CHAPTER-2

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC FLOW IMPROVERS

2.1 General

The Polymeric Flow Improvers or PPDs are polymers obtained from various discrete monomers. The performance of these polymeric additives depends on: Polymer Molecular Weight, Polymer Backbone, and length of pendant alkyl chain. Polymeric backbone has minor but statistically important effect on the efficacy of PPD's. Variation in monomers changes polymeric backbone and pendant chain length. The variation as well as control of polymer molecular weight can be brought about by changing reaction condition, concentration of initiator, etc. The interaction between additive and paraffin of the crude is very important and it has been found that the additive performs the best when it matches paraffin wax distribution in the crude oil. A low molecular weight, short chained polymer may not have sufficient molecular volume to alter the paraffin crystals dimension so that they can co-crystallize paraffin network. A long chained high molecular weight polymer due to its own dimension may interact with itself instead of paraffin from crude oil which leads to decrease in its solubility and subsequently initiate paraffin crystallization, raising crude oil's pour point. The molecular weight of alternating copolymer depends upon the concentration of activated complex. With rise in temperature, the complex concentration decreases which lowers the molecular weight of the co-polymer. The effect of solvent on the rate of polymerization has been attributed to complex formation. Gel Effect is common phenomenon observed for most of the polymerization. When the reaction condition is isothermal gel effect is seen. Due to above effect the average molecular weight of the polymer formed increases greatly. In free radical polymerization the molecular weight is controlled by methods such as:

1 Rise in polymerization temperature
2 Use of transfer agent
3 Method of weak inhibition [45]

Use of temperature control is not the only and accepted method for controlling molecular weight of the polymer formed. There are number of polymers which are temperature sensitive and change their properties under high temperature influence. In such cases weak inhibition method is employed. Use of transfer agents in the polymerization reaction makes low molecular weight polymers. Polymers of low molecular weight lead to increase in viscosity of reaction mass slowly than polymers of high molecular weight.

Most of the chemical additives consist of pendant alkyl side chains having length from C_2 to C_{30} carbons spaced along the polymeric backbone. These pendant chains co-crystallize with paraffins which decrease the crystal size and reduce its tendency to form gel structures. Some of the important features of such additives are that they should be effective in small quantities, should not produce unwanted by-products with its use and should be useful at all viscosities.[46]

One of the structural features associated with these polymers is that they are linear or copolymer with pendant alkyl side chain associated with specific length and nature. In copolymers one of the co-monomers may or may not contain pendant alkyl side chain. The structural formula for copolymers like polyalkyl acrylate and polyalkyl methacrylate is shown below in figure 2.1.

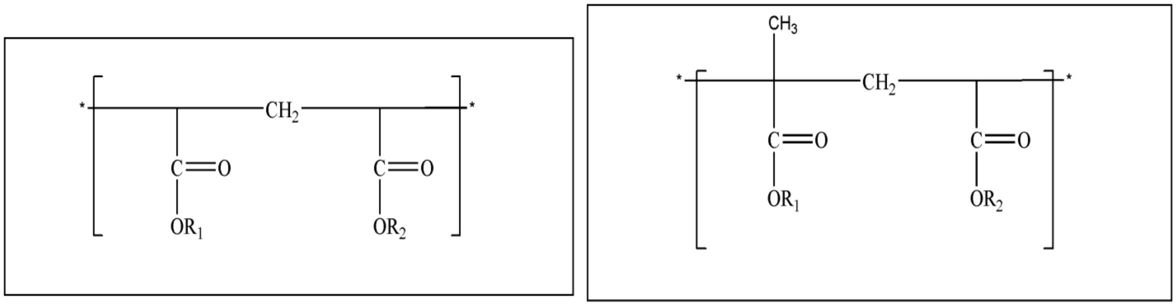


Fig. 2.1: Structure of Polyalkyl Acrylate and Polyalkyl Methacrylate

Based upon the type of R_1 and R_2 group attached a large variety of different polymers can be formed. Preferably the alkyl group $R_1$and R_2 is a straight chain having 10 to 30 carbon atoms.

2.2 Addition Polymerization

Free radical polymerization is one of the most common types of addition polymerization. Free radical is defined as an atom or group of atom possessing an unpaired electron. Free radicals have the tendency of accepting an electron since it is electron deficient. So it breaks the bond of another molecule by accepting an electron making that molecule free radical with an unpaired electron. Free radicals are often formed by division of molecules into fragments along a single bond. These are known as Initiators. Following is the example of Benzoyl Peroxide with undergoes breaking to form free radicals.

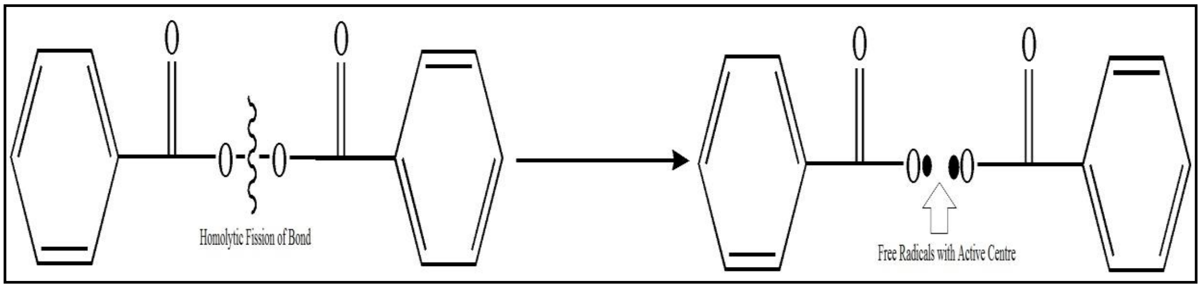


Fig. 2.2: Homolytic Fission of Benzoyl Peroxide

Stability of free radical plays an important role in monomers reactivity. An unstable free radical will readily combine with other molecules while a stable free radical interacts to lesser extent. The location of a unpaired electron on free radical represents active centre where reaction takes place.

In free radical polymerization the radical attacks a monomer subsequent to which electron migrates to other part of the molecule. This newly formed free radical attacks another monomer and the process is repeated. Thus the active centre shifts across the chain as polymerization occurs.

There are three stages involved in addition polymerization:

- i Initiation
- ii Propagation
- iii Termination

i Initiation

In this step initiator breaks into free radicals in presence of monomers. The high reactivity of double bond in the monomer makes it easy for free radical to attack the monomeric species. In this reaction, the active centre of the radical takes one electron from double bond of the monomer, leaving an unpaired electron to act as new active centre on completion of the reaction. Addition can take place at either end of the monomer. In a typical synthesis, 60 to 100% of free radical undergoes an initiation with a monomer. The rest of the free radicals may join with each other or with impurity. Self destruction of free radicals can be controlled by altering monomer to radical ratio.

ii Propagation

In propagation reaction the process of electron transfer and moving down of the active centre continues in the chain. Following diagram indicates (chain) as series of connected monomers and X refers to a substituent group specific to the monomer. For e.g. if X represents methyl group, monomer represented would be propylene and polymer represented would be polypropylene.

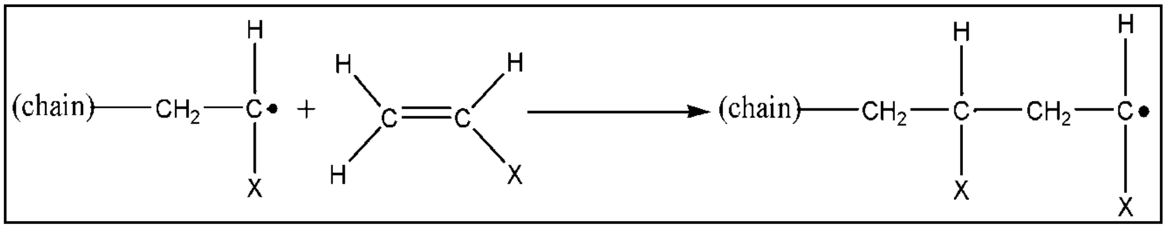


Fig. 2.3 Propagation Stage

The entire free reaction takes place in fraction of second with thousands of monomers added. This process stops when termination reaction takes place.

iii Termination

Theoretically, propagation reaction continues till monomer supply is continued. Such situation is less likely to take place. In most of cases, polymerization stops by termination reaction. Termination typically occurs in two ways: Combination and Disproportion.

(a) Combination: In this type of termination free electrons from growing chain joins to form single chain.

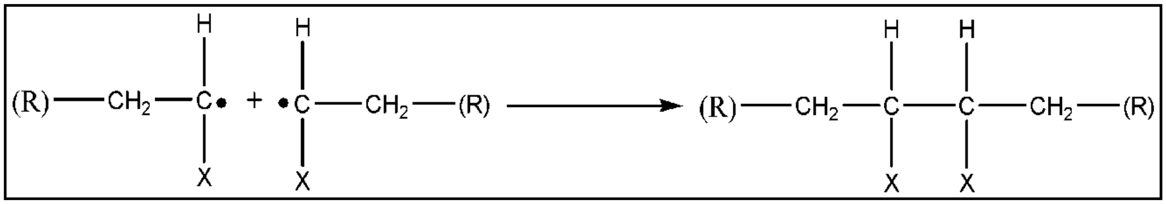


Fig. 2.4 (a) Termination Stage by way of combination

(b) Disproportionation: In this type of termination free radical strips hydrogen atom from active chain. A doubly bonded carbon appears in place of missing hydrogen.

