

Synthesis of Homo and Copolymerization of New Bicyclic Imide with Central Schiff Base Moiety

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ABSTRACT

In this work, seven new bisimide polymers containing Schiff base component were synthesized through performing many steps. The first step involved reaction of maleic anhydride with 4-amino acetophenone producing maleamic acid which in turn was converted in the second step to corresponding maleimide via dehydration reaction. Treatment with benzidine in the third step afforded Schiff base which subsequently introduced in reaction with citraconic anhydride affording citraconamic acid and this was converted to bisimide through reaction with acetic anhydride and sodium acetate. The newly synthesized monomer was introduced in free radical homo and copolymerization producing the target new polymers.

Keyword: Bisimide polymers, Copolymerization, Free radical polymerization, Maleamic acid.

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INTRODUCTION

Polyimides are widely known as high-performance polymers due to their excellent thermal and chemical stability, high mechanical performance and high radiation resistance.¹⁻³

These properties made polyimides used in various applications including aerospace industries, microelectronics, gas and chemical separation membrane and porous films.⁴⁻⁸

However, the further applications were limited because of their poor processability, high melting or glass transition temperatures and limited solubility in most organic solvents.

To overcome these problems different methods were followed^{9,10} like incorporation of bulky pendent groups or aliphatic and flexible units or by copolymerization.¹¹⁻¹³

Copolymerization¹⁴ is an excellent method for improving processability and solubility of polyimides beside preserving their good thermal and mechanical properties.

In the present work a new bisimide monomer containing both maleimide and citraconimide rings with central Schiff component was synthesized through multisteps then was introduced in copolymerization with different vinylic monomers producing new copolyimides with improved melting and solubility properties which may serve new applications.

MATERIAL AND METHODS

The chemicals were purchased from Merk, Fluka and BDH companies, fourier-transform infrared spectroscopy (FTIR) spectra were recorded on SHIMADZU FTIR 8400 Former

transform Infrared spectrophotometer. ¹H-NMR and ¹³C-NMR spectra were recorded on nuclear magnetic resonance Bruker 400 MHz. Melting points were measured on Gallen Kamp capillary melting point apparatus while softening points were measured on thermal microscope Riechert thermover apparatus.

Preparation of N-(4-acetyl phenyl) Maleamic Acid (1)¹⁵

A solution of 0.01 mol, 1.35 g of 4-amino acetophenone dissolved in acetone 25 mL was added drop by drop to solution of 0.01 mol, 0.98 g of maleic anhydride dissolved in acetone (20 mL) with cooling and stirring. The resulted mixture was stirred for additional 2 hours. then the formed solid was filtered, washed with acetone then with diethyl ether, dried and finally recrystallized from ethanol.

Preparation of N-(4-acetyl phenyl) Maleimide (2)¹⁶

A mixture of 0.1 mol, 2.33 g of N-(4-acetyl phenyl) maleamic acid in 25 mL of acetic anhydride and 5 to 10% by weight of anhydrous sodium acetate was refluxed with stirring for 2 hours. The resulted homogenous solution was cooled to room temperature then poured into excess cold water with vigorous stirring. The obtained precipitate was filtered, washed with water, dried and finally purified by recrystallization from acetone.

Synthesis of N-(4-(1-((4'-amino-[1,1'-biphenyl]-4-yl)imino)ethyl) phenyl) Maleimide (3)^{16,17}

A solution of N-(4-acetyl phenyl) maleimide (0.01 mol, 2.15 g) with few drops of glacial acetic acid in absolute ethanol 25 mL

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was added dropwise to solution of benzidine (0.01 mol, 1.84 g) in 15 mL absolute ethanol then the mixture was refluxed for 6 hours with stirring. The resulted mixture was cooled and the formed solid product was collected by filtration, washed with ether, dried then recrystallized from ethanol.

