

Synthesis and Copolymerization of Several New N-(allyloxy phenyl) tetrachlorophthalimides

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Abstract: A series of new copolyimides containing flexible allyloxy segments were synthesized via multisteps. In the first step four N-(hydroxyphenyl) tetra chloro phthalamic acids were prepared via reaction of amino phenols with tetra chloro phthalic anhydride. The obtained amic acids were dehydrated in the second step affording the corresponding N-(hydroxyphenyl) tetra chloro phthalimides. In the third step flexible allyloxy segments were introduced in the prepared imides via introducing the imides in reaction with allylchloride in basic medium producing N-(allyloxy phenyl)tetrachloro phthalimides and these in turn were introduced in the fourth step in free radical chain growth copolymerization with five vinylic monomers including acrylo nitrile , methacrylo nitrile, methyl acrylate, methyl meth acrylate and N-substituted acrylamide respectively producing fourteen new copolyimides having different physical properties which may serve different application. In this work both introducing of flexible allyloxy segment and copolymerization are efficient tools that furnish with new copolyimides having better solubility and process ability while maintaining their other excellent properties .

Keywords: copolyimides, allyloxy segment, tetrachlorophthalimides, vinylic monomers

1. Introduction

Aromatic polyimides are a class of polymers that have unique high thermal stability, high chemical resistance beside excellent mechanical and electrical properties ⁽¹⁻³⁾. However most polyimides have four processability and solubility due to high chain rigidity as a result of strong interchain forces ⁽⁴⁻⁶⁾. Thus significant efforts have been made to improve polyimides properties by chemical modifications ⁽⁷⁻¹⁰⁾. In this work we design and synthesize several new of copoly tetrachloro phthalimides with improve properties by performing two steps, First through introducing of soft segments flexible ether group (allyloxy group) into tetrachloro phthalimide monomers and second by introducing these monomers in copolymerization with different vinylic monomers. Both of these two steps introducing of soft segment ⁽¹¹⁾ and copolymerization ^(12,13) are efficient methods for improving polymers physical and mechanical properties. The present work reports synthesis of several N-(allyloxy phenyl)tetrachloro phthalimides then introduce them in free radical copolymerization producing new copolyimides with better solubility and processability properties fitted with different applications.

2. Experimental

Employed chemicals were purchased from Merk ,BDH and Fluka companies and used without further purification. FTIR spectra were recorded on a SHIMADZU FTIR 8400 Fourier transform Infrared spectrophotometer as KBr disk. ¹HNMR spectra were recorded on near magnetic resonance Bruker, ultrashield 300 MHz using DMSO-d₆ as solvent and tetramethyl silane as an internal standard. Melting points were determined by using Gallen Kamp capillary melting point apparatus and were uncorrected. Softening points were determined on thermal microscope Riechertthermover.

1) Synthesis of N-(hydroxy phenyl) tetrachlorophthalamic acids [1-4]

Amino phenol (0.01 mol) dissolved in (30 mL) of dry acetone was added dropwise to (0.01 mol, 2.86 g) of tetrachlorophthalic anhydride dissolved in (20 mL) of dry acetone with stirring and cooling ⁽¹⁴⁾. The resulted mixture was stirred for 2 h. at room temperature then the formed precipitate was filtered, washed with ether, dried and recrystallized from a suitable solvent. Physical properties of amic acids [1-4] are shown in table-1

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

Tetrachlorophthalamic acid (1 gm) was placed in a wide pyrex tube supplied with a thermometer and immersed in an oil bath ⁽¹⁵⁾. The oil bath was heated gradually until the complete fusion of amic acid then oil bath temperature was kept at ten degrees above melting point of the used amic acid for 2 h.

The fused product was cooled to room temperature and the obtained solid was recrystallized from a suitable solvent. Physical properties of imides [5-8] are shown in table-2

3) Synthesis of N-(allyloxyphenyl)tetrachlorophthalimides [9-12]

A mixture of (0.01 mol) of imides [5H-8H] and (0.0015mol) of sodium hydroxide was dissolved in (DMF) (15ml) then (0.01mol) of allyl chloride was added to the flask with stirring. The stirred mixture was refluxed for four hrs. then allowed to cool and poured onto ice water and left at 5°C over night. The resulted solid was filtered, washed with water, dried then purified by recrystallization from a suitable solvent. Physical properties of compounds [9-12] are shown in table-3.

