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Synthesis of New Pyromellitdiimde Homo and Copolymers Containing (N-AllylMethylol) Component

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Abstract--- *In this work six new pyromellitdiimde polymers containing (N-allylmethylol) component were synthesized through performing many steps. The first step involved treatment of pyromellitic anhydride with urea producing N-unsubstituted pyromellitdiimide(1) which inturn was converted in the second step to bis(N-methylol) pyromellitdiimide(2) via reaction with formaldehyde. Treatment of (2) with allyl bromide in the third step afforded bis(N-allylmethylol) pyromellitdiimde (3). Subsequently the new monomer (3) was introduced in free radical homo and copolymerization producing the target new polymers (4-9) which exhibit improved properties.*

Keywords--- *Allylmethylol, Pyromellitdiimde, Copolymerization.*

I. INTRODUCTION

Aromatic polyimides have been extensively studied and reported in literatures [1-5] due to their excellent mechanical and chemical properties, flame retardance beside their high thermal stability [6,7].In spite of all these excellent properties their low solubility and poor process ability limited their applications. Various structural modifications [8-10] were made to overcome this problem through incorporation of bulk components [11] or flexible segments like ester or ether moieties [12] in their polymeric chains or by copolymerization [13,14].In this work first we design and synthesize new pyromellitdiimide monomer containing flexible allylmethylol ether group then introduce this monomer in free radical homo and copolymerization producing new polymers with improved properties which may serve many applications.

II. MATERIALS AND METHODS

The employed chemicals were purchased from Merk, Fluka and BDH companies, FTIR spectra were reordered on SHIMADZU FTIR 8400 Former transform Infrared spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on nucler magnetic resonance Bruker 400 MHz. Melting points were measured on Gallen Kamp capillary melting point apparatus while softening points were measured on thermal microscope Riecherttherm over apparatus.

Preparation of Pyromellitdiimide (1) [15]

A mixture of pyromellitic anhydride (0.0125 mol, 2.72 g) and urea (0.025 mol, 1.5 g) was heated slowly to 260 °C until complete conversion to liquid. After cooling of resulted mixture white crystals were appeared and dispersed by adding cold water (250 mL) then filtered, washed with water, dried and recrystallized from ethyl acetate.

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Synthesis of Bis(N-Methylol) Pyromellitdiimide (2) [16]

To a suspension of pyromellitdiimide (0.05 mol, 10.8 g) in (10 mL) of 37% formaldehyde, 50 % sodium hydroxide solution (5 mL) was added with strring at 25 °C. The resulted mixture was stirred until complete dissolving of pyromellitdiimide then stirring was continued for 3 hrs.at room temperature. The obtained precipitate was filtered, washed with ethanol, dried then recrystallized from acetone.

Synthesis of Bis(N-AllylMethylol) Pyromellitdiimide (3) [12]

N-methylol pyromellitdiimide (0.01 mol, 2.78 g) was dissolved in acetone (25 mL) then potassium carbonate (0.02 mol, 2.7 g) was added with string. To the resulted mixture (0.02 mol) of allyl bromide was added then the mixure was heated in the range (60-70)°C for 10 hrs. With continuous stirring. The resulted precipitate was filtered, dried, and then recrystallized from ethanol. Physical properties of compounds (1-3) are shown in Table 1.

Synthesis of Bis(N-AllylMethylol) Pyromellitdiimide Homopolymer (4) [12]

In a suitable dry polymerization bottle (0.005 mol, 1.59 g) of the monomer bis(N-allylmethylol) pyromellitdiimide was dissolve in (10 mL) THF then (0.0002 g) of initiator AIBN (azobisisobutyronitrile) was added and the bottle was flushed with nitrogen before stoppering. The bottle contents were heated at (75°C) for 3 hrs. After completion of heating the resulted mixture was added to methanol and the precipitated polymer was filtered, washed with methanol and dried. Purification of the polymer was made by dissolving in THF followed by precipitation from methanol.