Synthesis of N-(4-(1-((4'-citraconamic acid-[1,1'-biphenyl]-4-yl)imino)ethyl)phenyl) maleimide (4)¹⁵

A solution of (0.005 mol, 1.9 g) of N-(4-(1-((4'-amino-[1,1'-biphenyl]-4-yl)imino)ethyl)phenyl) maleimide dissolved in acetone (20 mL) was added drop by drop to solution of (0.005 mol, 0.56 g) of citraconic anhydride dissolved in acetone (20 mL) with cooling and stirring. The resulted mixture was stirred for additional 3 hours, then the formed solid was filtered, washed with acetone then with diethyl ether, dried and finally recrystallized from ethanol.

Synthesis of N-(4-(1-((4'-citraconimide-[1,1'-biphenyl]-4-yl) imino)ethyl)phenyl) maleimide (5)¹⁵

A mixture of (0.005 mol, 2.465 g) of N-(4-(1-((4'-citraconamic acid-[1,1'-biphenyl]-4-yl)imino)ethyl)phenyl) maleimide in (15 mL) of acetic anhydride and (5–10) % by weight of anhydrous sodium acetate was refluxed with stirring for 2.5 hours. The resulted homogenous solution was cooled to room temperature then poured into excess cold water with vigorous stirring. The obtained precipitate was filtered, washed with water, dried and finally purified by recrystallization from ethanol.

Homopolymerization of monomer N-(4-(1-((4'-citraconimide-[1,1'-biphenyl]-4-yl)imino)ethyl)phenyl) maleimide (6)²

In a suitable dry and dark polymerization bottle (0.002 mol, 0.95g) of the monomer N-(4-(1-((4'-citraconimide-[1,1'-biphenyl]-4-yl)imino)ethyl) phenyl) maleimide was dissolved in (15 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 hours.

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.

Copolymerization of monomer N-(4-(1-((4'-citraconimide-[1,1'-biphenyl]-4-yl)imino)ethyl)phenyl) maleimide with vinylic monomers (7-12)¹³

The titled copolymers were prepared by following the same procedure steps used in synthesis of homopolymer [6] except using of monomer N-(4-(1-((4'-citraconimide-[1,1'-biphenyl]-4-yl)imino)ethyl)phenyl) maleimide and vinylic monomers including (acrylonitrile, methacrylonitrile, methyl acrylate, methyl meth acrylate, vinyl acetate and acryl amide). Purification of copolymers was performed by dissolving in THF followed by precipitation from methanol. Physical properties of polymers (6–12).

RESULTS AND DISCUSSION

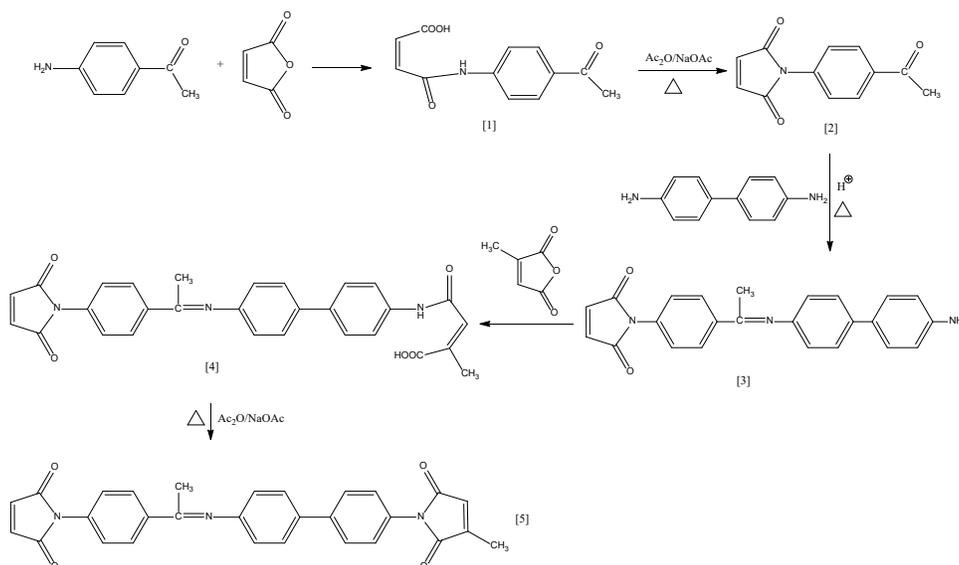
Strong interchain forces along backbone chains in polyimides lead to high thermal and chemical stability beside poor fusibility and solubility which caused poor processability.