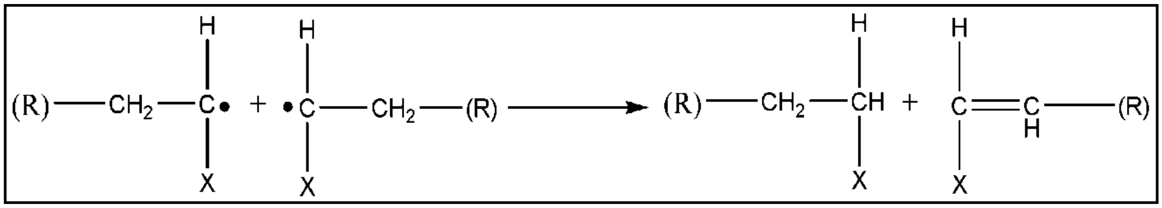


Fig. 2.4(b) Termination stage by way of disproportion

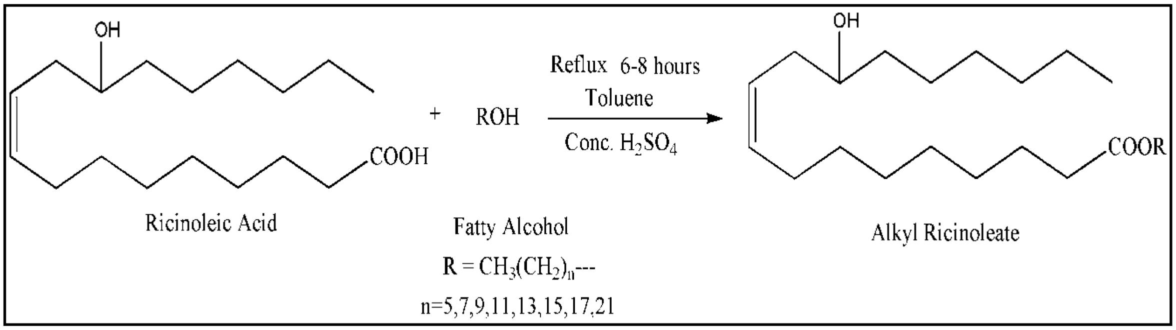
2.3 Synthesis of poly(octyl ricinolate-co-octadecyl maleimide-co-alkyl ricinolate)

2.3.1 Synthesis of alkyl ricinolate by esterification of Ricinoleic acid with fatty alcohols

Synthesis of esters is carried out by reaction between carboxylic acid having unsaturation and fatty alcohols with elimination of water. As esterification is reversible reaction for having complete conversion different methods used are azeotroping, desiccation and chemical means. Catalyst like hydrogen chloride, sulphuric acid, phosphoric acid, silica gel, sulphonic acid and cation exchange resins can be used effectively.

All esters of Ricinoleic acid is prepared by traditional acid catalyzed esterification with n-alkyl alcohols (where C number = 6,8,10,12,14,16,18,22) by azeotropic distillation using Dean and Stark apparatus. The amount of toluene as azeotropic agent is taken as 60 to 80% of the total weight of the reactants. In all esterification, conc. sulphuric acid was used as catalyst. 1 ml of sulphuric acid per mole of Ricinoleic acid was taken. Monitoring of esterification was done based on volume of water azeotrope collected in Dean and Stark apparatus. The duration of reaction was decided on the basis of volume of water separated in Dean and Stark apparatus where reaction was stopped when amount of water collected equaled theoretically calculated quantity of water separated during the entire reaction. Hence the total duration was found to be 6 to 8 hours based on batch size.

After completion of reaction, the crude esters obtained were neutralized with 10% sodium bicarbonate solution to remove acidity due to catalyst used and unreacted Ricinoleic acid. For esters of higher fatty alcohols like C_{16} to C_{22} dilution of crude esters with fresh toluene was needed to avoid crystallization and made work up easier. The neutralized crude solution was washed with de-mineralized water to remove impurities. The crude product was dried over anhydrous sodium sulphate and excess toluene was recovered by distillation under reduced pressure.



Scheme 2.1 Esterification of Ricinoleic acid with Fatty Alcohols

2.3.2 Characterization of alkyl ricinolate esters

The esters of Ricinoleic acid with different fatty alcohols were characterized using Infrared spectroscopy technique. For this purpose Shimadzu FTIR-8400S spectrophotometer was used. Following figure shows a representative FTIR spectrum for all alkyl ricinolate having similar pattern.

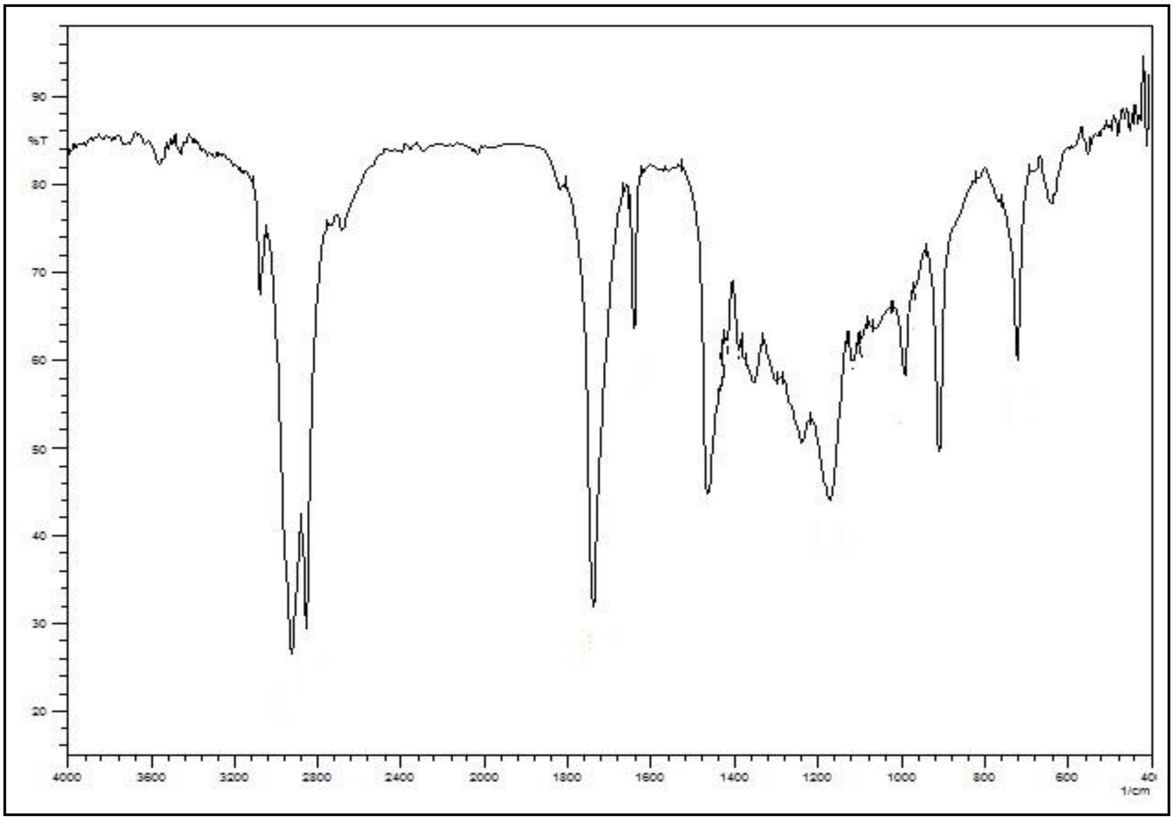


Fig. 2.5 FTIR spectrum of 8RA.

In Fig. 2.5 the C-H stretching vibration of $–CH_3$- and $–CH_2$- groups absorbed strongly 2924.18 cm^{-1} & 2852.81 cm^{-1}. The C=O ester absorption appears as strong peak at 1793.85 cm^{-1}. The characteristic C=C is observed at 1641.48 cm^{-1}. The presence of ester functional group was confirmed by C-O stretching vibration at 1172.76 cm^{-1}. A strong absorption of bending vibration of C-(CH*)-C of long alkyl chain of ester found at 721.40 cm^{-1}.

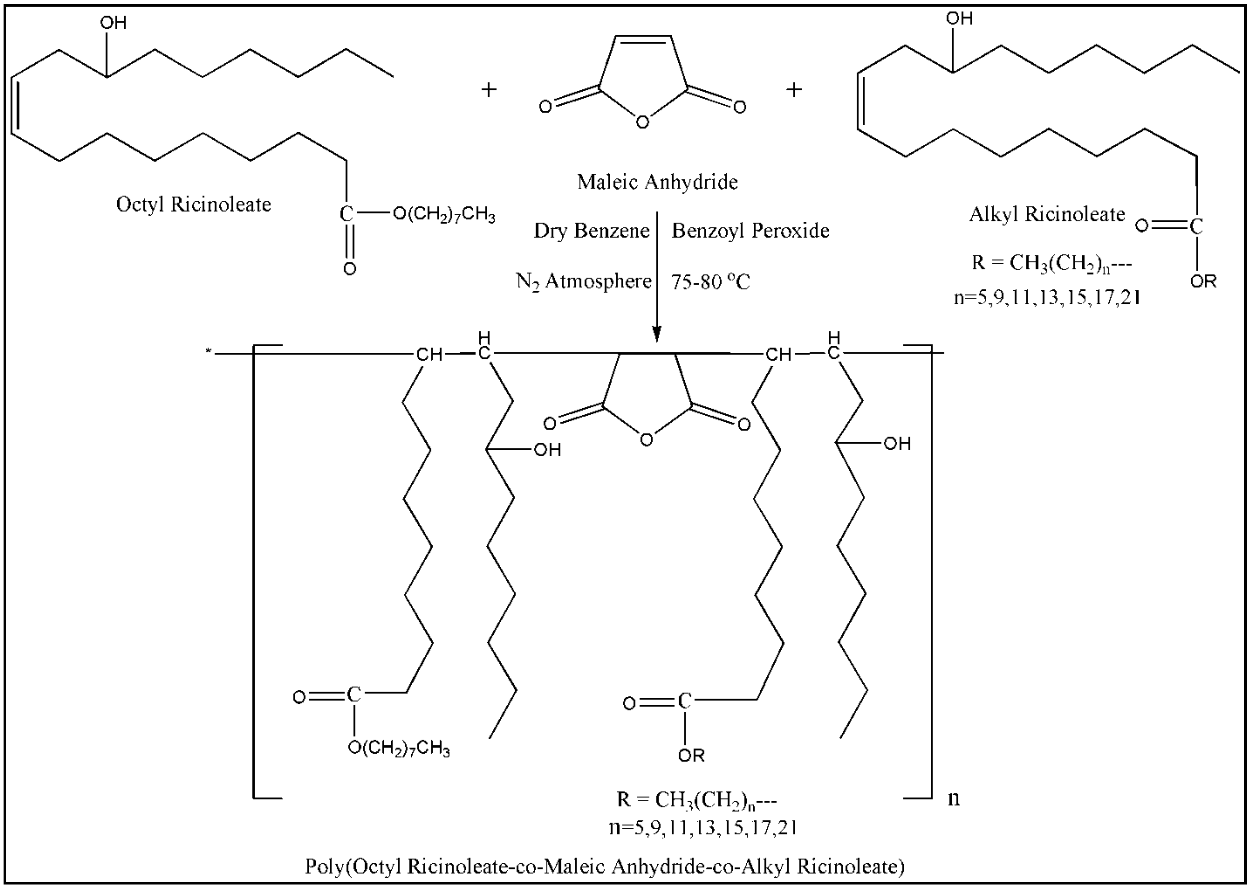
2.3.3 Synthesis of poly (Octyl ricinolate-co-maleic anhydride-co-alkyl ricinolate) Terpolymer

Free radical solution polymerization was employed to synthesize all terpolymers. The laboratory set up consists of four necked round bottom flask kept in electrically controlled rotamantle. The centered neck is fitted with water condenser while the remaining two necks are fitted with thermometer pocket and a purger for nitrogen inlet. The last free neck was fitted with pressure equalizing funnel.