Synthesis of Bis(N-AllylMethylol) pyromellitdiimide copolymers (5-9) [14]

The titled copolymers (5-9) were prepared by following the same procedure steps used in synthesis of homopolymer (4) except using of equimolar amounts of monomer (3) and vinylic monomers including (acrylonitrile, methacrylonitrile, methyl acrylate, methyl meth acrylate and vinyl acetate).Physical properties of polymers (4-9) are shown in Table 2.

III. RESULT AND DISCUSSION

The presence of strong inter chain forces in polyimides exhibit them high glass transition temperature beside insolubility in all known organic solvents and poor process ability and this inturn limited their applications. Thus various structural modifications were made to overcome these problems like incorporation of flexible segments in rigid polymeric chains or by copolymerization.

In this work we synthesize pyromellitdiimidemonomer containing flexible (allylmethylol) segment then introduce it in homo polymerization producing homopolymer (4). The second strategy that was used in this work is copolymerization which is an excellent tool in producing new polymers with improved properties, so we introduce monomer (3) in copolymerization with five vinylic monomers including acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate and vinyl acetate producing new five copolymers having improved solubility and fusibility. Many steps were made to perform the target of this work which are summarized in Schemes (1) and (2).

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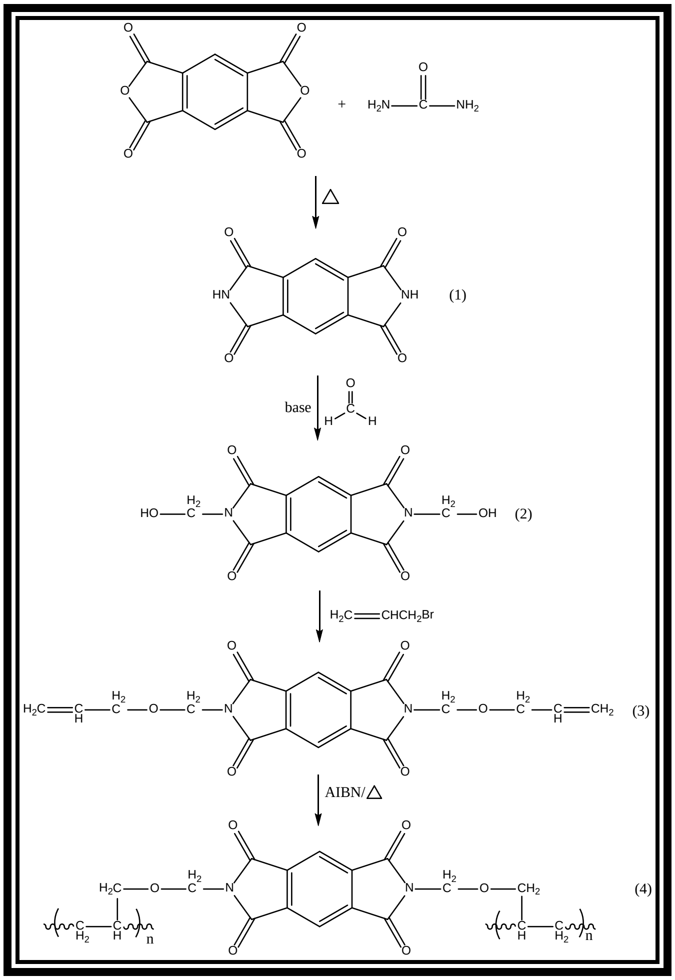
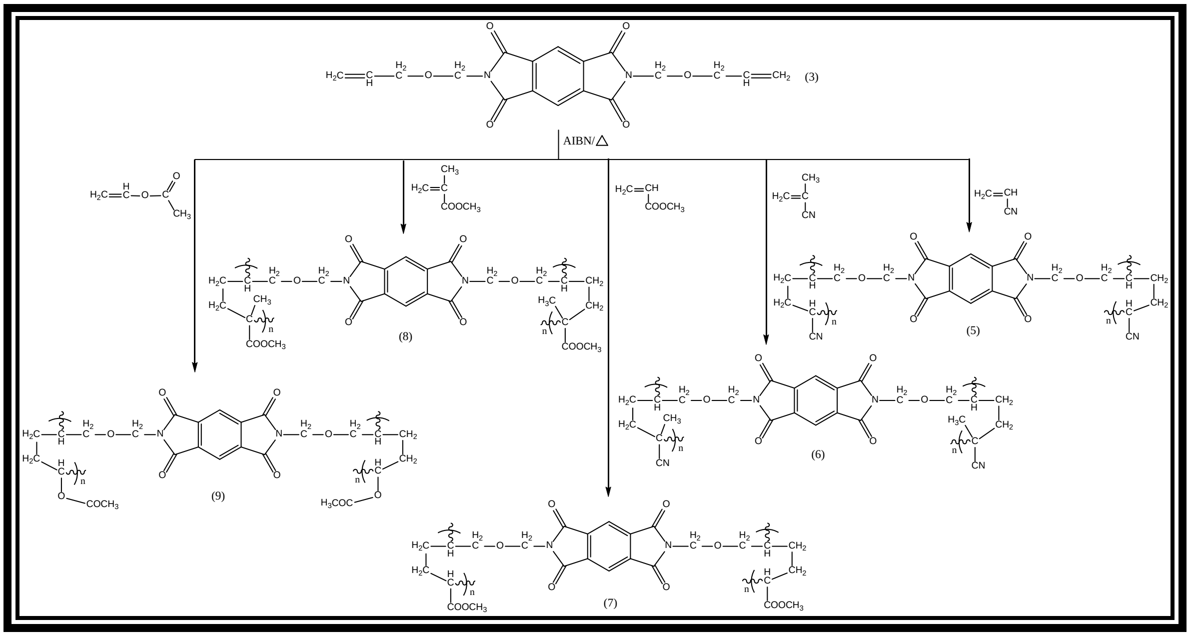