Thus, the core of the present work is to synthesize new polyimides with improving properties including improved processability, softening point and solubility.

Performing this target based on synthesis of new bisimide containing maleimide and citraconimide rings with central Schiff base moiety then introducing this monomer in chain growth copolymerization producing new copolyimides having improved desired properties.

Synthesis of the new bisimide monomer was performed by five synthetic steps which are shown in Scheme 1.

The first step involved preparation of amic acid¹ via reaction of 4-amino acetophenone with maleic anhydride. In the second step amic acid¹ was dehydrated to the corresponding maleimide² by using acetic anhydride and anhydrous sodium acetate as dehydrating agent. Maleimide² was introduced



Scheme 1: Synthesis route of compounds¹⁻⁵

in the third step in condensation reaction with benzidine in ethanol as solvent in presence of glacial acetic acid as catalyst producing Schiff base.³

Schiff base³ contain amino group which gave the chance for introducing this compound in the fourth step in reaction with citraconic anhydride producing the corresponding citraconamic acid⁴ and this inturn was dehydrated in the fifth step by using acetic anhydride and anhydrous sodium acetate as dehydrating agent producing the new target monomer.⁵

The newly synthesized monomer⁵ contain two imide rings maleimide and citraconimide with central Schiff base moiety. Physical properties of compounds [1-5] are listed in Table 1.

Chemical structures of the prepared compounds were proved by depending on FTIR, ¹H-NMR and ¹³C-NMR spectral data.

FTIR spectrum of compound [1] showed clear absorption bands at 3469, 3417 and 3269 cm⁻¹ due to $\nu(\text{O-H})$ carboxylic and $\nu(\text{N-H})$ amide. The spectrum showed also absorption bands at (1710) cm⁻¹, (1677) cm⁻¹ and (1633) cm⁻¹ which are attributed to $\nu(\text{C}=\text{O})$ carboxylic, $\nu(\text{C}=\text{O})$ ketone and $\nu(\text{C}=\text{O})$ amide, respectively.¹⁸

FTIR spectrum of compound [2] showed disappearance of absorption bands due to $\nu(\text{O-H})$ carboxyl, $\nu(\text{N-H})$ amide and $\nu(\text{C}=\text{O})$ amide and at the same time showed appearance of two absorption bands a shoulder band at (1778) cm⁻¹ and a clear strong band at 1714 cm⁻¹ belong to asym. and sym. $\nu(\text{C}=\text{O})$ imide. These points are clear proofs for success of dehydration reaction and formation of maleimide.² Other absorption bands appeared at 1679 cm⁻¹, 1379 cm⁻¹ and 1598 cm⁻¹ which are belong to $\nu(\text{C}=\text{O})$ ketone, $\nu(\text{C-N})$ imide and $\nu(\text{C}=\text{C})$ aromatic, respectively.¹⁹

FTIR spectrum of compound [3] showed appearance of two absorption bands at 3359 cm⁻¹ and 3201 cm⁻¹ due to asym. and sym. $\nu(\text{NH}_2)$.

The spectrum showed also disappearance of $\nu(\text{C}=\text{O})$ ketone and appearance of $\nu(\text{C}=\text{N})$ imine at 1658 cm⁻¹. These points proved success the formation of compound [3] which contain imine ($\text{C}=\text{N}$) group and amino group (NH_2).

¹H-NMR spectrum of compound [3] showed signal at ($\delta = 2.59$) ppm belong to (CH_3) protons, signal at ($\delta = 5.18$) ppm belong to (NH_2) protons, signal at ($\delta = 6.73$) ppm belong to vinylic protons in maleimide ring and signals at ($\delta = 7.21-7.3$) ppm belong to aromatic protons.

FTIR spectrum of compound [4] showed absorption bands at (3307) cm⁻¹ and (3203) cm⁻¹ due to $\nu(\text{O-H})$ carboxylic and $\nu(\text{N-H})$ amide. Beside the spectrum showed absorption bands due to $\nu(\text{C}=\text{O})$ carboxyl and $\nu(\text{C}=\text{O})$ amide appeared at (1683) cm⁻¹ and (1627) cm⁻¹, respectively.

