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Synthesis and Characterization of Several New Poly (Allyloxy Phenyl) Bearing pendenttetrachlorophthalimides

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Abstract: ***In this work a series of four new polly(allyloxy phenyl) havingpendent tetrachlorophthalimide groups in their repeating unit were synthesized. Synthesisof these polymerswas performed by many steps in the first step four N-(hydroxyphenyl) tetrachlorophthalamic acids wereprepared via reaction of ortho ,meta and p-amino phenols with tetra chlorophthalic anhydride. Dehydration of these amic acids by fusion in the second step afforded the corresponding N-(hydroxy phenyl) tetrachlorophthalimdesandtheseinturn were introduced in reaction with ally chloride in basic medium in the third step producing N-(allyloxy phenyl) tetra chlorophthalimides which introduced in free radical homopolymerization affording the target polymers . The presence of allyloxy groups in repeating units of the new polymers exhibit them flexibility leading to better solubility and processability with keeping good thermal stability.***

Keywords: allyloxygroup ,tetrachlorophthalimide ,homopolymerization

1. Introduction

Aromatic polyimides are a class of polymers known for their high thermal stabilitybesid excellent mechanical and electrical properties (1-3) but they have certiondisadvantages such as insolubility and infusibility and hence are difficult to process (4-7) . To solve these problems many efforts have been made to design and synthesize polyimides with improved properties (8-12) one of these methods involved incorporation of alkoxy groups in polymerbackbone (13) thus in the present work we introduce flexible allyloxy group into the chain of aromatic polytetrachloropphthalimide and this reduce polymer rigidity and improve solubility and fusibility with keeping good thermal stability and these properties make polyimides suitable for many applications.

2. Experimental

Commercially available chemicals and solvents were used as received from BDH and Merk . FTIR spectra were recorded on shimadzu FTIR 8400 Fourire Transform Infrared spectrophotometer as KBr disc.

^{1}H-NMR spectra were run on a Brukerultra shield 300 MHz NMR spectrometer using DMSO-d_6 as solvent and tetramethylsilane as internal standard .Uncorrected melting points were measured with a Gallen Kamp hot-block melting point apparatus . Softening point were determined on thermal microscope Riecherthermover.

1) Preparation of N-(hydroxy phenyl) tetra chlorophthalamicacids[1-4]

The titled amic acids were prepared according to literatures (14) via reaction of equimolar amounts of ortho , meta and para amino phenols with tetrachlorophthalic anhydride. Purification of amic acids [1-4] was made by recrystallization from ethanol.

2) Preparation of N-(hydroxy phenyl) tetrachlorophthalimides [5-8]

Thetitled imides were prepared according to literatures (15) via fusion of amic acid [1-4] to ten degrees above their melting points for 2hr . The obtained imides were recrystallized from cyclohexane.

3) Preparation of N-(allyloxy phenyl) tetrachlorophthalimides[9-12]

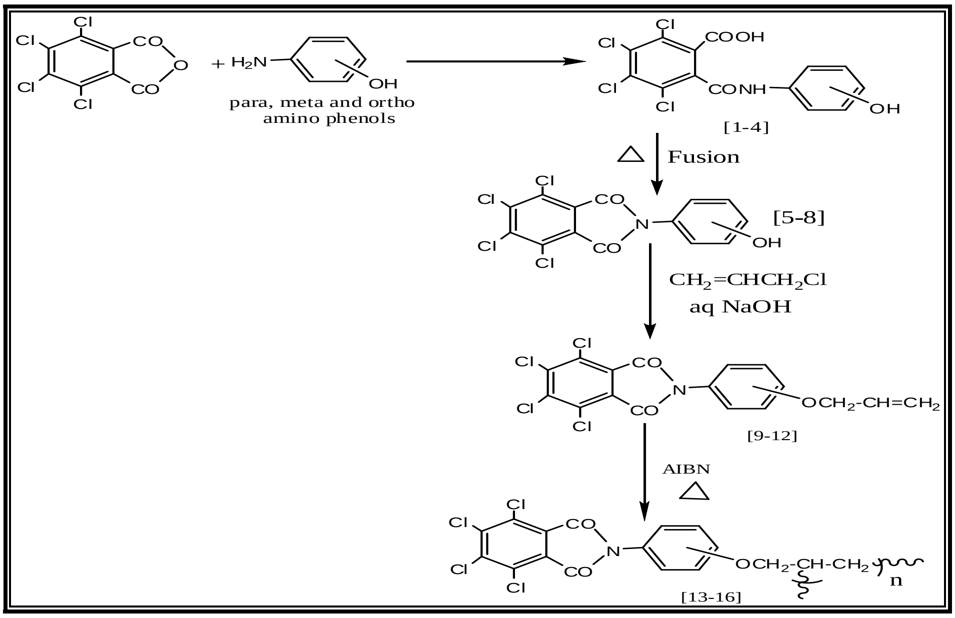
Allyl chloride (0.01mol,0.76g) was added dropwise to the mixture of (0.01mol) of imides [5-8] and (0.015mol ,0.6g) of sodium hydroxide dissolved in (15mL) of DMF with stirring . The resulted mixture was refluxed for 4hrs . Then allowed to cool and poured into ice water with stirring then was left over night at 5C°. The formed solid was filtered , washed with water, dried and recrystallized from a suitable solvent .