Scheme (1)



Scheme (2)

The first step involved preparation of N-unsubstituted pyromellitdiimide (1) through reaction of pyromelliticdianhydride with urea under heat. In the second step compound (1) was treated with formaldehyde in basic medium affording compound (2) bis(N-methylol) pyromellitdiimide so by this step we introduced methylol group in imide compound, the presence of alcoholic hydroxyl group in compound (2) gave the chance for introducing this compound in reaction with allyl bromide according to (Williamson Reaction) producing compound (3) N-(allylmethylol) pyromellitdiimide. By this step a flexible ether (allylmethylol) segment was introduced in imide structure beside creation of carbon-carbon double bond in allylic side chain which linked to imide moiety and ready to introduce in chain growth polymerization.

In the fourth step the newly synthesized monomer (3) was introduced in free radical addition polymerization using AIBN as initiator and THF as solvent under heating at (75°C) for 3 hrs. Affording the target homopolymer (4).

Beside copolymerization process was depended also in this work as excellent strategy that supplied us with new polymers having improved properties, thus the synthesized monomer (3) was introduced successfully in addition copolymerization with five vinylic monomers following the same steps that are used in homopolymerization producing new five copolymers having improved properties, they showed good solubility in most common organic solvents beside low softening points. Physical properties of compounds (1-3) and polymers (4-9) are listed in Tables (1) and (2) respectively. Chemical structures of the prepared compounds were confirmed by depending on FTIR, ^{1}H-NMR and ^{13}C-NMR spectral data.

FTIR spectrum of compound (1) gave clear absorption band at 3199 cm^{-1} due to ʋ(N-H) and absorption bands at (1772, 1718,1695) cm^{-1} due to asym. And sym. ʋ(C=O) imide and band at 1564 cm^{-1} due to ʋ(C=C) aromatic.

FTIR spectrum of compound (2) showed absorption bands at (3477 and 3379) cm^{-1} due to ʋ(O-H) and other bands at 1772 and 1714 cm^{-1} which are due to asym. And sym. ʋ(C=O) imide [17].

Beside the spectrum showed also absorption bands at 2964 cm^{-1} and 2862 cm^{-1} which belong to asym. and sym. ʋ(C-H) aliphatic. The appearance of these absorption bands and ʋ(O-H) absorption bands are good proofs for the formation of compound (2).