Firstly, the round bottom flask was dried completely. The glassware assembly was set up and then nitrogen gas was passed continuously to replace the oxygen and moisture. The charging of solvent benzene under stirring of magnetic needle was done. Then the short chain alkyl ester octyl ricinolate, long chain alkyl ester (carbon number ranging from 6 to 22) and re-crystallized maleic anhydride was charged in 1:1:1 mole ratio. The purging of nitrogen was continued to maintain inert atmosphere throughout the reaction time. Now the temperature was increased slowly by gradual heating till 75^oC and maintained throughout the reaction time. Then the initiator solution of 1 wt% of Benzoyl peroxide was added drop wise into the polymerization flask from pressure equalizing funnel at gap of every 15 minutes. Addition was completed in 2 hours time with slight exotherm observed. On completion of addition the temperature of the reaction was maintained between 75^oC to 80 ^oC for 10 hours. On completion of time duration, the reaction mass was cooled to room temperature and used for further purification.

All the synthesized terpolymers were purified by solvent non-solvent method. The reaction mass containing excess benzene was removed by vacuum distillation using rotaevaporator.

The terpolymer precipitation was done by pouring polymeric reaction mass free of benzene into 10-15 times the volume of the non-solvent under stirring. The precipitant must be miscible with solvent and non-solvent for terpolymer with solvent for initiator, oligomers and unreacted monomers. In this process solvent used was benzene while methanol was a non-solvent. The method of solvent non-solvent was employed 2 to 3 times. Then the terpolymers were recovered and dried under vacuum at 50^oC/25 mm Hg for 12 hours.



Scheme 2.2 Synthesis of poly (Octyl ricinolate-co-maleic anhydride-co-alkyl ricinolate) Terpolymer

The series represented by these terpolymers consists of seven polymers in which one monomer i.e. short chain ester octyl ricinolate was kept same while other long chain monomer of alkyl ricinolate was changed. The synthesized terpolymers were code named as 8-6RA, 8-10RA, 8-12RA, 8-14RA, 8-16RA, 8-18RA and 8-22RA. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. RA represents acid used was Ricinoleic acid for ester synthesis.

2.3.4 Characterization of poly (Octyl ricinolate-co-maleic anhydride-co-alkyl ricinolate) Terpolymer

2.3.4.1 FTIR spectra of poly (Octyl ricinolate-co-maleic anhydride-co-alkyl ricinolate) Terpolymer

Characterization of terpolymers was done using Shimadzu FTIR-8400S spectrophotometer. The FTIR spectrum of terpolymers representative for these polymers is shown in Fig. 2.6.

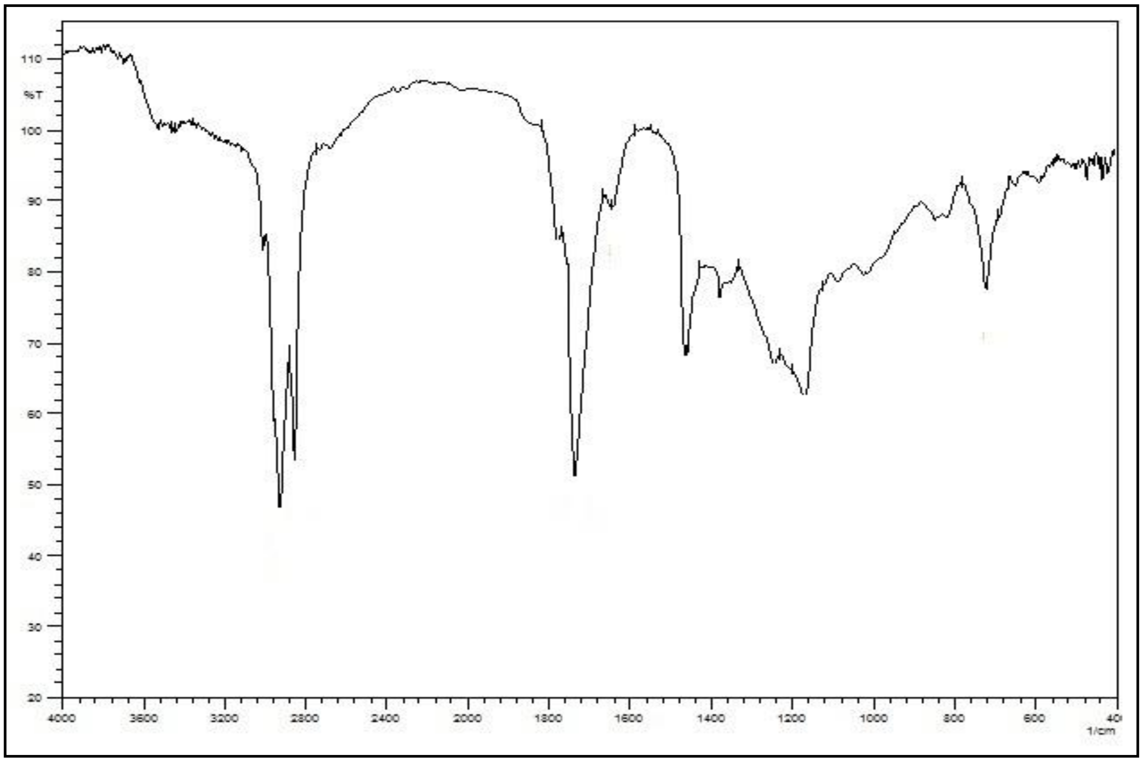


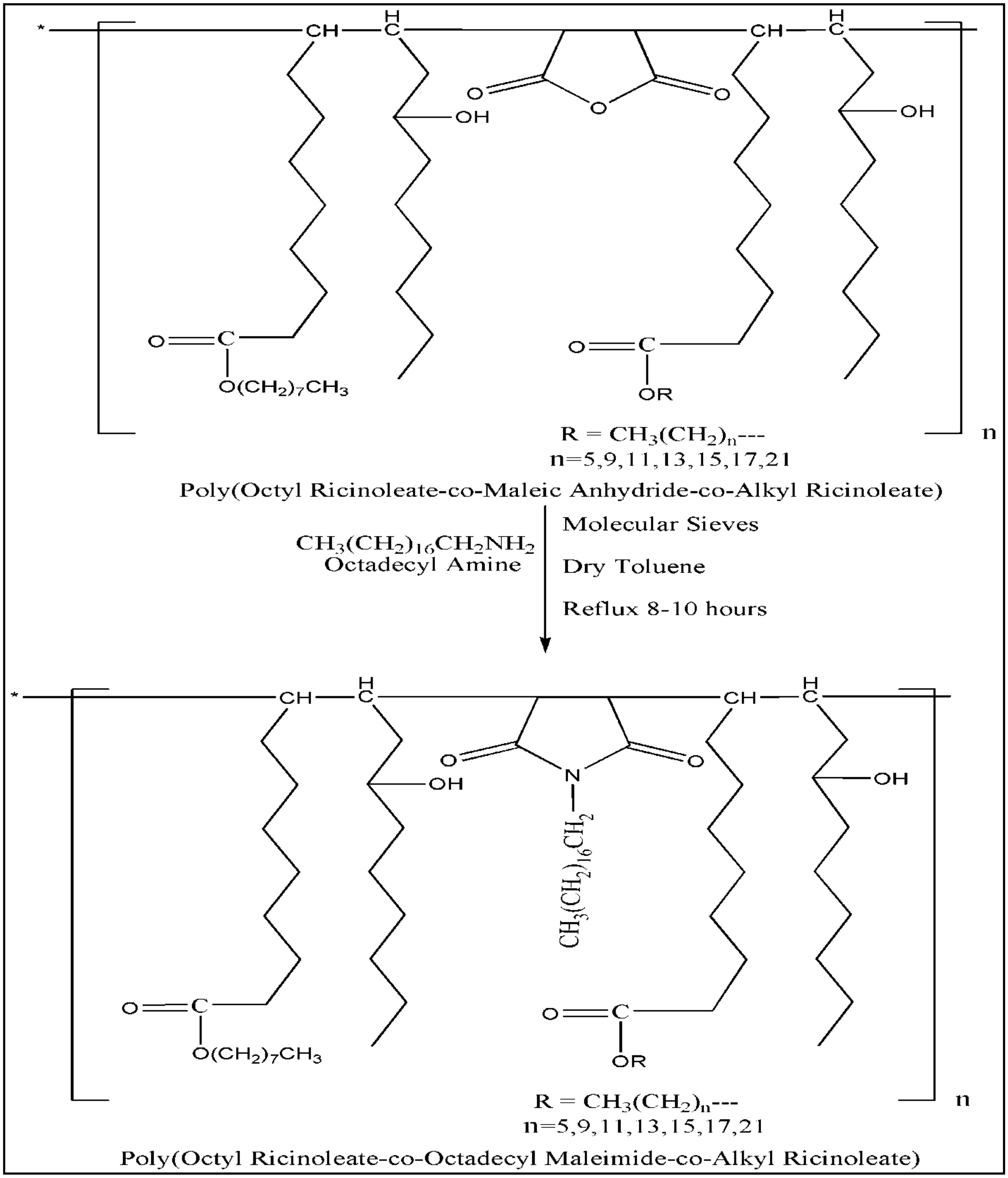
Fig. 2.6 FTIR spectrum of 8-18 RA (Terpolymer)

The above figure shows FTIR spectrum of 8-18RA having appearance of two characteristics peaks of C=O stretching of maleic anhydride shifted under the impact of carbonyl group of ricinolate ester to be found at 1774 $cm^{-1}$and 1735 cm^{-1} and the carbonyl group of ricinolate ester at 1641 cm^{-1}.

2.3.5 Synthesis of poly(Octyl Ricinolate-co-octadecyl maleimide-co-alkyl ricinolate)

In the final stage of synthesis all seven terpolymers were reacted with octadecyl amine to get polyimides. Solvent used was dry toluene. A round bottom flask completely clean and dried was used for this step where terpolymer and octadecyl amine was added in 1:1 mole ratio in presence of molecular sieves to trap water molecules. Dry toluene taken was 70 to 80 % of total volume of reactants. The time duration for reaction was 8-10 hours. On completion, the reaction mass was cooled to room temperature. Here also the product purification was done by solvent non-solvent method taking toluene as solvent and methanol non-solvent. The product obtained was vacuum dried for 6 to 7 hours. The obtained polyimides were code named as 8-6RA18N, 8-10RA18N, 8-12RA18N, 8-14RA18N, 8-16RA18N, 8-18RA18N and 8-22RA18N. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. RA represents acid used was Ricinoleic acid for ester synthesis.

And 18N shows imide formed by octadecyl amine.