4) Preparation of poly[N-(allyloxy phenyl) tetrachlorophthalimides [13-16]

In dry polymerization bottle (0.01mol) of compounds [9-12]was dissolved in (10mL) of THF then (0.0002g) of AIBN (azobisisobutyronitrile) initiator was added and the bottle was flushed with nitrogen then stoppered and maintained at (75C°) for 3hrs (16) . The resulted solution was filtered, washed with methanol and dried. Polymers [13-16] were purified by dissolving in methanol followed by precipitation from methanol.

3. Results and Discussion

Poor solubility and processability of polyimides lead to limit their applications thus in the present work we try to solve these problems by incorporation of flexible allyloxy units in aromatic poly tetrachlorophthalimides . This work was done by many steps which are summarized in scheme (1).



In the first step four N-(hydroxy phenyl) tetra chlorophthalamicacids[1-4] were prepared by reaction of ortho, meta and para- amino phenols with tetrachlorophthalic anhydride . In the next step amicacids[1-4] were dehydrated by fusion method producing the corresponding tetrachlorophthalimides [5-8]. The new imides [5-8] were introduced in the third step in nucleophilic substitution reaction with allylchloride in basic medium producing the corresponding N-(allyloxy phenyl) tetrachlorophthalimides[9-12].

By this step a flexible ether (allyloxy) segment was introduced in imides structure beside creation of carbon-carbon double bonds in the side chain which linked to imide moiety ready for addition polymerization.

In the fourth step the newly synthesized N-(allyloxy phenyl) tetra chlorophthalimides monomers [9-12] were introduced in free radical chain growth polymerization using THF as solvent and AIBN as initiator with heating at (75-80) °C for 3hrs. producing the new target homopolymers[13-16]. Physical properties of monomers [9-12]are shown in Table(1) while Physical properties of polymers[13-16]are shown in Table(2).

FTIR spectra of amic acids [1-4] showed clear absorption bands at (3184-3477) cm^{-1} which were attributed to υ(O-H) carboxylic , υ(O-H) phenolic and υ(N-H) amide. Absorption bands due to υ(C=O) carboxyl and υ(C=O) amide appeared at (1712-1716) cm^{-1} and (1650-1660) cm^{-1} respectively while absorption bands due to υ(C-H) aromatic , υ(C=C) aromatic and υ(C-Cl) appeared at (3020-3089)cm^{-1} , (1596-1620) cm^{-1} and (1030-1130) cm^{-1} respectively.^{1} H-NMR spectra of compound [1-4] showed signals at(δ=6.73-7.4)ppm belong to aromatic protons and singlet signal at (δ=8.95-9.34)ppm belong to NH amide proton. Signals belong to OH phenolic proton appeared at (δ=9.5-10.4)ppm. Other signals appeared at (δ=10.6- 14)ppm belong to OH carboxyl proton .

FTIR spectra of the new imides [5-8] showed two clear strong absorption bands at (1776-1787)cm^{-1} and (1704-1731)cm^{-1} due to asymmetric and symmetric υ (C=O) imide. Absorption bands due to υ (C=C) aromatic and υ (C-N) imide were appeared at (1598-1612)cm^{-1} and (1365-1367)cm^{-1}, while absorption bands due to υ (O-H)phenolic, υ (C-H) aromatic and υ (C-Cl) appeared at (3417-3480)cm^{-1}(3030-3078)cm^{-1} (1090-1099)cm^{-1} respectively. ^{1}H-NMR spectra of compounds [5-8] showed disappearance of υ (O-H) carboxyl, υ (N-H) amide signals. Signals of aromatic protons appeared as two doublets at (δ=6.88-7.22)ppm while signal for phenolic(OH) proton appeared at(δ=9.89)ppm(17).The target new homopolymers[13-16] were synthesized by free radical homopolymerization of monomers[9-12] and afforded in conversion ratio (62-71)% as coloured solids ranged from faint yellow to brown and . The new polymers showed partial solubility in chloroform but they are insoluble in methanol, benzene, dioxane , acetone, cyclohexane , ethanol and showed good solubility in THF, DMSO, DMF.

FTIR spectra of compounds [9-12] showed disappearance of υ(O-H) absorption bands present in FTIR spectra of phenolic imides[5-8]. The spectra showed also absorption bands at (2921-2927)cm^{-1}and (2815-2866)cm^{-1} due to asym. and sym. υ(C-H) aliphatic and other absorption bands at (1201-1274) cm^{-1} and (1000-1037)cm^{-1}due to υ(C-O) ether. All these points proved the success of ether formation. Other absorption bands appeared at (1778-1785)cm^{-1}, (1708-1726) cm^{-1}, (1608-1656) cm^{-1}, (1598-1600) cm^{-1}, (1353-1365) cm^{-1}and (1080-1099) cm^{-1} which are due to asym. and sym. υ(C=O)imide, υ(C=C) aliphatic and aromatic , υ(C-N) imide and υ(C-Cl) respectively.