FTIR spectrum of compound [5] showed disappearance of $\nu(\text{O-H})$ carboxyl, $\nu(\text{N-H})$ amide, $\nu(\text{C}=\text{O})$ carboxyl and $\nu(\text{C}=\text{O})$ amide absorption bands proving the success of citraconimide [5] formation. The spectrum showed absorption bands at (1768) cm⁻¹, (1712) cm⁻¹, (1647) cm⁻¹, (1502) cm⁻¹ and (1394) cm⁻¹ which are due to asym. $\nu(\text{C}=\text{O})$ imide, sym. $\nu(\text{C}=\text{O})$ imide, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C-N})$ imide, respectively.¹⁹

¹H-NMR spectrum of compound [5] showed signal at $\delta = 2.18$ ppm and $\delta = 2.61$ ppm belong to (CH_3) citracon protons and CH_3 bonded to imine group. Other signals appeared at $\delta = 5.89$ ppm and $\delta = 6.36$ ppm belong to vinylic protons in maleimide and citraconimide rings and signals at $\delta = 6.95-7.95$ ppm belong to aromatic protons.

Table 1: Physical properties of compounds (1-5).

Comp. No.	Compound structure	Color	Yield %	Melting point °C	Recrystallization solvent
1		Yellow	94	200–203°C	Ethanol
2		Dark red	96	279–281°C	Acetone
3		Brown	65	75–78°C	Ethanol
4		Brown	88	278–280°C	Ethanol
5		Brown	90	150–152°C	Ethanol

^{13}C -NMR spectrum of compound [5] showed signals at ($\delta = 210.85$) ppm and ($\delta = 26.78$) ppm belong to two methyl groups carbons and signals at ($\delta = 119.26$) ppm, ($\delta = 169.62$) ppm and ($\delta = 170.49$) ppm belong to aromatic carbons, ($\text{C} = \text{N}$) carbon and ($\text{C} = \text{O}$) imide carbons, respectively.

Compound [5] represents a new monomer containing two imide rings with central Schiff base moiety beside presence of two vinylic bonds ready for chain growth polymerization.

Thus compound [5] was introduced in free radical chain growth homopolymerization using THF as solvent and (AIBN) as initiator producing homopolymer [6].

Homopolymer (6) is a pale brown solid with high softening points and showed no solubility in all common organic solvents except DMF and DMSO.

On the other side since copolymerization is an excellent method for producing polymers with improved physical and mechanical properties we introduce the newly synthesized monomer (5) in chain growth copolymerization with six vinylic monomers including acrylo nitrile, methacrylo nitrile, methyl acrylate, methyl methacrylate, vinyl acetate and acryl amide producing new six copolymers with better fusibility and solubility.

The synthesized copolymers are either gummy products or solids with low softening points beside all of them showed good solubility in all tested organic solvents.

Physical properties of polymers [6-12] are shown in Table 2 while their solubility properties are shown in Table 3 (Scheme 2).

FTIR spectrum of homopolymer [6] showed absorption bands at ($1770, 1716$) cm^{-1} due to asym. and sym. $\nu(\text{C} = \text{O})$ imide and other bands at ($1652, 1606$ and 1373) cm^{-1} due to $\nu(\text{C} = \text{N})$, $\nu(\text{C} = \text{C})$ and $\nu(\text{C}-\text{N})$ imide respectively.