Scheme 2.3: Synthesis of poly (Octyl Ricinolate-co-octadecyl maleimide-co-alkyl ricinolate)

2.3.6 Characterization of Polyimides

2.3.6.1 FTIR spectra of Polyimides

Confirmation of Nitrogen incorporation in the copolymers was done through IR spectral analysis. Following figure shows representative FTIR spectrum of 8-18RA18N. The appearance of the characteristics peak for imide N-C stretching at 1701.27 cm^{-1} and C=O stretching at 1737.92 cm^{-1}.

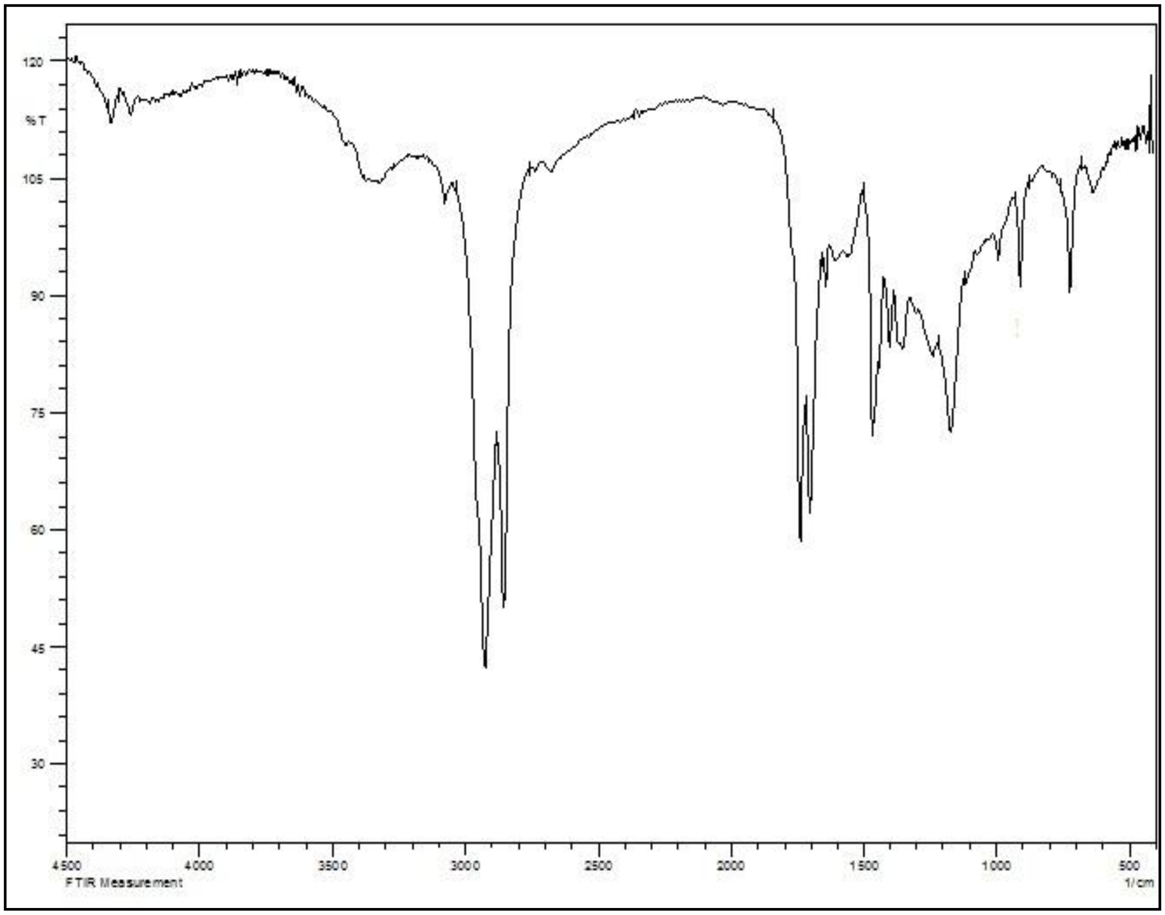


Fig. 2.7 FTIR spectrum of 8-18RA18N

2.3.6.2 GPC results of polyimides

The synthesized polyimides were analyzed for their molecular weight and Polydispersity index using Gel Permeation Chromatography Technique. Polystyrene was used as molecular weight standards. The GPC apparatus used was of Perkin Elmer make having Model No. Turbo Matrix-40. The HPLC grade THF solvent was used with stayragel HR4 column, and 1ml/min flow rate at 25^{o}C. Molecular weights of terpolymers are as shown in the Table 2.1.

Table 2.1 Molecular Weights of poly (Octyl ricinolate-co-octadecyl maleimide-co-alkyl ricinolate)

S. No.	Polymer Code	Weight Average Molecular Weight (M_w)	Number Average Molecular Weight (M_n)	Polydispersity Index (M_w/M_n)
1	8-6RA18N	15866	10043	1.5798
2	8-10RA18N	19782	12793	1.5463
3	8-12RA18N	29470	16147	1.8251
4	8-14RA18N	32491	17247	1.8838
5	8-16RA18N	27631	15955	1.7318
6	8-18RA18N	31263	17195	1.8181
7	8-22RA18N	26130	16818	1.5536

2.4 Synthesis of poly (octyl oleate-co-octadecyl maleimide-co-alkyl oleate)

2.4.1 Synthesis of alkyl oleate by esterification of oleic acid with fatty alcohols

All esters of oleic acid was prepared by traditional acid catalyzed esterification with n-alkyl alcohols (where C number = 6,8,10,12,14,16,18,22) by azeotropic distillation using Dean and Stark apparatus. The amount of toluene as azeotropic agent is taken as 60 to 80% of the total weight of the reactants. In all esterification conc. sulphuric acid was used as catalyst. 1ml of sulphuric acid per mole of oleic acid was taken. Monitoring of esterification was done based on volume of water azeotrope collected in Dean and Stark apparatus. The duration of reaction was decided on the basis of volume of water separated in Dean and Stark apparatus where reaction was stopped when amount of water collected equaled theoretically calculated quantity of water separated during the entire reaction. Hence the total duration was found to be 6 to 8 hours based on batch size.

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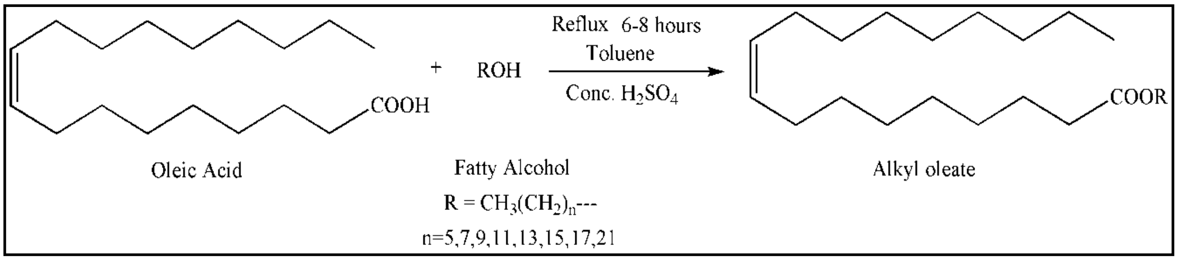

Scheme 2.4 Esterification of Oleic Acid with Fatty Alcohols

2.4.2 Characterization of alkyl oleate esters

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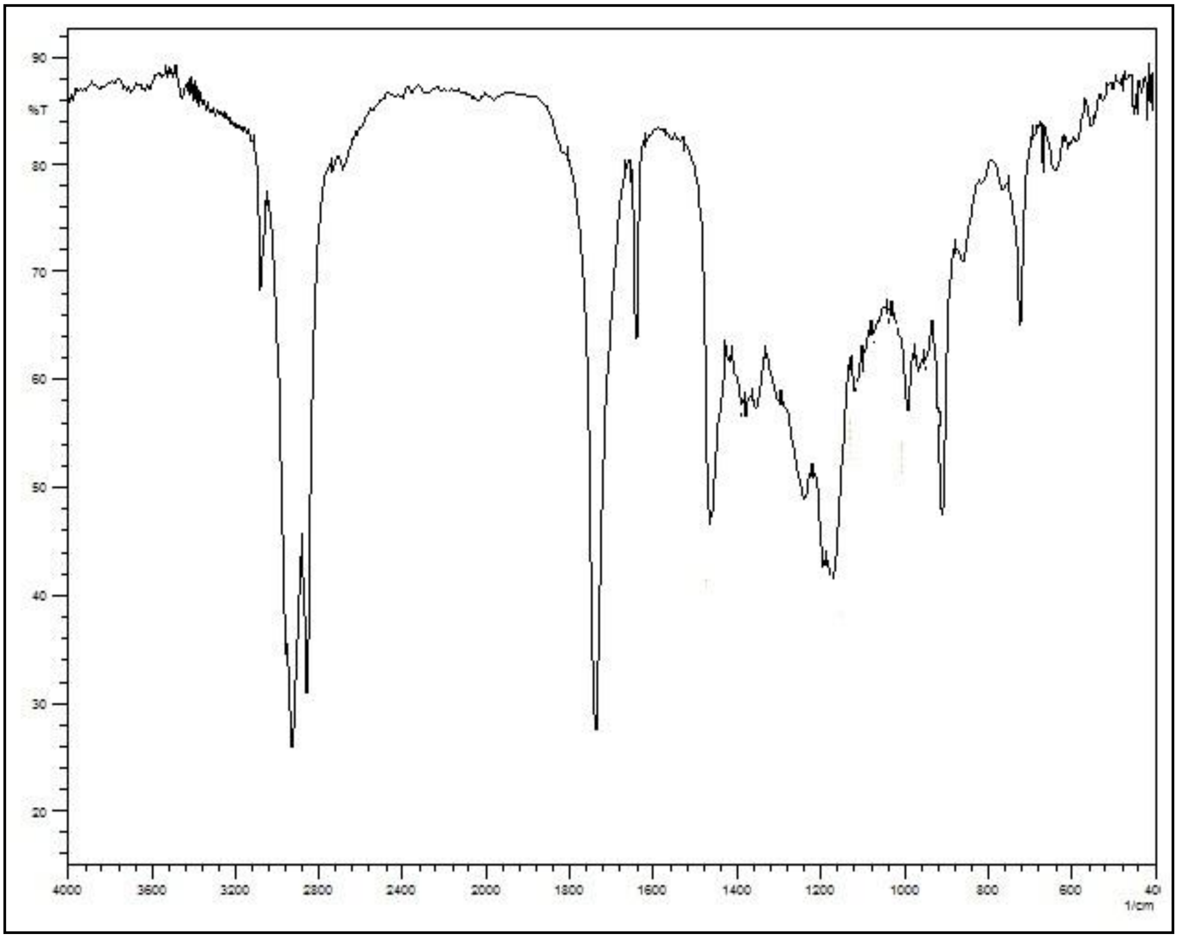

Fig. 2.8 FTIR spectrum of 8OA

In Fig. 2.8 the C-H stretching vibration of –CH_3- and –CH_2- groups absorbed strongly 2926.11 cm^{-1} & 2854.74 cm^{-1}. The C=O ester absorption appears as strong peak at 1735.99

cm^{-1}. The characteristics C=C is observed at 1641.48 cm^{-1}. The presence of ester functional group was confirmed by C-O stretching vibration at 1172.76 cm^{-1}. A strong absorption of bending vibration of C-(CH*)-C of long alkyl chain of ester found at 723.33 cm^{-1}.

