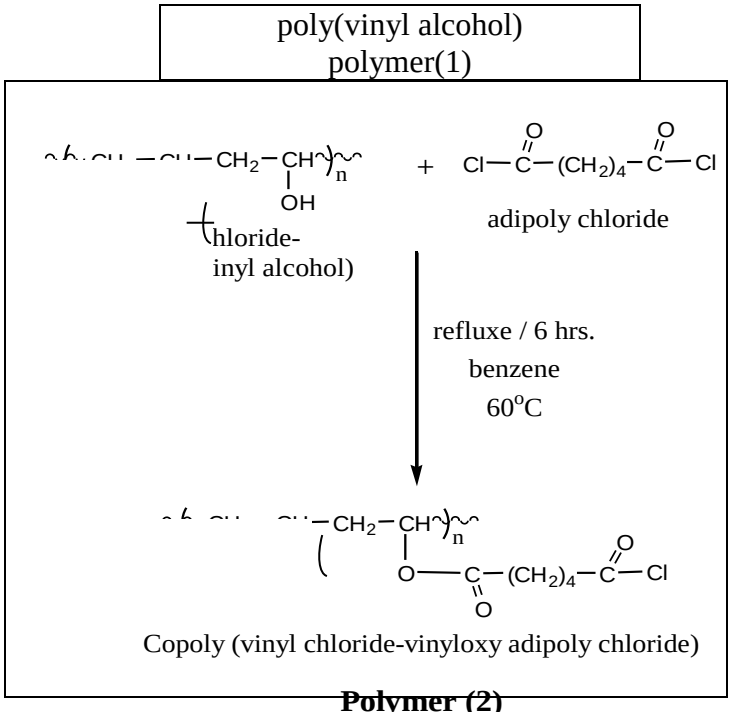
Reaction of poly (vinyl alcohol) with adipoly dichloride in presence of benzene gave copoly (vinyloxy adipoly chloride).This is the first step.The second step included the reaction of the prepared copolymer with ethanol to give copolymers(vinyloxy adipoly ester) which containing pendant esters group on polymeric chain.

The prepared copolymers were identified by FT-IR and ^{1}H –NMR spectra, and by studing the physical properties such as softening or melting points and solubility.

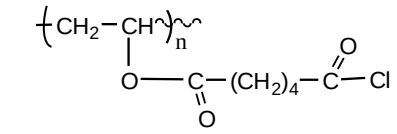
Introduction

poly(vinyl alcohol) [(1)] was used with adipoly dichloride in benzene as asolvent for six hours refluxe, this is the second step to give copoly (vinyl oxy adipoly chloride) [(2)].

The third step include formation of copoly (vinyl oxy adipoly ester) with ethanol under reflux for six hours to obtain new copoly esters[(3,4,5)].

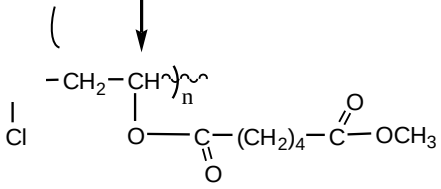


Scheme(1)



Copoly (vinyl chloride-vinyloxy adipoly chloride)

MeOH / 6 hrs.
refluxe



Copoly (vinyl chloride-vinyloxy adipoly methylate)

Polymer (3)

Scheme(2)

Expermintal

Melting point were determined on Gallen kamp Melting points apparatus(MFB-600),softening points were determined using Reichert thermovar,SP,10\0.25,160.

Structures conformation of new prepared copolymer ,were proved by FT-IR spectroscopy and other physical properties including softening points, melting points, solubility of copolymers were measured.

All physical properties are usted in Table(1) Fig(1)^{1}H-NMR and Fig(2) -^{13}C

1. Preparation of poly (vinyloxy adipoly chloride).

Mixture 0.01 mole of poly (vinyl alcohol) and o.o1 mole of adipoly chloride in benzene used as a solvent were refluxed for 6 hours at 60 ^{0}C to give new ester poly (vinyloxy adipoly chloride) forming black precipitate, purified by using THF. Conversition of yield 89%.Softening point 189-201^{0}C and melting point 203-205^{0}C

All physical properties are usted in Table(1)