On the other hand FTIR spectrum of compound (3) showed disappearance of ʋ(O-H) absorption bands and appearance of strong absorption bands at 1176 cm^{-1} and 1078 cm^{-1} due to asym. and sym. ʋ(C-O-C)ether. These two points are clear proofs for the formation of compound (3).All details of FTIR spectral data for compounds (1-3) are listed in Table (3).^{1}H-NMR spectrum of compound (3) showed signals at (δ=3.99, 4.80 and 5.10) ppm belong to (OCH_2) protons, (N-CH_2-O-) protons and vinylic protons respectively [18]. Signals belong to aromaticprotons appeared at (δ=7.25-8.31) ppm.

^{13}C-NMR spectrum of compound (3) showed signals at (δ=60.18 and 62.86) ppm belong to (OCH_2) and (N-CH_2-O-) carbons. Other signals appeared at δ=(113.83, 134.31and 166.91) ppm which are belong to vinylic carbons, aromatic carbons and (C=O) imide carbons respectively.

FTIR spectrum of homopolymer (4) showed strong absorption bands at 2983 cm^{-1} and 2879 cm^{-1} due to asym. and sym. ʋ(C-H) aliphatic. The appearance of these bands proved the presence of aliphatic CH_2 groups indicating

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success of polymer formation. The spectrum showed also absorption bands at (1699, 1595, 1382, 1182 and 1039) cm^{-1}which are due to ʋ(C=O) imide, ʋ(C=C), ʋ(C-N) imide, asym. and sym. ʋ(C-O-C) ether respectively.

^{1}H-NMR spectrum of polymer (4) showed the appearance of multisignals at (δ=1.29-1.86) ppm belong to (CH-CH_2-) protons and disappearance of vinylic protons signal at (δ=5.1) ppm. These two points are clear proofs for polymer formation. Other signals appeared at (δ=4.15, 4.75 and (7.19-8.68)) ppm which are belong to (OCH_2) protons, (N-CH_2O-) protons and aromatic protons.

FTIR spectra of copolymers (5) and (6) showed clear, important characteristic absorption band at (2235-2243) cm^{-1} due to ʋ(C≡N). Also strong absorption bands appeared at (2927-2952) cm^{-1} and (2856-2879) cm^{-1} due to asym. and sym. ʋ(C-H) aliphatic [17]. Other absorption bands appeared at (1772-1778) cm^{-1}, (1720) cm^{-1}, (1595-1633) cm^{-1}, (1371) cm^{-1}, (1178-1180) cm^{-1} and (1076-1078) cm^{-1} which are due to asym. and sym. ʋ(C=O) imide, ʋ(C=C), ʋ(C-N) imide, asym. and sym. ʋ(C-O) ether, respectively.

^{1}H-NMR spectrum of copolymer (5) showed multisignals at (δ=0.99-2.13) ppm belong to (-CH_2-$CHCH_2$) protons which indicate polymer formation.Other signals appeared at (δ=3.98, 4.19 and (7.25-8.15)) ppm which are belong to (OCH_2) protons, (N-CH_2-O) protons and aromatic protons [18].

FTIR spectra of copolymers (7), (8) and (9) showed clear strong absorption bands at (2952-2977) cm^{-1} and (2850-2880) cm^{-1} due to asym. and sym. ʋ(C-H) aliphatic. Beside strong absorption band appeared at (1731-1737) cm^{-1} due to ʋ(C=O), ester and clear absorption bands at (1242-1261) cm^{-1} and (1149-1178) cm^{-1} due to asym. and sym. ʋ(C-O) ester. FTIR spectral data details of polymers (4-9) are listed in Table (4).

^{1}H-NMR spectrum of copolymer (7) showed multisignals at (δ=1.36-1.90) ppm belong to (-CH-CH_2-CH_2-) protons and at (δ=2.39) ppm belong to (-$CHCOOCH_3$)protons. Signals belong to (-OCH_2-), (OCH_3) and (-N-CH_2-O-) protons appeared at (δ=3.69) and (δ=3.73-3.76) ppm while signals for aromatic protons appeared at (δ=7.89-8.3).