4) Synthesis of N-(allyloxyphenyl)tetrachlorophthalimide-CO-acrylonitrile Copolymers [13-15]

In the screw capped polymerization bottle using equimolar amounts of monomers [9-12] and acrylonitrile were

dissolved in (15mL) of THF then (0.0002g) of AIBN was added as initiator⁽¹⁶⁾. The bottle was flushed with nitrogen for few minutes then firmly stoppered and maintained at (75°C) for 3hrs. the resulted solution was poured into (25mL) of methanol and the precipitated polymer was filtered, washed with methanol and dried. Physical properties of copolymers [13-15] are shown in table -4.

5) Synthesis of [N-(allyloxyphenyl)tetrachloro phthalimide-CO-methacrylonitrile] Copolymers [16,17]

The titled copolymers were synthesized by following the same procedure used in preparation of copolymers [13-15] using equimolar amounts of monomers [9-12] and methacrylonitrile dissolved in THF in the presence of AIBN initiator. Physical properties of copolymers [16,17] are shown in table-5.

6) Synthesis of [N-(allyloxyphenyl)tetrachloro phthalimide-CO-methyl acrylate] Copolymers [18,19]

The titled copolymers were synthesized by following the same procedure used in preparation of copolymers [13-15] using equimolar amounts of monomers [9-12] and methyl acrylate dissolved in THF in the presence of AIBN initiator. Physical properties of copolymers [18,19] are shown in table-6.

7) Synthesis of [N-(allyloxyphenyl)tetrachloro phthalimide-CO-methyl meth acrylate] Copolymers [20-22]

The titled copolymers were synthesized by following the same procedure used in preparation of copolymers [13-15] using equimolar amounts of monomers [9-12] and methyl acrylate dissolved in THF in the presence of AIBN initiator. Physical properties of copolymers [20-22] are shown in table-7.

8) Synthesis of [N-(allyloxyphenyl)tetrachloro phthalimide-CO-N-(2-methyl-6-chlorophenyl) acrylamide] Copolymers [23-26]

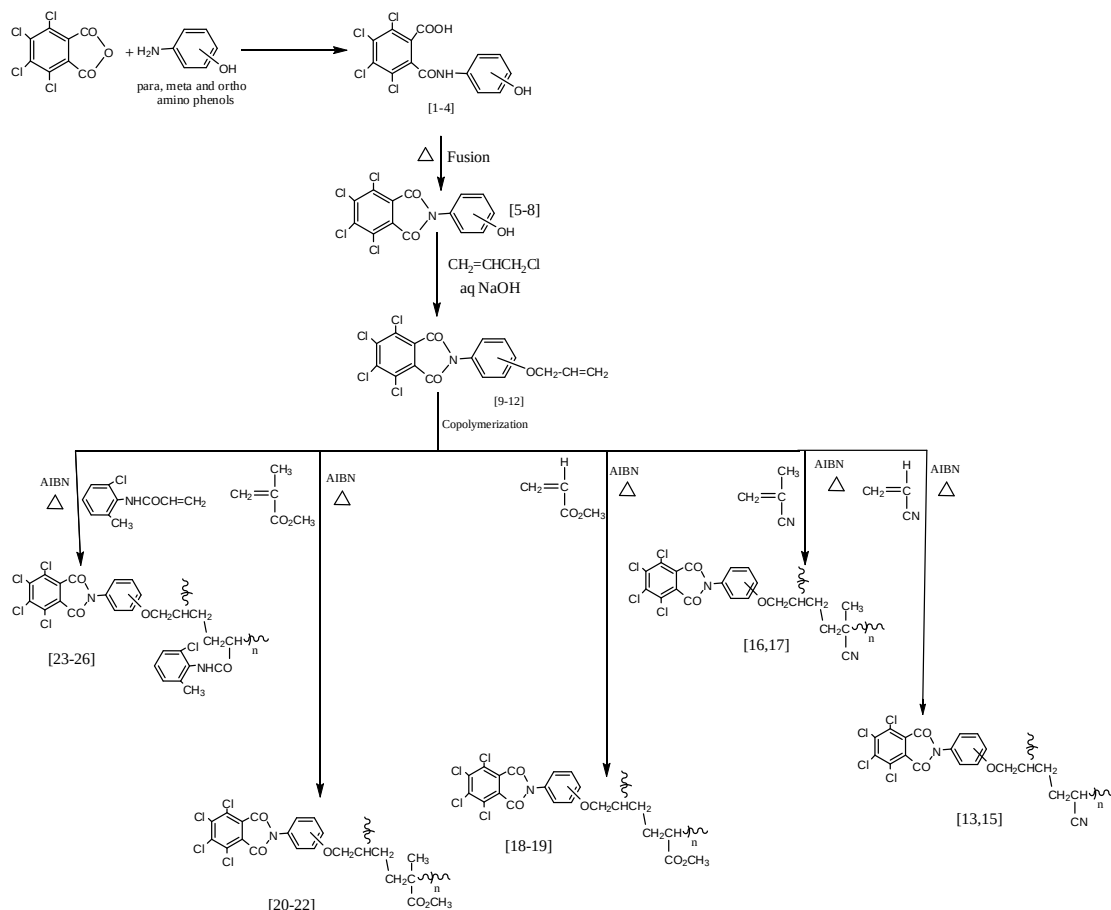
The titled copolymers were synthesized by following the same procedure used in preparation of copolymers [13-15] using equimolar amount of monomers [9-12] and N-(2-methyl-6-chlorophenyl) acrylamide dissolved in THF in the presence of AIBN initiator. Physical properties of copolymers [23-26] are shown in table-8.