2. Preparation of poly (vinyloxy adipoly methylate) [6,7,8].

Mixture 0.01 mole of poly (vinyloxy adipoly chloride) with o.o1 mole of ethanol were refluxed for 6 hours at 62 ^{0}C to give new ester (gray precipitate), which was purified by THF. Conversition of yield 84%.Softening point 175-190^{0}C and melting point 185-189^{0}C

physical properties of new bhpoly table(1-3),FT-IR shown in Table(3-3)

3. Preparation of plasticizer

Mixture of solid I gm of PVC[9] with different weight of new ester copoly[4,5,6] (vinyloxy adipoly Ethylate) 0.1gm,0.2 gm,0.3 gm,0.4 gm,0.5 gm,o.6gm,0.7gm,0.8gm,0.9gm,1gm of ester with 1 gm of PVC give new physical properties Softening point of PVC with copoly(vinyloxy adipoly ethylate as shown in Fig(3) and relation ship between weight of plasticizer in PVC[10,11,12,13] with softening point shown in curve No.(1)

Result and discussion

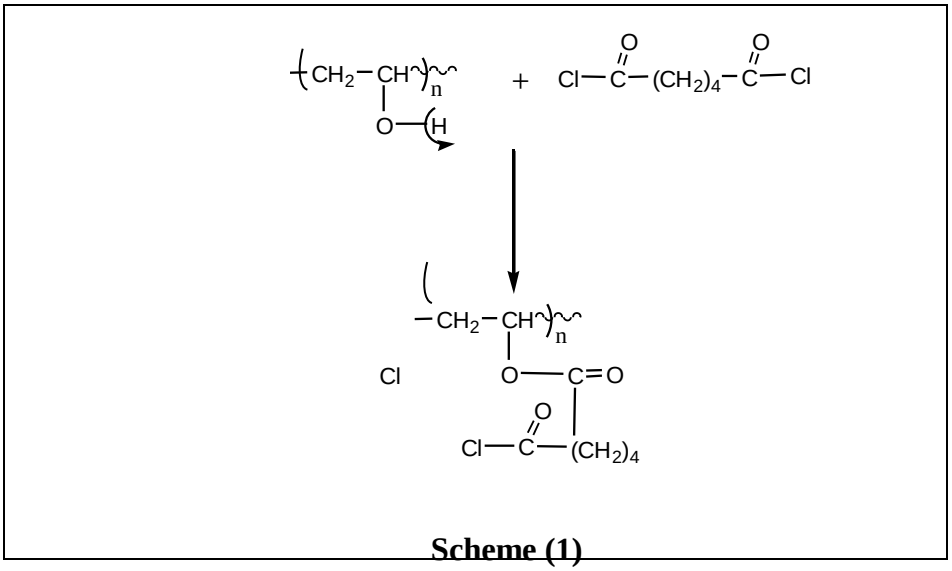
One of the suitable procedure for preparation of poly(vinyl alcohol) from (vinyl acetate)[1]by hydrolysis in acidic medium with acetone under refluxe.All physical properties listed in Table(1-3).The FT-IR spectrum show absorption band at(3250-3600) cm^{-1} for OH group and at 680cm^{-1} forC-Cl and 1250 cm^{-1} for C-O alcohol

The FT-IR spectra for poly(vinyloxy adipoly chloride)[2]

This new ester polymer show absorption band at 617 cm^{-1} for C-Cl group, and at 1280cm^{-1} for O-C-O ester group, and at 1697$cm^{-1}$for C=O ester group, and at 2916cm^{-1} for C-H group.

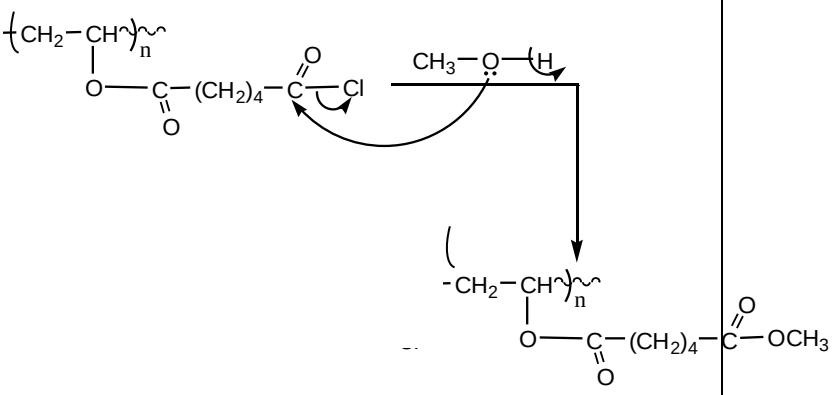
Mechansim of reaction is shown in scheme(1)