^{13}C-NMR spectrum of copolymer (7) showed signals at (δ=25.40-30.88) ppm belong to (-CH-CH_2-CH_2-) carbons and signals at (δ=34.13-34.81) ppm belong to (-$CHCOOCH_3$) carbon. Other signals appeared at (δ=51.32, 51.52and 66.77) ppm belong to (-O-CH_2-) carbon, (OCH_3) and (-N-CH_2-O-) carbons and signals at (δ=129.73-132.0) ppm and (172.66) ppm belong to aromatic carbons and (C=O) imide and ester carbons.

^{1}H-NMR spectrum of copolymer (8) showed multisignals at (δ=0.83-1.55) ppm belong to (-CH-CH_2-CH_2-) protons and signals at (δ=1.85-2) ppm belong to two methyl protons. Other signal appeared at (δ=3.66-3.77) ppm, (4.89) ppm and (8.2) ppm which are belong to (-OCH_2) and (OCH_3) protons, (-N-CH_2-O-) protons and aromatic protons respectively [18].

^{13}C-NMR spectrum of copolymer (8) showed signals at (δ=16.0-28.70) ppm and (δ=29.19-30.37) ppm belong to (-CH-CH_2CH_2-) carbons and two methyl carbons. The spectrum showed also other signals at (δ=43.81-44.53) ppm, (51.45-52.62) ppm, (55.73) ppm, (113-129) ppm, (176.17-176.48) ppm and (177.16-177.37) ppm which are belong to (-OCH_2-) carbon, (OCH_3) carbons, (-N-CH_2-O-) carbons, aromatic carbons, (C=O) imide and (C=O) ester carbons respectively.

Finally ^{1}H-NMR spectrum of copolymer (9) showed multisignals at (δ=1.11-1.93) ppm belong to (-CH-CH_2CH_2-) protons and signals at (δ=2.15-2.23) ppm belong to two (CH_3) protons. Other signals appeared at (δ=4.1) ppm belong to (-CH_2-O-) protons and (-CHO-CO-CH_3) proton and signals at (δ=4.95) ppm and (δ=8.07-8.2) ppm belong to (-N-CH_2-O-) protons and aromatic protons [17].

^{13}C-NMR spectrum of copolymer (9) showed signals at (δ=19.81-26.36) ppm belong to (-CH-CH_2CH_2-) carbons and signal at (δ=28.65) ppm belong to two (CH_3) carbons. Signal belong to (-CH_2O-), (-$CHOCOCH_3$) and (N-CH_2-O) carbons appeared at (δ=60) and (62.30) ppm while signals belong to aromatic carbons, (C=O) imide and ester carbons appeared at (δ=122.33-133.23) ppm and (168.18-170) ppm.

Table 1: Physical Properties of Compounds (1-3)

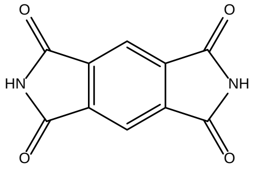
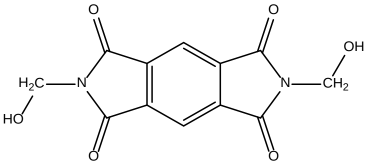
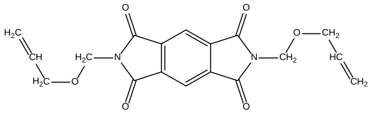
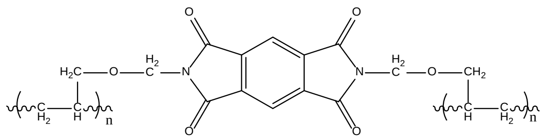
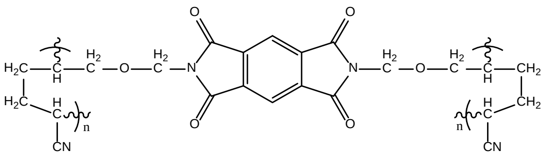
Comp. No.	Compound structure	Color	Yield %	Melting point °C	Recrystallization solvent
1		White	85	>300	Ethyl acetate
2		Bright gray	81	>300	Acetone
3		Gray	72	221-223	Ethanol