2.4.3 Synthesis of poly (Octyl oleate-co-maleic anhydride-co-alkyl oleate) Terpolymer

Free radical solution polymerization was employed to synthesize all terpolymers. The laboratory set up consists of four necked round bottom flask kept in electrically controlled rotamantle. The centered neck is fitted with water condenser while the remaining two necks are fitted with thermometer pocket and a purger for nitrogen inlet. The last free neck was fitted with pressure equalizing funnel.

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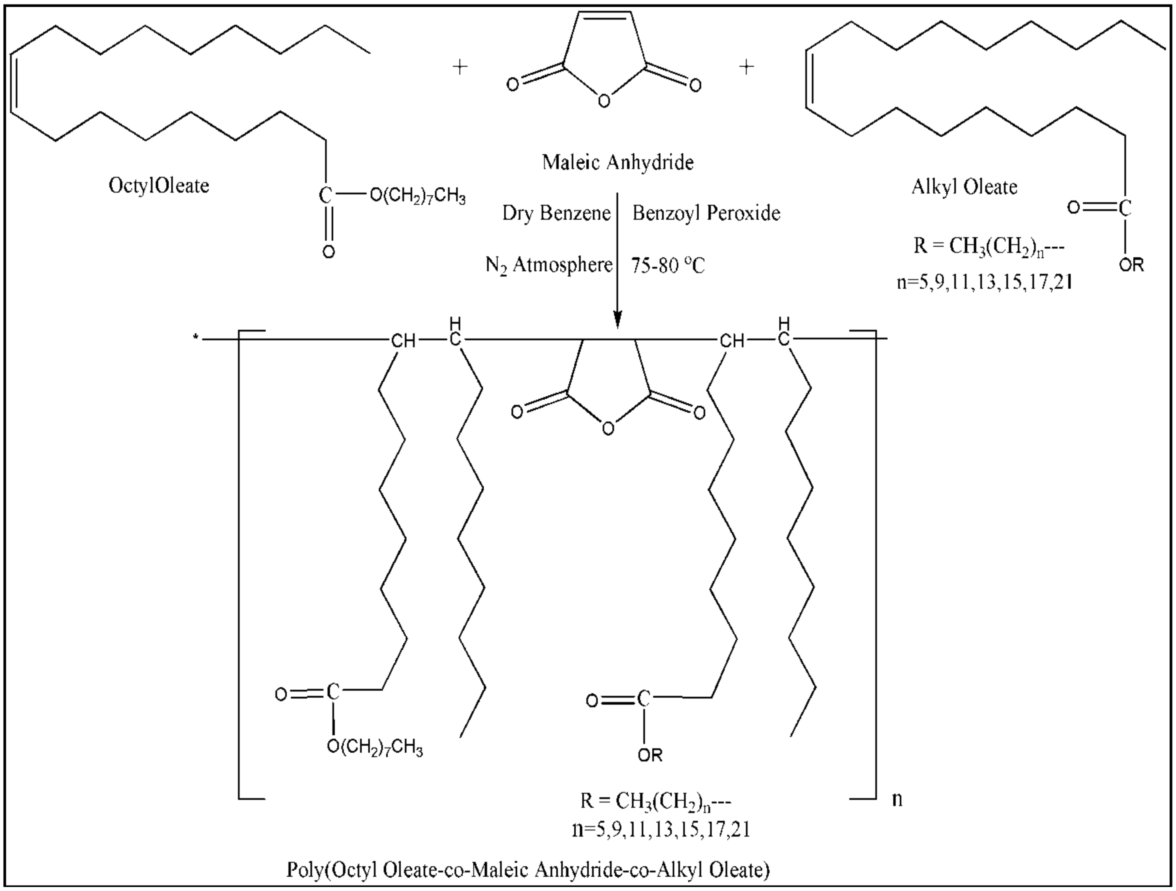
The terpolymer precipitation was done by pouring polymeric reaction mass free of benzene into 10-15 times the volume of the non-solvent under stirring. The precipitant must be miscible with solvent and non-solvent for terpolymer with solvent for initiator, oligomers and unreacted monomers. In this process solvent used was benzene while methanol was a non-solvent. The method of solvent non-solvent was employed 2 to 3 times. Then the terpolymers were recovered and dried under vacuum at 50^{o}C/25 mm Hg for 12 hours.



Scheme 2.5 Synthesis of poly (Octyl oleate-co-maleic anhydride-co-alkyl oleate) Terpolymer

The series represented by these terpolymers consists of seven polymers in which one monomer i.e. short chain ester octyl oleate was kept same while other long chain monomer of alkyl oleate was changed. The synthesized terpolymers were code named as 8-6OA, 8-10OA, 8-12OA, 8-14OA, 8-16OA, 8-18OA and 8-22OA. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. OA represents acid used was oleic acid for ester synthesis.

2.4.4 Characterization of poly (Octyl oleate-co-maleic anhydride-co-alkyl oleate) Terpolymer

2.4.4.1 FTIR spectra of poly (Octyl ricinolate-co-maleic anhydride-co-alkyl ricinolate) Terpolymer

Characterization of terpolymers was done using Shimadzu FTIR-8400S spectrophotometer. The FTIR spectrum of terpolymers representative for these polymers is shown in Fig. 2.9.

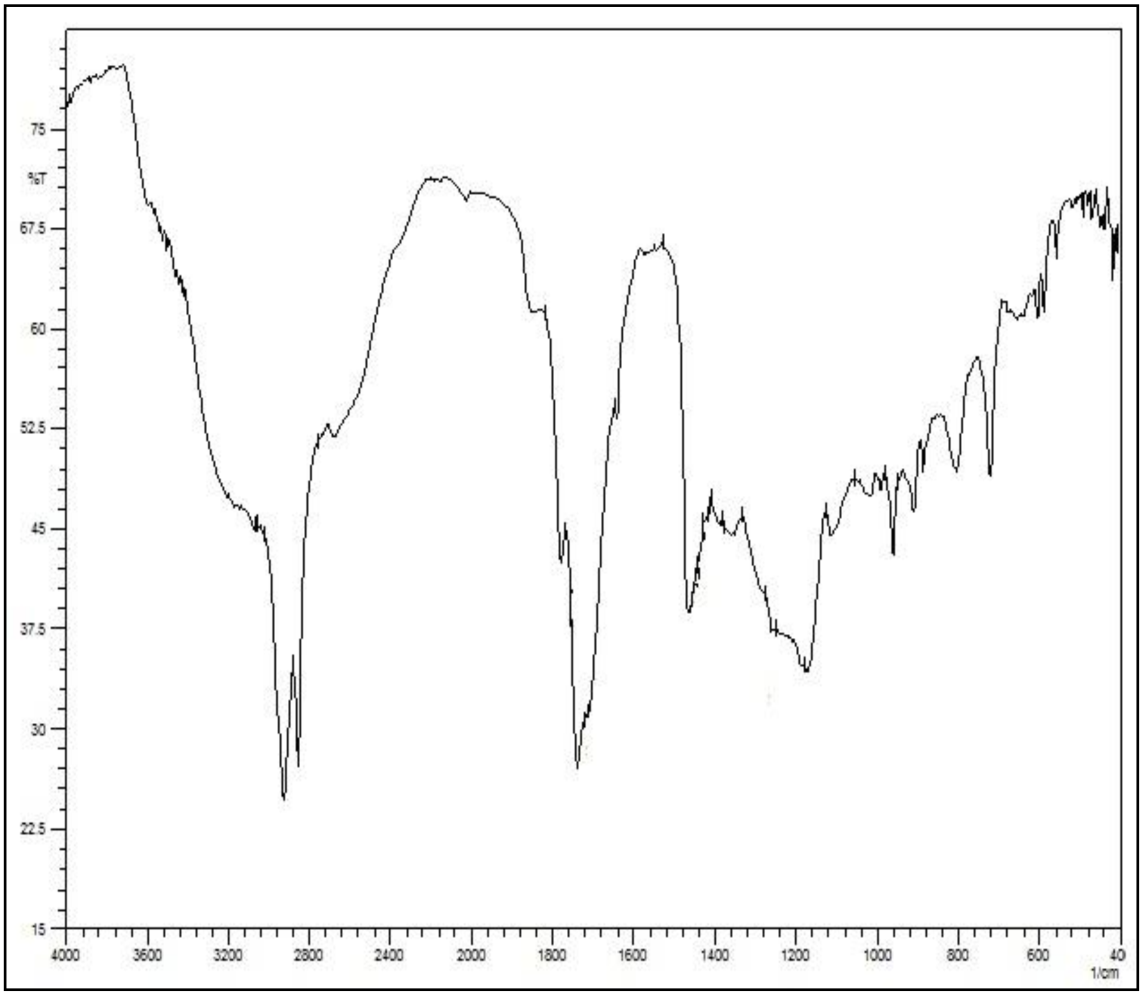
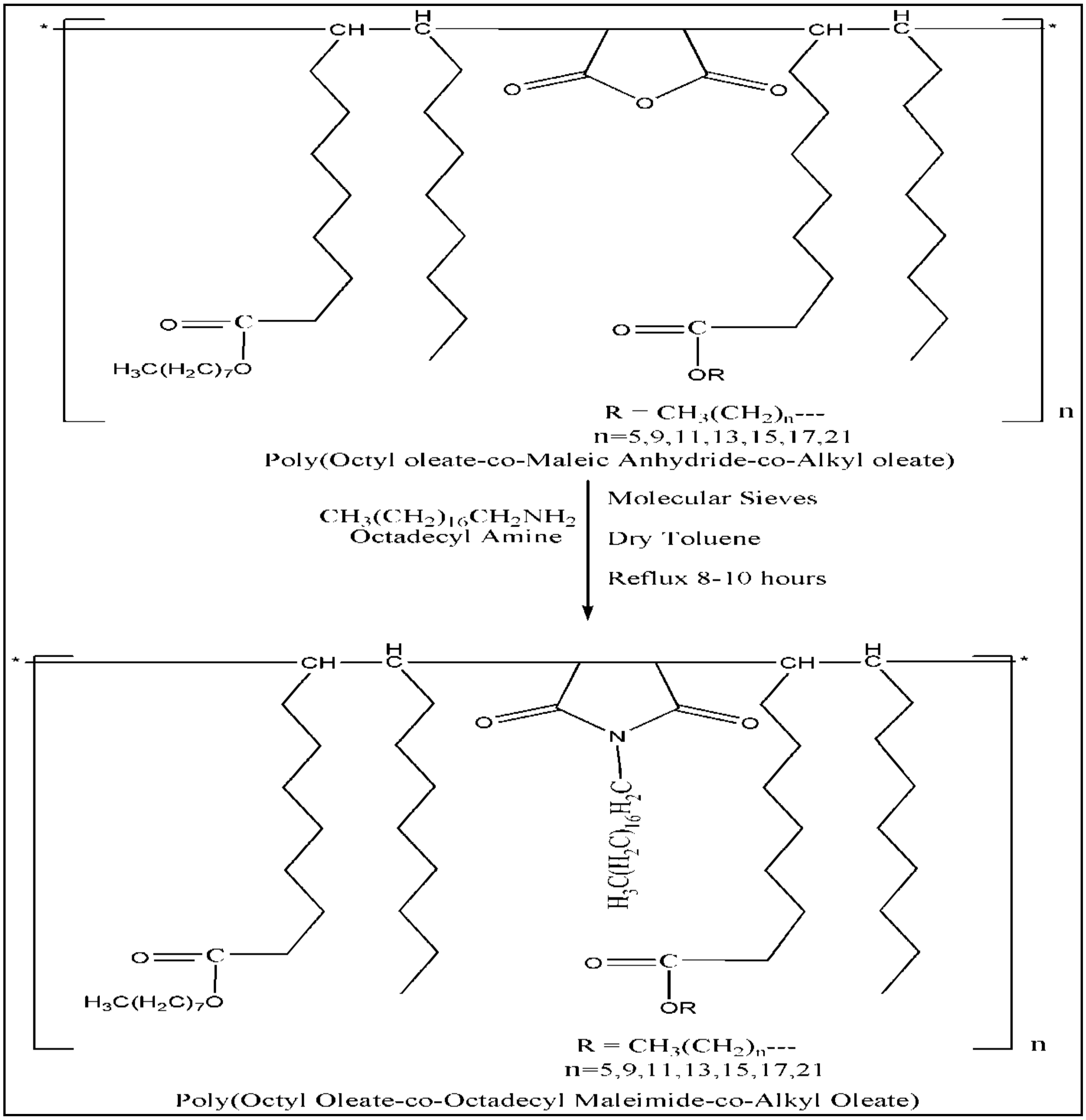