3. Results and Discussion

In general high chains rigidity in polyimides leads to high glass transition temperature, poor solubility and processability. These properties in turn limit polyimides applications. To overcome this limitation, incorporation of alkoxy segment in polyimides backbone chains or introducing imides themselves in copolymerization with suitable monomers will establish flexibility in polyimides chains besides improving solubility and processability.

Thus in the present work a series of new poly tetrachloro phthalimides with improved properties were synthesized first by introducing alkoxy flexible segment (allyloxy group) in tetrachloro phthalimides monomers and second by introducing the synthesized monomers in copolymerization with suitable monomers since both of these two points are efficient methods for improving polymers physical and mechanical properties leading to wide spectrum of applications.

The target of this work was performed by many steps which are summarized in scheme-1



Scheme-1

In the first step four N-(hydroxyl phenyl) tetra chloro phthalamic acids [1-4] were synthesized via equimolar amounts ortho, meta and para- amino phenols with tetrachlorophthalic . In the next step amic acids[1-4] were dehydrated by fusion method to produce the corresponding tetrachloro phthalimides [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) tetra chloro phthalimides[9-12]. By this step a flexible alkoxy segments were introduced in imides structure and the same time this alkoxy segments having carbon-carbon double bonds ready for introducing in chain growth copolymerization.

In the fourth step the newly synthesized N-(allyloxy phenyl) tetra chloro phthalimides 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 copolymers[13-26]. Physical properties of amic acids, imides, allyloxy monomers and copolymers are listed in tables (1),(2),(3),(4),(5) and (6).

FTIR spectra of amic acids [1-4] showed clear absorption bands at (3184-3477) cm^{-1} which were attributed to ν (O-H) carboxylic , ν (O-H) phenolic and ν (N-H) amide. Absorption bands due to ν (C=O) carboxyl and ν (C=O) amide appeared at (1712-1716) cm^{-1} and (1650-1660) cm^{-1} respectively while absorption bands due to ν (C-H) aromatic , ν (C=C) aromatic and ν (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)ppmbelong 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 ν (C=O) imide. Absorption bands due to ν (C=C) aromatic and ν (C-N) imide were appeared at (1598-1612) cm^{-1} and (1365-1367) cm^{-1} , while absorption bands due to ν (O-H) phenolic, ν (C-H) aromatic and ν (C-Cl) appeared at (3417-3480) cm^{-1} (3030-3078) cm^{-1} (1090-1099) cm^{-1} respectively. ¹H-NMR spectra of compounds [5-8] showed disappearance of ν (O-H) carboxyl, ν (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⁾.

FTIR spectra of compounds [9-12] showed disappearance of ν (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. ν (C-H) aliphatic and other absorption bands at (1201-1274) cm^{-1} and (1000-1037) cm^{-1} due to ν (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. ν (C=O)imide, ν (C=C) aliphatic and aromatic , ν (C-N) imide and ν (C-Cl) respectively.

¹H-NMR spectra of compounds [9-12] showed signals at (δ = 2.55- 2.58) ppm belong to aliphatic protons and two doublet signals at (6.9 -7.15) ppm belong to aromatic protons. Details of FTIR spectral data of amic acids, imides, and N-(allyloxy phenyl) tetra chloro phthalimides are listed in tables (7), (8) and (9).