The FT-IR spectra for new poly(vinyloxy adipoly etheyl ester) show absorption band [14] at 1735 cm^{-1} C=O for ester group, and at 694 cm^{-1} for C-Cl group, and at 2923cm^{-1} for C-H aliphatic group , and at 1242 $cm^{-1}$for O-C-O ester group show in table (3-3): FTIR absorption spectra data $(cm)^{-1}$ of new polymers.Mechansim of reaction is shown in scheme(2)



Scheme (1)

Scheme(3)



Scheme (2)

Scheme(4)

Table(1-3)
Physical properties for new poly (vinyl alcohol) and new ester derivatives)

No.	poly	time	% Yield	colour	Meltig point	Softing point
1	poly(vinyl alcohol)	6 hrs.	78	Pink.	186-188	161-171
2	poly (vinyloxy adipoly chloride)	6 hrs.	89	Black	203-205	189-201
3	poly (vinyloxy adipoly ester)	6 hrs.	84	gray	185-189	175-190

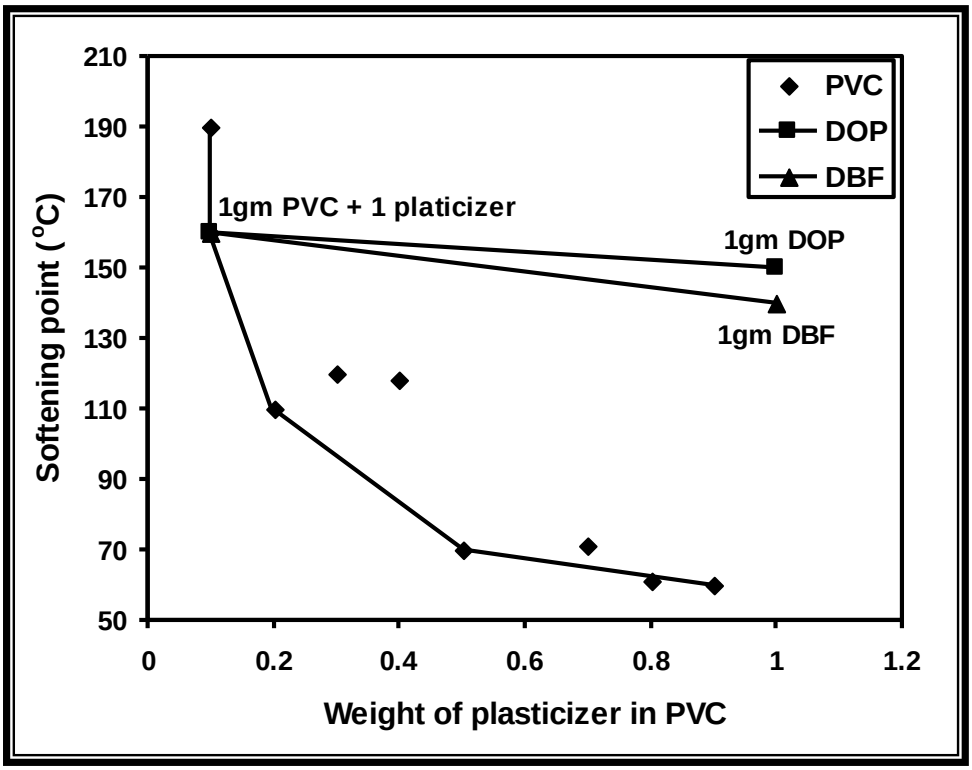
Table (3-3): FTIR absorption spectra data $(cm)^{-1}$ of new Polymers

Comp. No.	Fig. No.	ν C-OH	νC-O	νC-Cl	νC-H aliphatic	νC=O
1	1	3250-360	1250	_	2990	_
2	2	_	1280	617	2916	1697
3	3	_	1242	694	2923	1735