Fig. 2.9 FTIR spectrum of 8-12OA (Terpolymer)

The above figure shows FTIR spectrum of 8-18RA having appearance of two characteristics peaks of C=O stretching of maleic anhydride shifted under the impact of carbonyl group of ricinolate ester to be found at 1778.43 cm^{-1}and 1737.92 cm^{-1} and the carbonyl group of ricinolate ester at 1710.92 cm^{-1}.

2.4.5 Synthesis of poly(Octyl oleate-co-octadecyl maleimide-co-alkyl oleate)

In the final stage of synthesis all seven terpolymers were reacted with octadecyl amine to get polyimides. Solvent used was dry toluene. A round bottom flask completely clean and dried was used for this step where terpolymer and octadecyl amine was added in 1:1 mole ratio in presence of molecular sieves to trap water molecules. Dry toluene taken was 70 to 80 % of total volume of reactants. The time duration for reaction was 8-10 hours. On completion the reaction mass was cooled to room temperature. Here also the product purification was done by solvent non-solvent method taking toluene as solvent and methanol non-solvent. The product obtained was vacuum dried for 6 to 7 hours. The obtained polyimides were code named as 8-6OA18N, 8-10OA18N, 8-12OA18N, 8-14OA18N, 8-16OA18N, 8-18OA18N and 8-22OA18N. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. OA represents acid used was oleic acid for ester synthesis. And 18N shows imide formed by octadecyl amine.



Scheme 2.6 Synthesis of poly (Octyl oleate-co-octadecyl maleimide-co-alkyl oleate)

2.4.6 Characterization of Polyimides

2.4.6.1 FTIR spectra of Polyimides

Confirmation of Nitrogen incorporation in the copolymers was done through IR spectral analysis. Following figure shows representative FTIR spectrum of 8-12OA18N. The appearance of the characteristics peak for imide N-C stretching at 1701.27 cm^{-1} and C=O stretching at 1737.92 cm^{-1}.

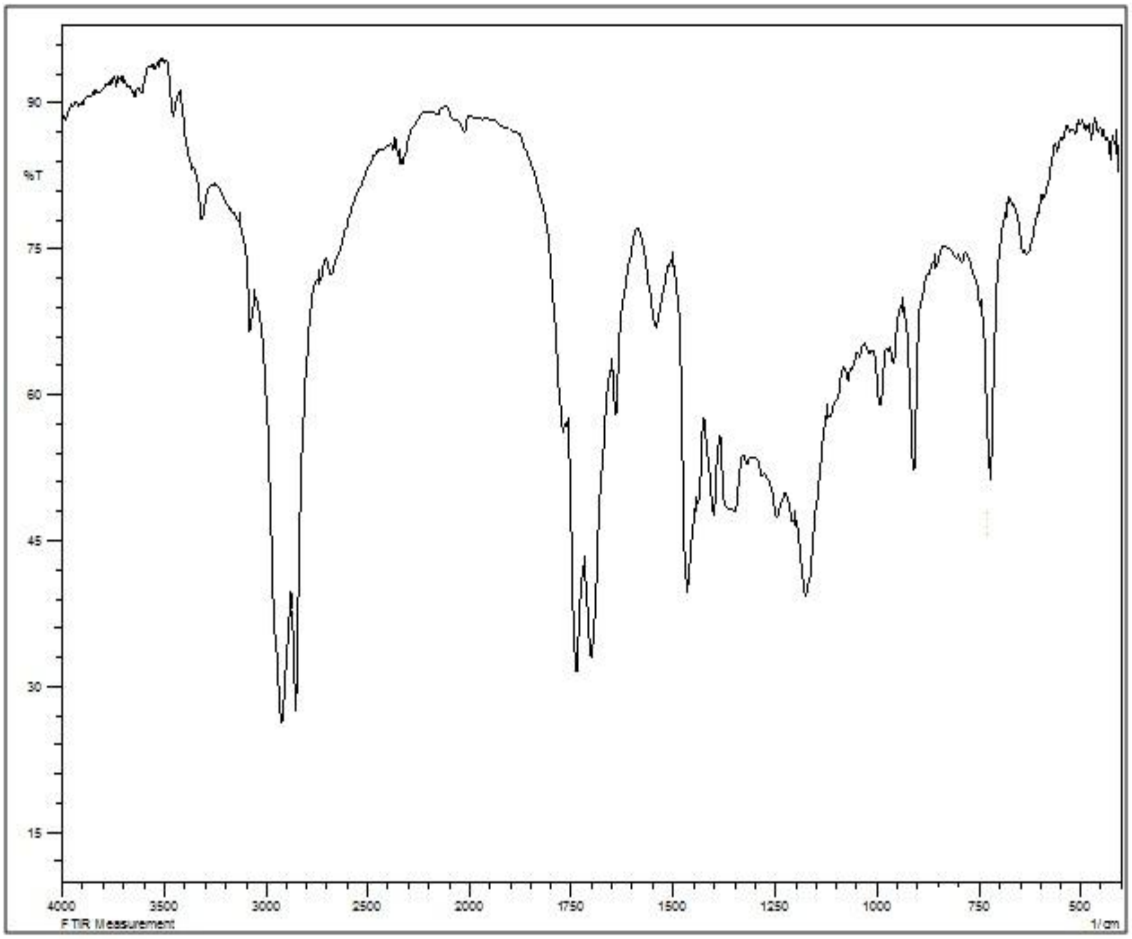


Fig. 2.10 FTIR spectrum of 8-12OA18N

2.4.6.2 GPC results of Polyimides

The synthesized polyimides were analyzed for their molecular weight and Polydispersity index using Gel Permeation Chromatography Technique. Polystyrene was used as molecular weight standards. The GPC apparatus used was of Perkin Elmer make having Model No. Turbo Matrix-40. The HPLC grade THF solvent was used with stayragel HR4 column, and 1ml/min flow rate at 25^{o}C. Molecular weights of terpolymers are as shown in the Table 2.2.

Table 2.2 Molecular Weights of poly (Octyl oleate-co-octadecyl maleimide-co-alkyl oleate)

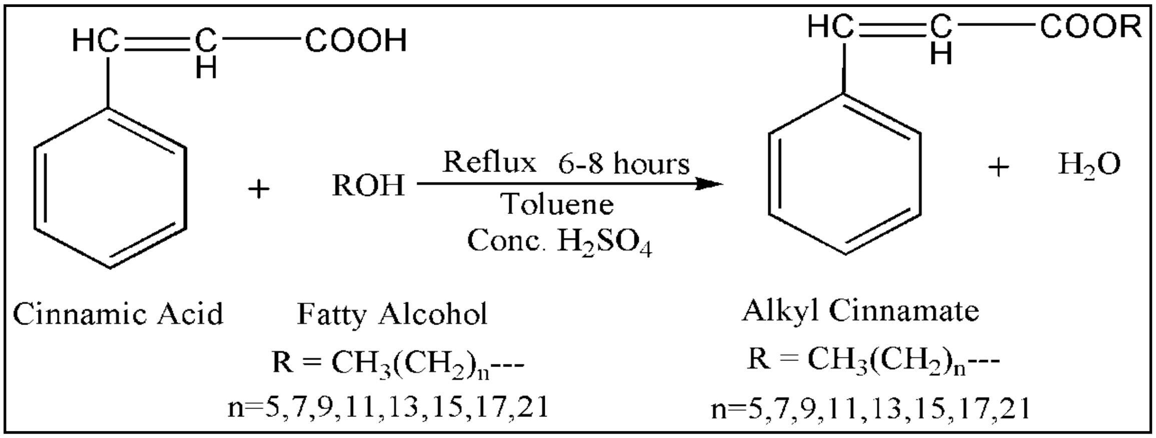
S. No.	Polymer Code	Weight Average Molecular Weight (M_w)	Number Average Molecular Weight (M_n)	Polydispersity Index (M_w/M_n)
1	8-6OA18N	17050	8849	1.9267
2	8-10OA18N	25620	11670	2.1953
3	8-12OA18N	22849	10465	2.1833
4	8-14OA18N	16299	8686	1.8764
5	8-16OA18N	22807	9845	2.3166
6	8-18OA18N	29869	13260	2.2525
7	8-22OA18N	25479	12886	1.9772

2.5 Synthesis of poly (octyl cinnamate-co-octadecyl maleimide-co-alkyl cinnamate)

2.5.1 Synthesis of alkyl cinnamate by esterification of Cinnamic acid with fatty alcohols

All esters of Cinnamic acid was prepared by traditional acid catalyzed esterification with n-alkyl alcohols (where C number = 6,8,10,12,14,16,18,22) by azeotropic distillation using Dean and Stark apparatus. The amount of toluene as azeotropic agent is taken as 60 to 80% of the total weight of the reactants. In all esterification conc. sulphuric acid was used as catalyst. 1ml of sulphuric acid per mole of Cinnamic acid was taken. Monitoring of esterification was done based on volume of water azeotrope collected in Dean and Stark apparatus. The duration of reaction was decided on the basis of volume of water separated in Dean and Stark apparatus where reaction was stopped when amount of water collected equaled theoretically calculated quantity of water separated during the entire reaction. Hence the total duration was found to be 6 to 8 hours based on batch size.