Synthesis of target copolymers was performed by free-radical chain growth copolymerization of monomers [9-12] with different vinylic monomers including acrylonitrile, meth acrylonitrile , methylacrylate , methylmethacrylate ,and N-substituted acryl amide producing copolymers [13-15] ,[16,17],[18,19] ,[20-22], and [23-26] respectively.it was noticeable that introduction of flexible allyloxy group in to the chain of phthalimide followed by copolymerization gave copolymers with remarkable solubility in polar amidic solvent such as DMF.The prepared copolymers [13-26] showed partial solubility in chloroform and good solubility in DMSO, DMF, and acceptable solubility in hot THF, but they are insoluble in methanol, benzene, acetone, ethanol, diethyl ether and cyclohexane.

FTIR spectra of acrylo and methacrylo nitrile copolymers [13-17] showed clear absorption band at (2235-2243) cm^{-1} due to ν ($\text{C}\equiv\text{N}$) and this is an excellent proof for the success of copolymerization reaction. Absorption bands due to asym. and sym. ν (C-H) aliphatic appeared at (2920-2981) cm^{-1} and (2845-1891) cm^{-1} while bands for asym. and sym. ν (C=O) imide appeared at (1776-1785) cm^{-1} and (1708-1724) cm^{-1} . Details of FTIR spectral data of copolymers [13-17] are listed in table-10

¹H-NMR spectrum of compounds [13-15] showed signals at δ =(2-2.15), 2.7 and 2.8 ppm belong to aliphatic protons, signal at δ =(3.1) ppm belong to (-CHCN) proton and two

doublet signals at δ =(6.8 and 7.35) ppm belong to aromatic protons.

¹H-NMR spectra of compounds [16,17] showed signals at δ =(1.47-1.51) and (1.7-1.76) and 2.55 ppm belong to (CH_3)and aliphatic protons, signals at δ =(6.8 and 7.21) ppm belong to aromatic protons.

FTIR spectra of methyl acrylate and methyl methacrylate copolymers [18-22] showed clear absorption bands at (1728-1735) cm^{-1} and (1149-1164) cm^{-1} due to ν (C=O) ester and ν (C-O) ester respectively and this is a good proof for the success of copolymerization. Other FTIR spectral data of copolymers[18-22] are listed in table -11

¹H-NMR spectra of copolymers [18-22] showed signals at δ = (1.55-1.8) , 2.7 and 2.9 ppm belong to aliphatic protons. Singlet signal appeared at (δ =3.6)ppm belong to (OCH_3) protons and signals at (δ =6.85-7.4)ppm belong to aromatic protons.

FTIR spectra of copolymers [23-26] showed two important clear absorption bands at (3261-3269) cm^{-1} and (1660-1662) cm^{-1} which are attributed to ν (N-H) amide and ν (C=O) amide respectively and this is an important proof for success of copolymers [23-26] formation.

Other details of FTIR spectral data of copolymers [23-26] are listed in Table 12.

¹H-NMR spectra of copolymers [23-26] showed signals at (δ = (1.09-1.72), 2.31, (2.6-2.7) and 2.97) ppm belong to aliphatic protons and (CH_3) protons. Other signals appeared at δ = (6.65-7.67) and δ = (9.62-9.97) ppm which are belong to aromatic protons and (NH) proton respectively.

Table 1: Physical properties of Compounds [1-4]

Comp. No.	Compound structure	Color	Yield %	Melting points $^{\circ}\text{C}$	Recrystallization solvent
1		Gray	78	166-168	Ethanol
2		Bluish green	81	186-187	Ethanol
3		Faint green	76	170-172	Ethanol
4		Yellowish green	88	184-186	Ethanol

Table 2: Physical properties of Compounds [5-8]

Comp. No.	Compound structure	Color	Yield %	Melting points °C	Recrystallization solvent
5		Deep gray	80	231-233	Acetone
6		Deep yellow	95	195 Dec.	Cyclohexane
7		Deep green	88	210-212	Cyclohexane
8		yellow	93	205 Dec.	Cyclohexane

Table3: 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 4: Physical properties of Copolymers [13-17]

Polym. No.	Polymer structure	Color	Conversion ratio	Soft. point °C
13		Off White	69	229-238
14		Off white	64	230-246