Table(2-3)
Solubility of new polymer

No.	Benzene	DMF	DMSO	THF	Water	CCl4	Acetone	EtOH
1	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S
2	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S
3	V.S	V.S	V.S	V.S	P.S	P.S	V.S	V.S

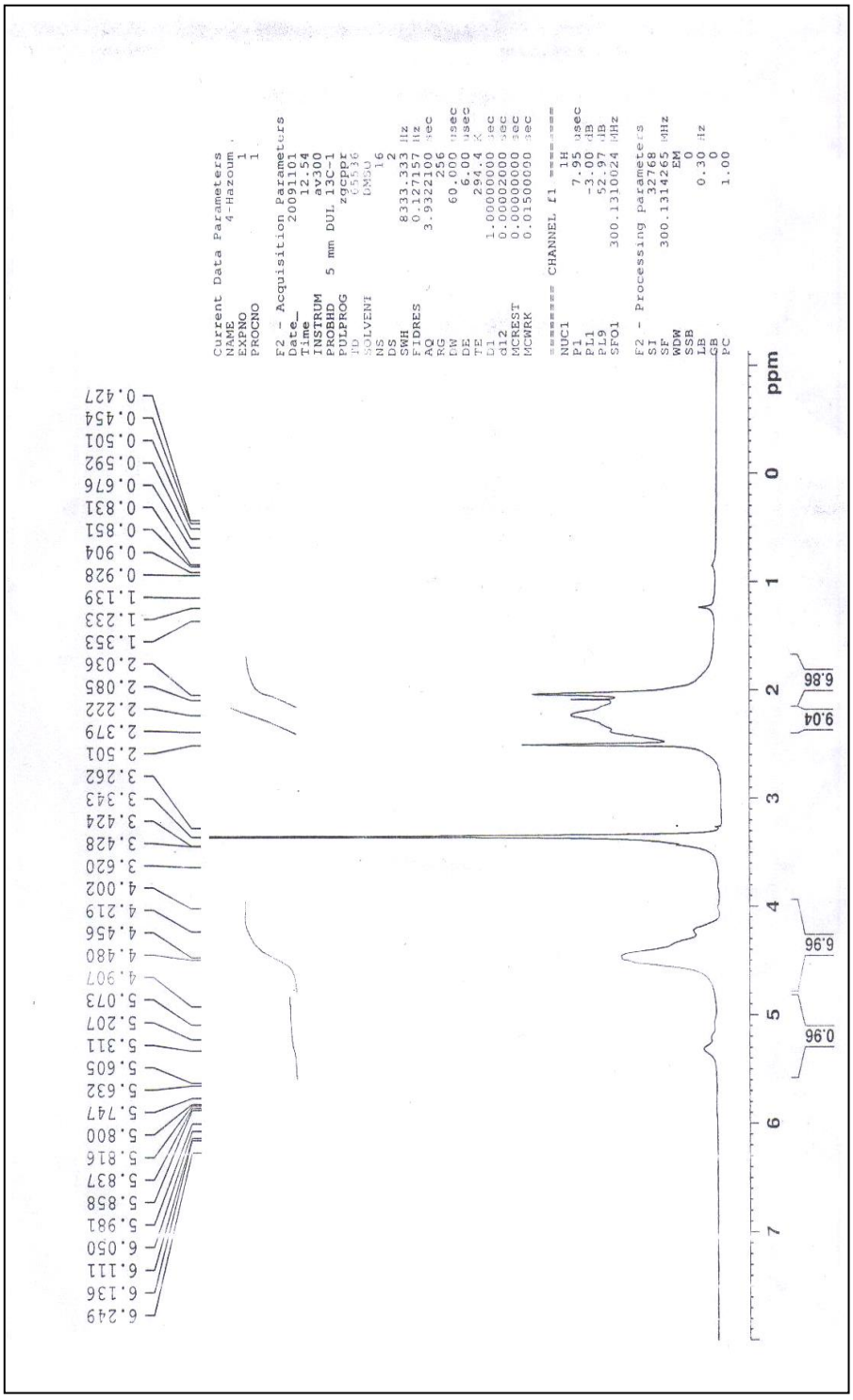
plasticizer	Weight%	Softening point C°
poly (vinyloxyadipoly diester).which is used with pvc	0.1 gm+1gm pvc	(180-210)
	0.2 gm+1gm pvc	(110-130)
	0.3 gm+1gm pvc	(120-166)
	0.4 gm+1gm pvc	(118-148)
	0.5 gm+1gm pvc	(70-81)
	0.6 gm+1gm pvc	(115-205)
	0.7 gm+1gm pvc	(71-92)
	0.8 gm+1gm pvc	(61-81)
	0. 9 gm+1gm pvc	(60-79)
	1 gm+1gm pvc	(160-162)