After completion of reaction the crude esters obtained were neutralized with 10% sodium bicarbonate solution to remove acidity due to catalyst used and unreacted Cinnamic acid. For esters of higher fatty alcohols like C_{16} to C_{22} dilution of crude esters with fresh toluene was needed to avoid crystallization and made work up easier. The neutralized crude solution was washed with de-mineralized water to remove impurities. The crude product was dried over anhydrous sodium sulphate and excess toluene was recovered by distillation under reduced pressure.



Scheme 2.7 Esterification of Cinnamic Acid with Fatty Alcohols

2.5.2 Characterization of Alkyl Cinnamate Esters

The esters of Undecylinic acid with different fatty alcohols were characterized using Infrared spectroscopy technique. For this purpose Shimadzu FTIR-8400S spectrophotometer was used. Following figure shows a representative FTIR spectrum for all alkyl cinnamate having similar pattern.

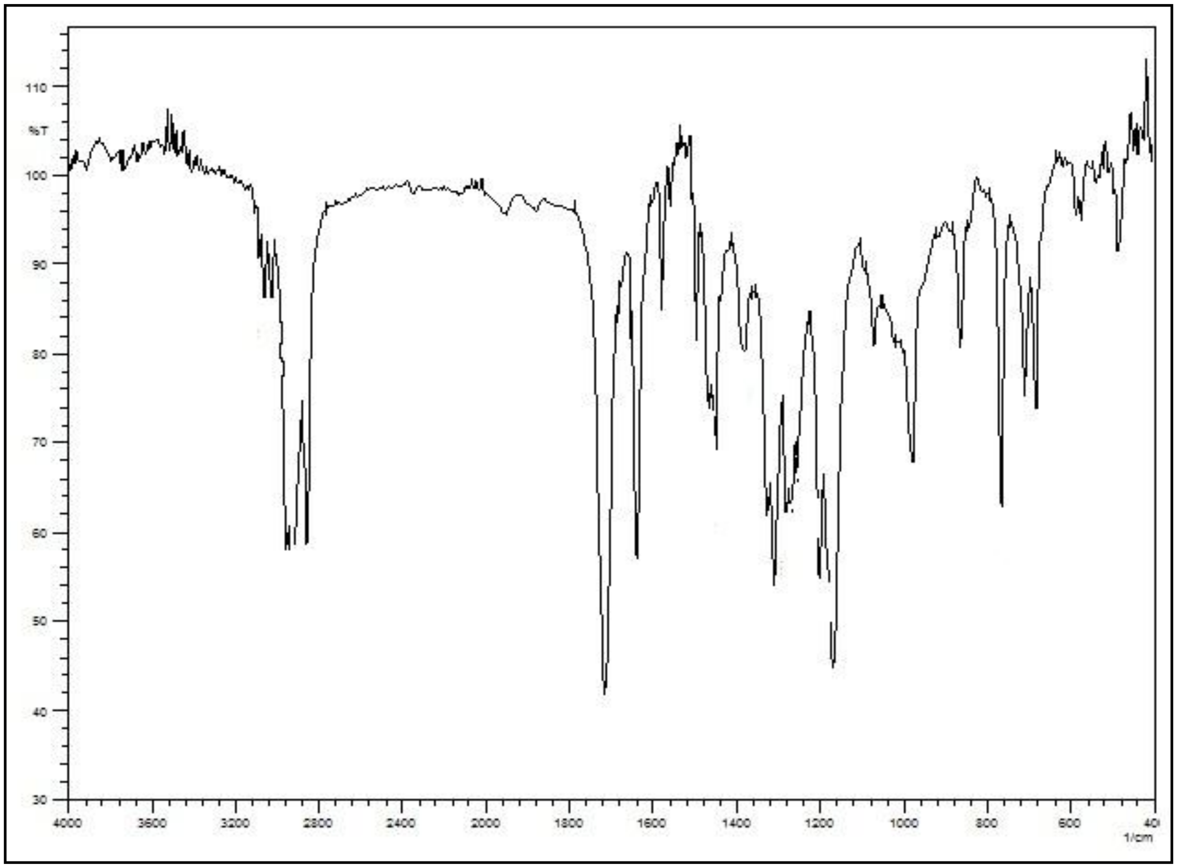


Fig. 2.11 FTIR spectrum of 8CA

In Fig. 2.11 the C-H stretching vibration of $–CH_3$- and $–CH_2$- groups absorbed strongly 2926.04 cm^{-1} & 2854.74 cm^{-1}. The C=O ester absorption appears as strong peak at 1716.70 cm^{-1}. The characteristics C=C is observed at 1637.62 cm^{-1}. The presence of ester functional group was confirmed by C-O stretching vibration at 1168.90 cm^{-1}.

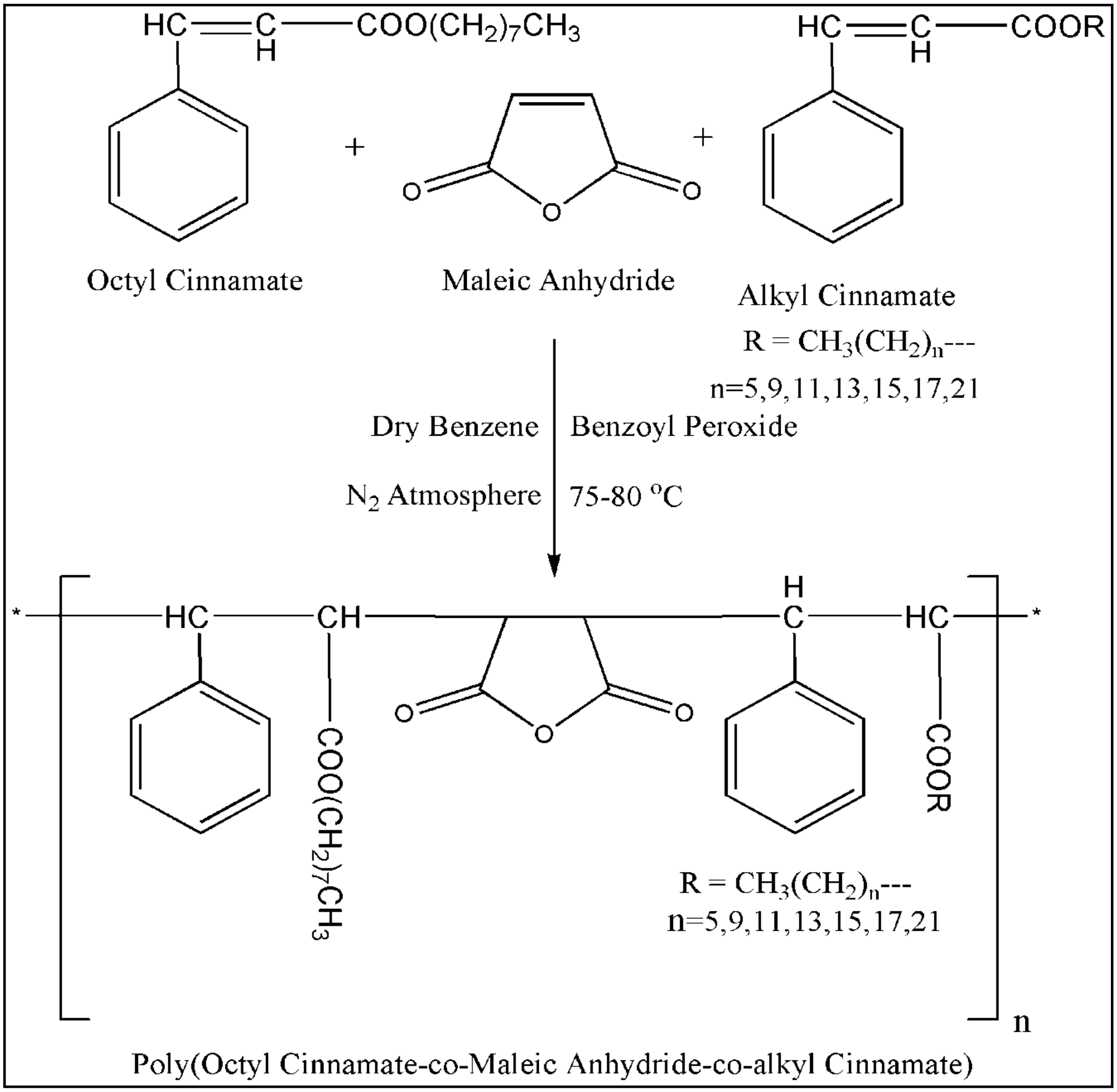
2.5.3 Synthesis of poly (Octyl cinnamate-co-maleic anhydride-co-alkyl cinnamate) Terpolymer

Free radical solution polymerization was employed to synthesize all terpolymers. The laboratory set up consists of four necked round bottom flask kept in electrically controlled rotamantle. The centered neck is fitted with water condenser while the remaining two necks are fitted with thermometer pocket and a purger for nitrogen inlet. The last free neck was fitted with pressure equalizing funnel.

Firstly the round bottom flask was dried completely. The glassware assembly was set up and then nitrogen gas was passed continuously to replace the oxygen and moisture. The charging of solvent benzene under stirring of magnetic needle was done. Then the short chain alkyl ester octyl cinnamate, long chain alkyl ester (carbon number ranging from 6 to 22) and re-crystallized maleic anhydride was charged in 1:1:1 mole ratio. The purging of nitrogen was continued to maintain inert atmosphere throughout the reaction time. Now the temperature was increased slowly by gradual heating till 75^{o}C and maintained throughout the reaction time. Then the initiator solution of 1 wt% of Benzoyl peroxide was added drop wise into the polymerization flask from pressure equalizing funnel at gap of every 15 minutes. Addition was completed in 2 hours time with slight exotherm noted. On completion of addition the temperature of the reaction was maintained between 75^{o}C to 80 ^{o}C for 10 hours. On completion of time duration, the reaction mass was cooled to room temperature and used for further purification.

All the synthesized terpolymers were purified by solvent non-solvent method. The reaction mass containing excess benzene was removed by vacuum distillation using rotaevaporator.