Table 2: Physical Properties of Polymers (4-9)

poly. No.	polymer structure	Color	Conv. Ratio %	Softening point °C	Purification
4		Brown	75	245-258	By dissolving in THF then precipitation by methanol
5		Brown	82	62-77	

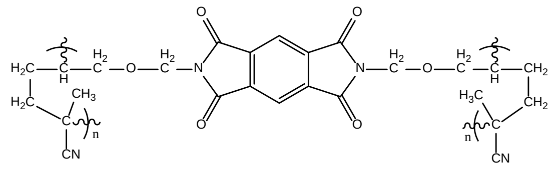
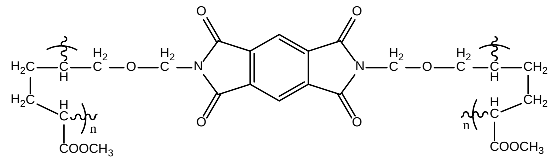
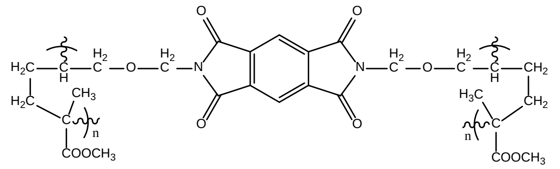
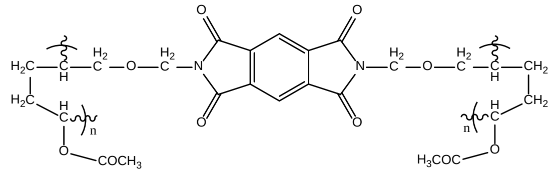
6		Pale yellow	77	45-57	
7		Gray	85	Gummy	
8		Yellow	87	32-45	
9		Yellow	84	28-50	

Table 3: FTIR Spectral Data (cm-1) of Compounds (1-3)

Comp. No.	υ(O-H)	υ(N-H)	υ(C-H) Aromatic	υ(C-H) Aliphatic	υ(C=O) Imide	υ(C=C)	υ(C-N) imide	υ(C-O) Ether
1	-	3199	3066	-	1772 1718 1695	1564	-	-
2	3477 3379	-	3031	2964 2862	1772 1714	1560	1352	-
3	-	-	3020	2958 2837	1780 1718	1633	1380	1176 1078

Table 4: FTIR Spectral Data (cm-1) of Polymers (4-9)

poly. No.	υ(C-H) Aromatic	υ(C-H) Aliphatic	υ(C=O) Imide	υ(C=C)	υ(C-N) imide	υ(C-O) Ether	Others
4	3078	2983 2879	1699	1616 1596	1382	1182 1039	-
5	3053	2952 2879	1772 1720	1631 1595	1371	1180 1076	υ(C≡N) 2243
6	3097	2927 2856	1778 1720	1633 1602	1371	1178 1078	υ(C≡N) 2235
7	3040	2954 2850	1699	1614 1595	1382	1178 1043	υ(C=O)Ester 1737 υ(C-O)Ester 1261
8	3070	2952 2880	1731	1620 1598	1390	1191 1068	υ(C=O) Ester 1731 υ(C-O) Ester

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							1242,1149
9	3080	2977 2875	1770 1672	1616 1585	1371	1155 1047	υ(C=O) Ester 1737 υ(C-O) Ester 1242,1184

Table 5: Solubility of Polymers in Different Organic Solvents.

Poly. No.	solvents										
	THF	DMF	DMSO	Acetone	Methanol	Ethanol	Dioxane	chloroform	n-hexane	Petr. ether	Et_2O
4	s	s	s	sh	ins	ins	s	sh	ins	ins	ins
5	s	s	s	sh	ins	ins	s	sh	ins	ins	ins
6	s	s	s	sh	ins	ins	s	sh	ins	ins	ins
7	s	s	s	sh	ins	ins	s	sh	ins	ins	ins
8	s	s	s	sh	ins	ins	s	sh	ins	ins	ins
9	s	s	s	sh	ins	ins	s	sh	ins	ins	ins

*s= soluble, sh= soluble hot and ins=insoluble.

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