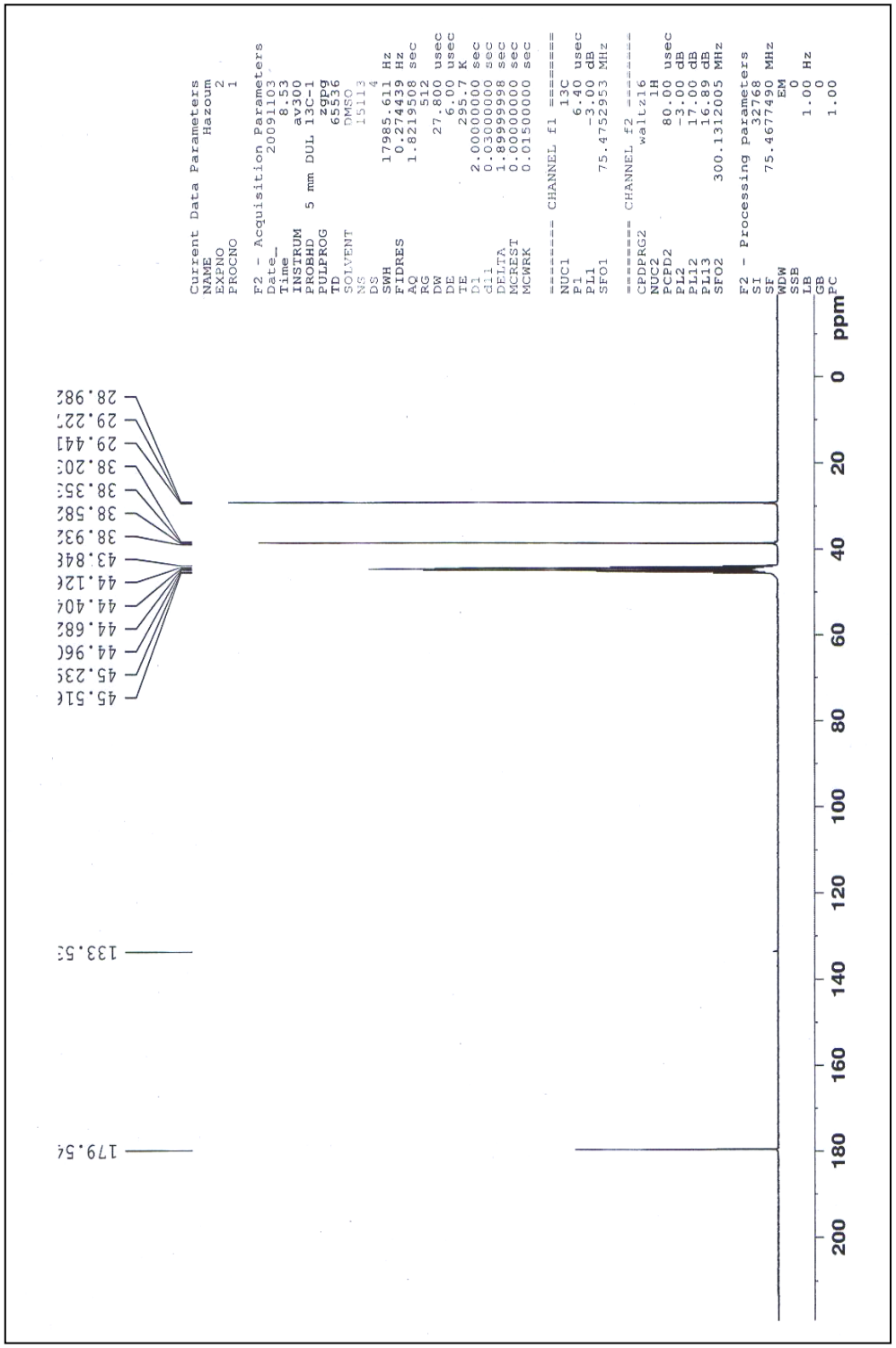
Fig(3)
DEP 132-142°CCurve(1) Curve(1)
DOP 135-150°C