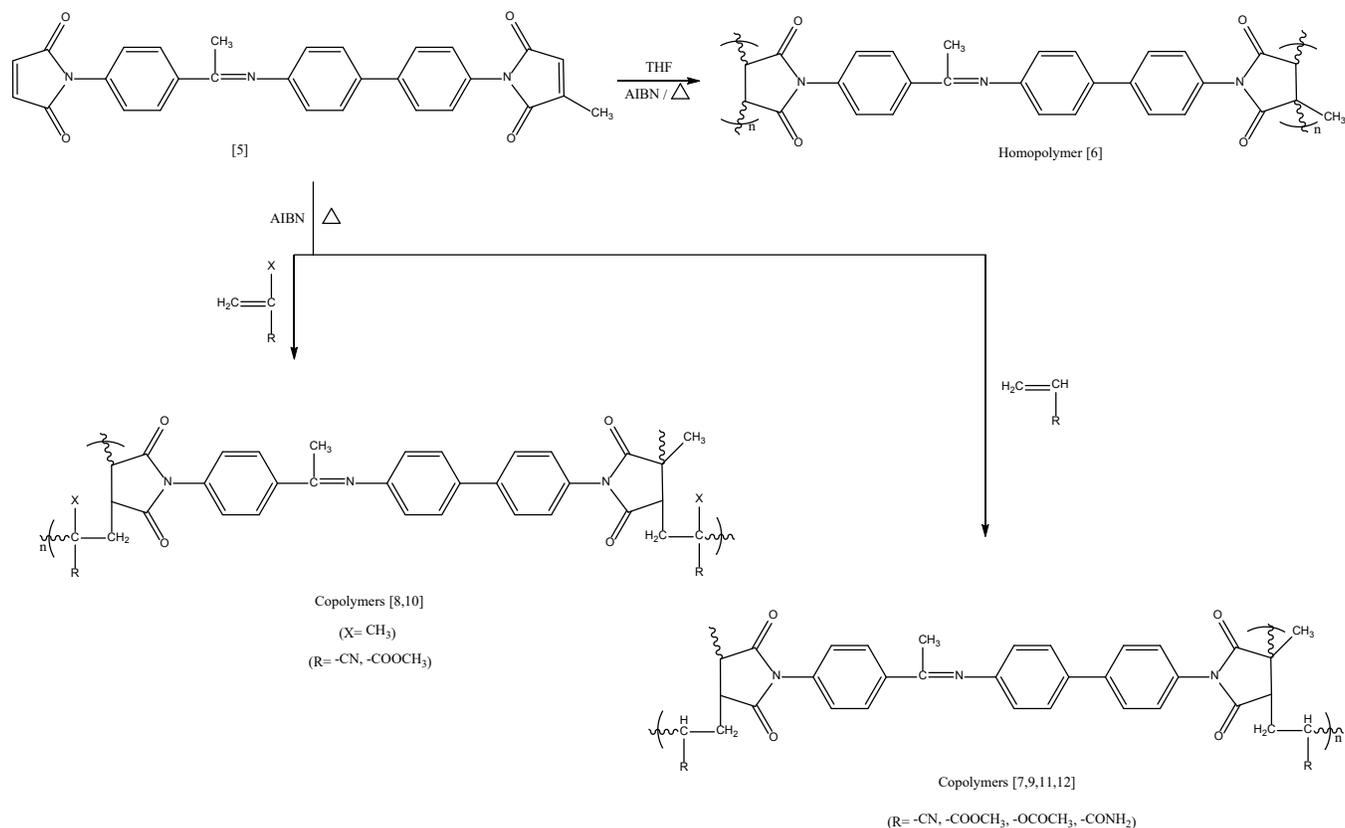
Besides the spectrum showed also important strong bands at ($2981, 2929, 2873$) cm^{-1} due to asym. and sym. $\nu(\text{C}-\text{H})$ aliphatic indicating presence of aliphatic ($\text{C}-\text{H}$) bonds formed due to the success of polymerization.

FTIR spectra of copolymers with acrylo nitrile [7] and methacrylo nitrile [8] showed clear absorption bands at ($2937-2987$) cm^{-1} and ($2875-2879$) cm^{-1} due to asym. and sym. $\nu(\text{C}-\text{H})$ aliphatic. Besides the spectra of copolymers [7] and [8] showed very important characteristic band at ($2237-2243$) cm^{-1} due to $\nu(\text{C}\equiv\text{N})$. These two points are good proofs for success the formation of copolymers [7] and [8].

^1H -NMR spectrum of copolymer [7] showed signals at ($\delta = 1.48-1.97$) ppm belong to aliphatic protons, signal at ($\delta = 2.13$) ppm belong to citracon methyl protons, signal at ($\delta = 2.59$) ppm belong to ($\text{CH}_3\text{C} = \text{N}$) protons and signals at ($\delta = 7.45-7.9$) ppm belong to aromatic protons.