FTIR spectra of polymers [13-16] showed absorption bands at (2918-2927) cm^{-1} and (2812-2877) cm^{-1} due to asym. andsym.υ(C-H) aliphatic and bands at (1778-1787) cm^{-1} and (1708-1730) cm^{-1} due to asym. andsym.υ(C=O) imide. Other absorption bands appeared at (1353-1371) cm^{-1} ,(1083-1099) cm^{-1},(1199-1274) cm^{-1} and (1012-1018) cm^{-1} which are due to .υ(C-N) imide , .υ(C-Cl) and asym. and sym. .υ(C-O) ether respectively the spectra showed also disappearance or atrophy of .υ(C=C) aliphatic which are present in FTIR spectra of monomers [9-12] proving success of polymerization. FTIR spectral data of polymers [13-16] are listed in table (4) .

^{1}H-NMR spectrum of polymer [13-16] showed signals at (δ=2.55 and 2.63) ppm belong to aliphatic protons and signals at (δ=6.9and 7.2)ppm and (δ=7.3- 7.45)ppm.belong to aromatic protons.

Table 1: Physical properties of Compounds [9-12]

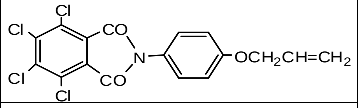
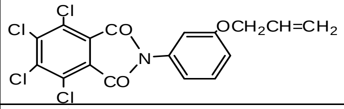
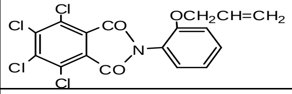
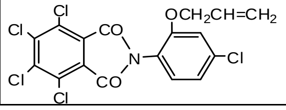
Comp. No.	Compound structure	Color	Yield %	Melting points °C	Recrystallization solvent
9		Off white	81	182-183	Acetone
10		Faint yellow	70	188-190	Acetone
11		Faint yellow	77	195 Dec.	Dioxane
12		Off white	75	192 Dec.	Dioxane

Table 2: Physical properties of Compounds [13-16]

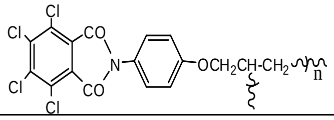
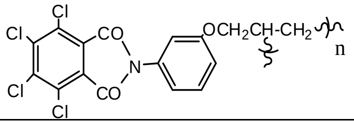
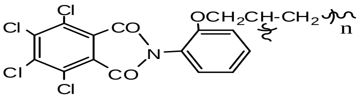
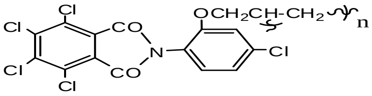
Polym. No.	Polymer structure	Color	Conver. ratio %	Soft. points °C	Recrystallization solvent
13		Faint yellow	65	225-235	Dissolving in THF then precipitation by MeOH
14		Faint yellow	63	222-230	Dissolving in THF then precipitation by MeOH
15		Brown	71	215-220	Dissolving in THF then precipitation by MeOH
16		Faint yellow	62	235-240	Dissolving in THF then precipitation by MeOH

Table 3: FTIR spectral data (cm^{-1}) of copolymers [9-12]

Comp. No.	ν(C-H) aromatic	ν(C-H) aliphatic	ν(C=O) imide	ν(C=C)	ν(C-N) imide	ν(C-O)	ν(C-Cl)
9	3033	2921 2815	1778	1612 1600	1353	1274 1016	1099
10	3087	2923	1782 1712	1608 1598	1365	1261 1000	1080
11	3020	2927 2852	1785 1726	1645 1600	1363	1271 1037	1095
12	3078	2925 2866	1784 1724	1656 1598	1365	1201 1018	1085

Table 4: FTIR spectral data (cm^{-1}) of copolymers [13-16]

Comp. No.	ν(C-H) aromatic	ν(C-H) aliphatic	ν(C=O) imide	ν(C=C) aromatic	ν(C-N) imide	ν(C-O)	ν(C-Cl)
13	3020	2923 2812	1778 1708	1600	1353	1274 1014	1099
14	3074	2918 2854	1784 1718	1600	1367	1201 1018	1097
15	3035	2927	1785 1724	1600	1365	1199 1018	1095
16	3018	2923 2877	1787 1730	1581	1371	1236 1012	1083

4. Conclusion

In this work incorporation of allyloxy groups in poly tetrachlorophthalimides structure is very important strategy to improve poly tetrachlorophthalimides solubility and fusibility leading to good processability and this inturn made the new polymers suitable for wide spectrum of applications.

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