Table (3): ^{1}H-NMR spectra for selected copolymers

Comp. No.	^{1}H-NMR parameters (ppm) δ-H
1	3.2 (t, 2H, -CH2);2.5 (m, 1H, -CH),
3	7.89 (s, 1H, -NH); 6.9 (s, 2H, NH2); 3.4 (m, 2H, -CH2); 3.1 (t, 2H, -H2);2.8(m,1H,-)


Current Data Parameters
NAME 4-Hazoum
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091101
Time 12.54
INSTRUM av300
PROBHD 5 mm DUL 13C-1
PULPROG zgcppr
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8333.333 Hz
FIDRES 0.127157 Hz
AQ 3.9322100 sec
RG 256
DW 60.000 usec
DE 264.4 usec
TE 294.4 K
D1 1.00000000 sec
d12 0.00002000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.95 usec
PL1 -3.00 dB
PL9 52.97 dB
SFO1 300.1310024 MHz
F2 - Processing parameters
SI 32768
SF 300.1314255 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
6.86
9.04
6.96
0.96

Fig(1) ^{1}H -NMR


Current Data Parameters
NAME Hazoum
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091103
Time 8.53
INSTRUM av300
PROBHD 5 mm DUL 13C-1
PULPROG zgpg
TD 65536
SOLVENT DMSO
NS 1511 4
DS
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 512
DW 27.800 usec
DE 6.00 usec
TE 295.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 6.40 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.00 dB
PL13 16.89 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
ppm
28.982
29.227
29.441
38.203
38.353
38.582
38.932
43.848
44.124
44.404
44.682
44.960
45.239
45.516
133.53
179.54

Fig(2) ^{13}C

Reference:-

1. Bell,V.L.,(1966),polymer "J.poly.sci.",Vol.13,5.
2. Encyclopediaof polymer science and Technology.,(1969),vol.11, p.p.62-128.
3. Coleman,L.E and Dunn,1959,polymer,J.Org.Chem.,24,135.

4.Rodriguez,F., (1983), "Principle of polymer system" 2nd. ed.McGraw-Hill Book company

5.Billmeyer,F.W.,(1970), "Text book of polymer science"Wiley inter science,New York.

6. Pyriadi,T.M.,(1985), "Practical polymer chemistry" University of Mousel press,Iraq.

7.Roderick,W.R., and Bhatia,P.L(1963),Polymer,J.Org.chem.,28.

8.Rehbery,C.E.;Fisher,C.H.,(1948),Polymer,Ind.Eng.chem.40,(1429).

9.Darby,J.R. and.Sears,J.K.,(1969),"Plasticizers" in encyclopedia of polymer science and Technology vol.10,p.228.

10. Campbell,A.W.,and Tryon,P.F.,(1953),Ind.Eng.chem.54,125.

11.Gould,R.F.,(1965),(Ed.),plasticization and plasticizer processes ,Advance in chemistry series NO.48,American chemical socity,Washington,D.C.

12.MISRA,G.S.,(1993), "Introduction polymer chemistry"EX-Director,Indian loc Research Institute Namkum,Ranchi.

13.Doolittle,A.K.,(1954), " The Technology of solvents and plasticizer "p.870,New york,John wiley and sons,inc.

14.williams,D.H. and Fleming,I.,(1958), "Spectroscopic method inorgani chemistry"Jon wiely and Sons New York.

تحضيرمشتقات بوليمرية جديدة من بوليمرات (كحول الفاينيل)

هزوم مولى المياحي
كلية العلوم /جامعة بغداد

الخلاصة :

تم في هذا البحث تحضير بوليمرات جديدة (vinyloxy adipoly chloride) من تفاعل(vinyl alcohol) مع adipoly chloride بوجود البنزين. في الخطوة الثانية تـــم مفاعلة البـــوليمر المحضر(2) مع الايثانول و اجراء عملية الاسترة لمجموعة الهيدروكسيل. تم تشخيص الاسترات المحضرة بالطرق الطيفية و تمت دراسة قابلية البولي استرات المحضرة الجديدة على تلدين PVC ومتابعة تأثير التلدين على الخصائص الفيزيائية