^{13}C -NMR spectrum of copolymer [7] showed signals at ($\delta = 14.10-26.44$) ppm belong to ($-\text{CH}_2-\text{CH}-$) carbons and carbons in imide rings.

Signals at ($\delta = 27.98$) ppm and ($\delta = 30.92$) ppm belong to two methyl carbons, signal at ($\delta = 67.05$) ppm belong to ($\text{C}\equiv\text{N}$) carbon, signals at ($\delta = 119-138$) ppm belong to aromatic carbons and signals at ($\delta = 153-158$) ppm belong to ($\text{C} = \text{N}$) and ($\text{C} = \text{O}$) imide carbons.



Scheme 2: Synthesis route of polymers⁶⁻¹²

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Table 2: Physical properties of polymers (6-12).

Poly. No.	Polymer structure	Color	Conv. Ratio %	Softening point °C	Purification
6		Pale brown	83	120–133°C	
7		Brown	85	Gummy	
8		Pale brown	78	Gummy	
9		Brown	81	Gummy	By dissolving in THF then precipitation by methanol
10		Dark orange	77	41–55°C	
11		Brown	79	Gummy	
12		Dark brown	82	137–150°C	

Table 3: Solubility of polymers in different organic solvents.

Poly. No.	Solvents									
	THF	DMF	DMSO	Acetone	Methanol	Ethanol	Dioxane	Chloroform	Petr. ether	Et ₂ O
6	sh	s	s	ins	ins	ins	ins	sh	ins	ins
7	s	s	s	s	ins	sh	s	s	ins	ins
8	s	s	s	s	ins	sh	s	s	ins	ins
9	s	s	s	s	ins	sh	s	s	ins	ins
10	s	s	s	s	ins	sh	s	s	ins	ins
11	s	s	s	s	ins	sh	s	s	ins	ins
12	s	s	s	s	ins	sh	s	s	ins	ins

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

FTIR spectra of copolymers with methyl acrylate [9], methyl methacrylate [10] and vinyl acetate [11] showed strong absorption bands at 2952-2981 cm^{-1} and 2856-2883 cm^{-1} due to asym. and sym. $\nu(\text{C-H})$ aliphatic, strong absorption band at 1714-1735 cm^{-1} due to $\nu(\text{C}=\text{O})$ ester and strong clear absorption bands at 1240-1269 cm^{-1} and 1149-1172 cm^{-1} due to asym. and sym. $\nu(\text{C-O})$ ester. All these points are excellent proofs for success of copolymerization process and formation of copolymers.⁹⁻¹¹

$^1\text{H-NMR}$ spectrum of copolymer [9] showed strong clear signals at $\delta = 1.36\text{-}1.8$ ppm, $\delta = 1.98$ ppm and $\delta = 2.06$ ppm belong to aliphatic protons and two methyl groups (citracon and methacrylate) protons. Other signals appeared at $\delta = 2.62$, 3.78 and 7.4-7.35 ppm which are belong to (CH_3) imine protons, (OCH_3) protons and aromatic protons respectively.

$^{13}\text{C-NMR}$ spectrum of copolymer [9] showed signals at $\delta = 26.56\text{-}28.66$ ppm, 30.77-30.88 ppm and 33.45-34.81 ppm which are belong to carbon of $(-\text{CH}_2-)$ group, carbons in imide rings and carbons of two methyl groups.

Signals appeared at $\delta = 51.31$ ppm and $\delta = 66.77$ ppm belong to $(-\text{CH-COOCH}_3)$ and (OCH_3) carbons, signals at $\delta = 127.37\text{-}132$ ppm belong to aromatic carbons and signals at $\delta = 140$ ppm, $\delta = 172.60$ ppm and $\delta = 174.33$ ppm belong to $(\text{C}=\text{N})$, $(\text{C}=\text{O})$ imide and $(\text{C}=\text{O})$ ester respectively.