15		Off White	65	238-250
16		Dark green	66	220-230
17		Faint green	68	232-241

Table 5: Physical properties of Copolymers [18-22]

Comp. No.	Polymer structure	Color	Conversion ratio %	Soft. point °C
18		Faint brown	63	237-240
19		Faint brown	62	236-243
20		Dark green	83	227-235
21		Dark green	61	234-240
22		Faint brown	70	243-253

Table 6: Physical properties of Copolymers [23-26]

Comp. No.	Polymer structure	Color	Conversion ratio %	Soft. point °C
23		Brown	72	Gummy
24		Brown	53	286-290
25		Deep green	62	231-236
26		Brown	70	237-250

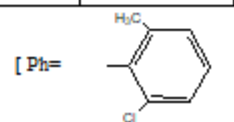


Table 7: FTIR spectral data (cm⁻¹) of Compounds[1-4]

Comp. No.	v(O-H) and v(N-H)	v(C-H) aromatic	v(C=O) carboxyl	v(C=O) amide	v(C=C) aromatic	v(C-Cl)	Others
1	3267	3040	1712	1650	1620 1610	1030	-
2	3477 3394 3267	3089	1714	1654	1606	1043	-
3	3417 3274 3261	3020	1712	1650	1618	1103	p-sub. 825
4	3379 3184	3037	1716	1660	1596	1089	p-sub. 815

Table 8: FTIR spectral data (cm⁻¹) of Compounds [5-8]

Comp. No.	v(O-H) phenolic	v(C-H) aromatic	v(C=O) imide	v(C=C) aromatic	v(C-N) imide	v(C-Cl)	Others
5	3421	3078	1787 asy. 1731 sy.	1598	1365	1097	-
6	3417	3060	1778 asy. 1710 sy.	1612 1600	1367	1099	-
7	3419	3030	1776 asy. 1704 sy.	1612 1600	1367	1099	p-sub. 833
8	3480	3060	1780 asy. 1720 sy.	1605	1365	1090	p-sub. 822

Table 9: FTIR spectral data (cm⁻¹) of compounds [9-12]

Comp. No.	v(C-H) aromatic	v(C-H) aliphatic	v(C=O) imide	v(C=C) aromatic	v(C-N) imide	v(C-O)	v(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 10: FTIR spectral data (cm⁻¹) of copolymers[13-17]

Polym. No.	v(C-H) aromatic	v(C-H) aliphatic	v(C≡N)	v(C=O) imide	v(C=C) aromatic	v(C-N) imide	v(C-O) ether	v(C-Cl)
13	3093	2920 2870	2243	1776 1710	1562	1369	1205 1018	1099
14	3070	2921 2945	2243	1784 1708	1596	1365	1236 1014	1080
15	3040	2937 2873	2243	1785 1724	1600	1365	1199 1016	1095
16	3001	2950 2891	2235	1780 1710	1517	1369	1276 1018	1101
17	3010	2981 2890	2235	1784 1708	1596	1365	1234 1015	1095

Table 11: FTIR spectral data (cm⁻¹) of copolymers[18-22]

Polym no.	v(C-H) aromatic	v(C-H) aliphatic	v(C=O) ester	v(C=O) imide	v(C=C) aromatic	v(C-N) imide	v(C-O)	v(C-Cl)
18	3080	2954 2850	1730	1784 1708	1596	1365	1164	1058
19	3068	2952 2850	1731	1787 1731	1502	1388	1164	1037
20	3095	2952	1735	1774 1722	1558	1369	1149	-
21	3040	2950 2842	1730	1782 1720	1596	1365	1149	1058
22	2995	2950 2839	1728	1785 1728	1602	1367	1149	1097

Table 12: FTIR spectral data (cm⁻¹) of copolymers [23-26]

Comp. No.	v(N-H) amide	v(C-H) aromatic	v(C-H) aliphatic	v(C=O) imide	v(C=O) amide	v(C=C) aromatic	v(C-N) imide	v(C-O) ester	v(C-Cl)
23	3267	3056	2918 2866	1776 1712	1660	1581	1371	1263 1022	1087
24	3263	3070	2960 2842	1780 1712	1662	1581	1369	1261 1018	1087
25	3269	3033	2970 2866	1782 1722	1662	1581	1365	1199 1024	1093
26	3261	3078	2970 2885	1785 1728	1660	1581	1373	1201 1020	1087

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