$^1\text{H-NMR}$ spectrum of copolymer [10] showed strong clear signals at $\delta = 0.85\text{-}1.71$ ppm, $\delta = 1.80$ ppm and $\delta = 1.91$ ppm belong to aliphatic protons and two methyl groups (citracon and methacrylate) protons. Other signals appeared at $\delta = 2.63$, 3.67 and 6.7-7.9 ppm which are belong to (CH_3) imine protons, (OCH_3) protons and aromatic protons respectively.

$^{13}\text{C-NMR}$ spectrum of copolymer [10] showed signals at $\delta = 15.93\text{-}25.45$ ppm belong to $(-\text{CH}_2-)$ carbons and carbons

in imide rings, signals at $\delta = 29.14\text{-}30.37$ ppm belong to four methyl groups protons, signals at $\delta = 44.18$ ppm belong to $(\text{CH}_3\text{C-CO-})$ carbons and signals at $\delta = 51.77\text{-}53.75$ ppm belong (OCH_3) carbons.

Other signals appeared at $\delta = 124.89\text{-}127.60$ ppm belong to aromatic carbons and signals at $\delta = 177.18$ and $\delta = 178$ ppm belong to $(\text{C}=\text{N})$, $(\text{C}=\text{O})$ imide and $(\text{C}=\text{O})$ ester carbons.

$^1\text{H-NMR}$ spectrum of copolymer with vinyl acetate [11] showed signals at $\delta = 1.11\text{-}1.75$ ppm, $\delta = 1.84$ ppm, $\delta = 2.19$ ppm and $\delta = 2.6$ ppm which are belong to aliphatic protons, (CH_3) citracon protons, $(\text{CH}_3\text{CO-})$ protons and (CH_3) imine protons respectively. Other signals appeared at $\delta = 3.80$ ppm and $\delta = 7.43\text{-}7.96$ ppm belong to $(-\text{CH-O-COCH}_3)$ protons and aromatic protons.

$^{13}\text{C-NMR}$ spectrum of copolymer [11] showed signals at $\delta = 19.22\text{-}26.77$ ppm belong to $(-\text{CH}_2-)$ carbons and carbons in imide rings, signals at $\delta = 28.51$ ppm, $\delta = 29.10$ ppm and $\delta = 30.37$ ppm belong to (CH_3) citracon, (CH_3CO) and (CH_3) imine carbons.

Other signals appeared at $\delta = 66.77$ ppm belong to $(-\text{CH-O-CO-})$ carbons, signals at $\delta = 119.28\text{-}129.60$ ppm belong to aromatic carbons, signal at $\delta = 139.26$ ppm belong to $(\text{C}=\text{N})$ carbon and signals at $\delta = 175$ ppm and $\delta = 177.86$ ppm belong to $(\text{C}=\text{O})$ imide and $(\text{C}=\text{O})$ ester carbons.

Copolymer with acryl amide [12] is a dark brown solid with softening point 137-150°C. The presence of amide groups in this copolymer gave the chance for formation of hydrogen bonding between polymeric chains leading to increase softening point in comparison with gummy polymers (copolymers 9, 10, 11) which have on hydrogen bonding but instead have ester groups which exhibit flexibility and lowering softening points.

Table 4: FTIR spectral data (cm^{-1}) of compounds (1-3).

Comp. No.	$\nu(\text{O-H})$ $\nu(\text{N-H})$	$\nu(\text{C-H})$ Aromatic	$\nu(\text{C-H})$ Aliphatic	$\nu(\text{C}=\text{O})$ Carboxyl	$\nu(\text{C}=\text{O})$ Ketone	$\nu(\text{C}=\text{O})$ Amide	$\nu(\text{C}=\text{C})$
1	3469 3414 3269	3087	2920 2860	1710	1677	1633	1537
2		$\nu(\text{C-H})$ Aromatic	$\nu(\text{C-H})$ Aliphatic	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{O})$ Ketone	$\nu(\text{C-N})$ Imide	$\nu(\text{C}=\text{C})$
3		3053	2916 2880	1787 1714	1679	1379	1598
4		$\nu(\text{C-H})$ Aromatic	$\nu(\text{C-H})$ Aliphatic	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	Others
5		3029	2927 2867	1778 1710	1658	1606	$\nu(\text{NH}_2)$ 3359 3201
6	$\nu(\text{O-H})$ $\nu(\text{N-H})$	$\nu(\text{C-H})$ Arom./Aliph.	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C-N})$ Imide	$\nu(\text{C}=\text{C})$
7	3307 3203	3062 2929 2831	1770 1726	1683 Caboxyl 1627 Amide	1569	1330	1525
8		$\nu(\text{C-H})$ Aromatic	$\nu(\text{C-H})$ Aliphatic	$\nu(\text{C}=\text{O})$ Imide	$\nu(\text{C}=\text{N})$	$\nu(\text{C-N})$ Imide	$\nu(\text{C}=\text{C})$
9		3093	2940 2880	1768 1712	1647	1394	1502

Table 5: FTIR spectral data (cm⁻¹) of polymers (6-12).

<i>Poly. No.</i>	<i>v(C-H)</i> <i>Aromatic</i>	<i>v(C-H)</i> <i>Aliphatic</i>	<i>v(C = O)</i> <i>Imide</i>	<i>v(C = N)</i>	<i>v(C = C)</i>	<i>v(C-N)</i> <i>Imide</i>	<i>Others</i>
6	3080	2929 2873	1770 1716	1652	1606	1373	-
7	3058	2975 2941 2875	1762 1714	1685	1519	1373	$\nu(\text{C}\equiv\text{N})$ 2243
8	3089	2987 2937 2879	1774 1714	1637	1502	1394	$\nu(\text{C}\equiv\text{N})$ 2237
9	3020	2952 2883	1735	1635	1500	1394	$\nu(\text{C} = \text{O})$ Ester 1735 $\nu(\text{C}-\text{O})$ Ester 1257,1166
10	3062	2952 2856	1730	1649	1541	1388	$\nu(\text{C} = \text{O})$ Ester 1730 $\nu(\text{C}-\text{O})$ Ester 1269,1149
11	3064	2981 2883	1714	1650	1500	1380	$\nu(\text{C} = \text{O})$ Ester 1714 $\nu(\text{C}-\text{O})$ Ester 1240,1172
12	3070	2925 2866	1712	1616	1500	1369	$\nu(\text{N}-\text{H})$ Amide 3433, 3363 $\nu(\text{C} = \text{O})$ Amide 1664

FTIR spectrum of copolymer [12] showed clear strong absorption bands at 3433 cm⁻¹ and 3363 cm⁻¹ due to asym. and sym. $\nu(\text{NH}_2)$ and band at 1664 cm⁻¹ due to $\nu(\text{C} = \text{O})$ amide. These points beside presence of strong absorption bands at 2925 cm⁻¹ and 2866 cm⁻¹ due to asym. and sym. $\nu(\text{C}-\text{H})$ aliphatic are good proofs for success of copolymerization with acryl amide.

All details of FTIR spectral data of the prepared compounds and polymers are listed in Tables 4 and 5.

¹H-NMR spectrum of copolymer [12] showed signals at ($\delta = 1.40$ -2.0) ppm belong to (-CH₂-) and aliphatic protons in imide rings.

Signals appeared at ($\delta = 2.2$) ppm, ($\delta = 2.62$) ppm and ($\delta = 3.82$) ppm which are belong to (CH₃) citracon protons, (CH₃) imine protons and (-CH-CONH₂) protons.

Other signals appeared at ($\delta = 6.88$ -7.95) ppm and signals at ($\delta = 8.6$ -8.65) ppm belong to aromatic protons and (NH₂) amide protons.

¹³C-NMR spectrum of copolymer [12] showed signals at ($\delta = 21.99$ -25.74) ppm belong to (-CH₂-) carbons and carbons in imide rings.

Signals appeared at ($\delta = 30.69$ -31.90) ppm and ($\delta = 35.53$) ppm are belong to (CH₃) citracon carbon and (CH₃) imine carbon while signal at ($\delta = 66.69$) ppm belong to (-CH-CONH₂) carbon.

Other signals appeared at ($\delta = 125.49$ -131.98) ppm, ($\delta = 148$) ppm and ($\delta = 175$) ppm which are belong to aromatic protons, (C = N) carbon and (C = O) imide and amide carbons respectively.

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