The terpolymer precipitation was done by pouring polymeric reaction mass free of benzene into 10-15 times the volume of the non-solvent under stirring. The precipitant must be miscible with solvent and non-solvent for terpolymer with solvent for initiator, oligomers and unreacted monomers. In this process solvent used was benzene while methanol was a non-solvent. The method of solvent non-solvent was employed 2 to 3 times. Then the terpolymers were recovered and dried under vacuum at 50^{o}C/25 mm Hg for 12 hours.



Scheme 2.8 Synthesis of poly (Octyl cinnamate-co-maleic anhydride-co-alkyl cinnamate) Terpolymer

The series represented by these terpolymers consists of seven polymers in which one monomer i.e. short chain ester octyl cinnamate was kept same while other long chain monomer of alkyl cinnamate was changed. The synthesized terpolymers were code named as 8-6CA, 8-10CA, 8-12CA, 8-14CA, 8-16CA, 8-18CA and 8-22CA. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. CA represents acid used was Cinnamic acid for ester synthesis.

2.5.4 Characterization of poly (Octyl cinnamate-co-maleic anhydride-co-alkyl cinnamate) Terpolymer

2.5.4.1 FTIR spectra of poly (Octyl cinnamate-co-maleic anhydride-co-alkyl cinnamate) Terpolymer

Characterization of terpolymers was done using Shimadzu FTIR-8400S spectrophotometer. The FTIR spectrum of terpolymers representative for these polymers is shown in Fig. 2.12.

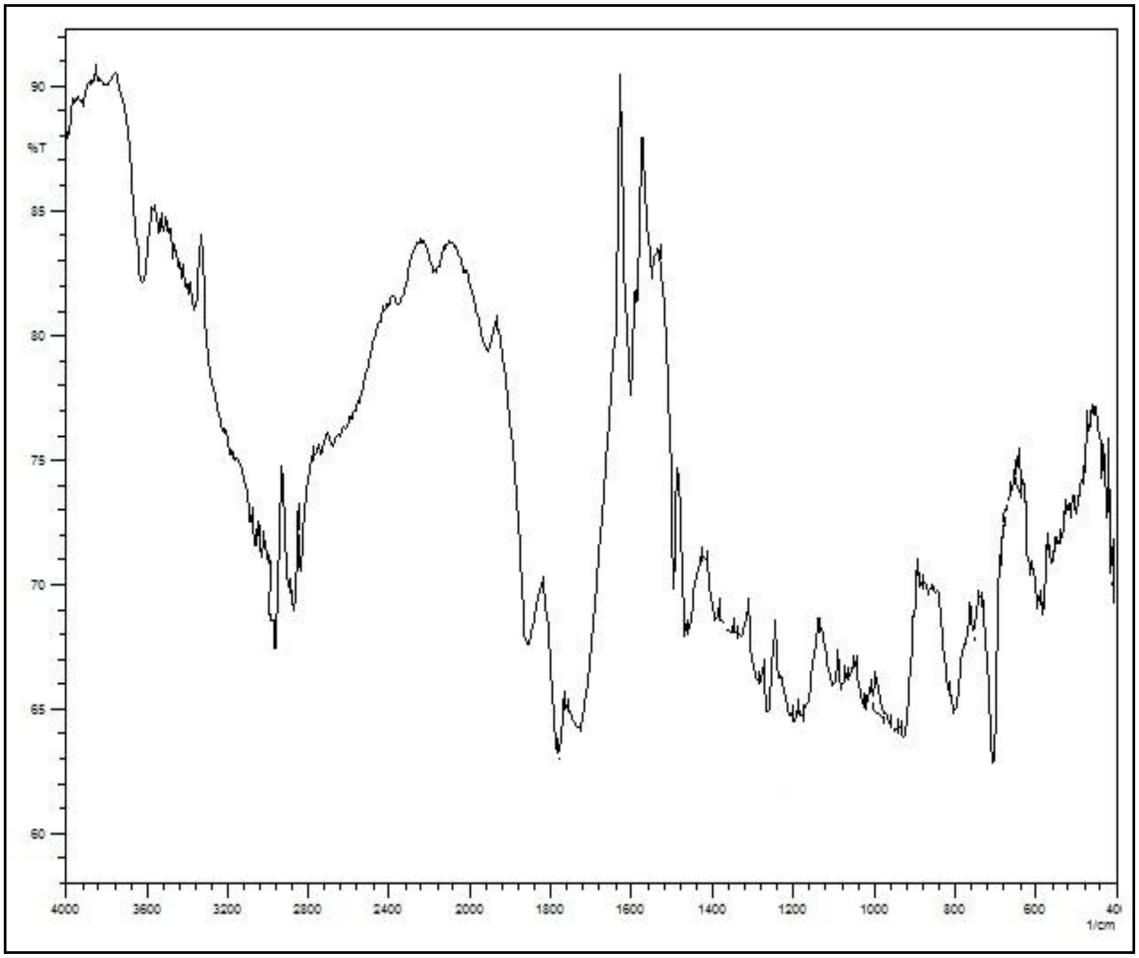
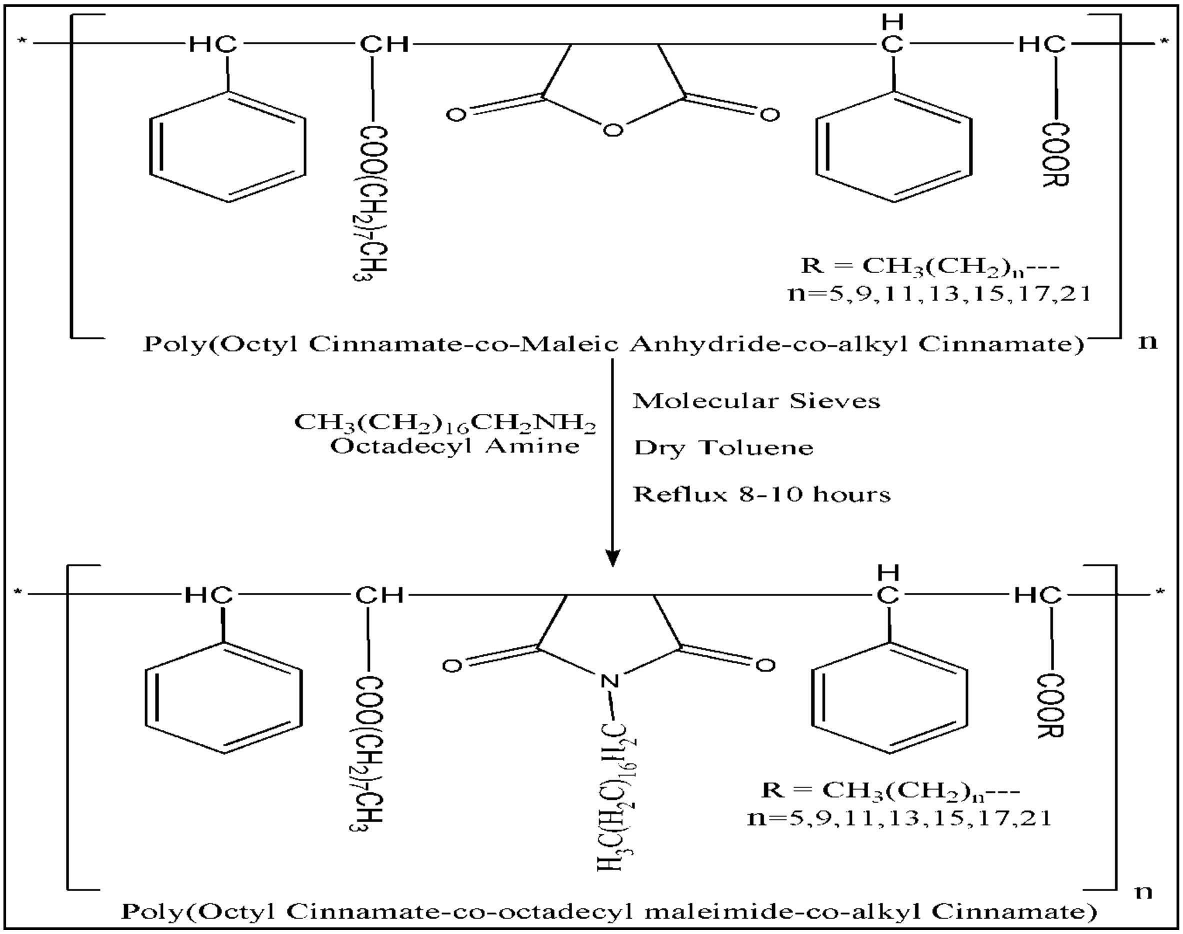


Fig. 2.12 FTIR spectrum of 8-12CA (Terpolymer)

The above figure shows FTIR spectrum of 8-12CA having appearance of two characteristics peaks of C=O stretching of maleic anhydride shifted under the impact of carbonyl group of cinnamate ester to be found at 1857.51 and 1778.43 cm^{-1} and the carbonyl group of Undecylinate ester at 1726.35 cm^{-1}.

2.5.5 Synthesis of poly(Octyl Cinnamate-co-octadecyl maleimide-co-alkyl cinnamate) Polyimides

In the final stage of synthesis all seven terpolymers were reacted with octadecyl amine to get polyimides. Solvent used was dry toluene. A round bottom flask completely clean and dried was used for this step where terpolymer and octadecyl amine was added in 1:1 mole ratio in presence of molecular sieves to trap water molecules. Dry toluene taken was 70 to 80 % of total volume of reactants. The time duration for reaction was 8-10 hours. On completion the reaction mass was cooled to room temperature. Here also the product purification was done by solvent non-solvent method taking toluene as solvent and methanol non-solvent. The product obtained was vacuum dried for 6 to 7 hours. The obtained polyimides were code named as 8-6CA18N, 8-10CA18N, 8-12CA18N, 8-14CA18N, 8-16CA18N, 8-18CA18N and 8-22CA18N. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. CA represents acid used was Cinnamic acid for ester synthesis. And 18N shows imide formed by octadecyl amine.



Scheme 2.9 Synthesis of poly (Octyl cinnamate-co-octadecyl maleimide-co-alkyl cinnamate)

2.5.6 Characterization of poly(Octyl cinnamate-co-octadecyl maleimide-co-alkyl cinnamate) Polyimides

2.5.6.1 FTIR spectra of poly(Octyl cinnamate-co-octadecyl maleimide-co-alkyl cinnamate) Polyimides

Confirmation of Nitrogen incorporation in the copolymers was done through IR spectral analysis. Following figure shows representative FTIR spectrum of 8-12CA18N. The appearance of the characteristics peak for imide N-C stretching at 1701.27 cm^{-1} and C=O stretching at 1737.92 cm^{-1}.

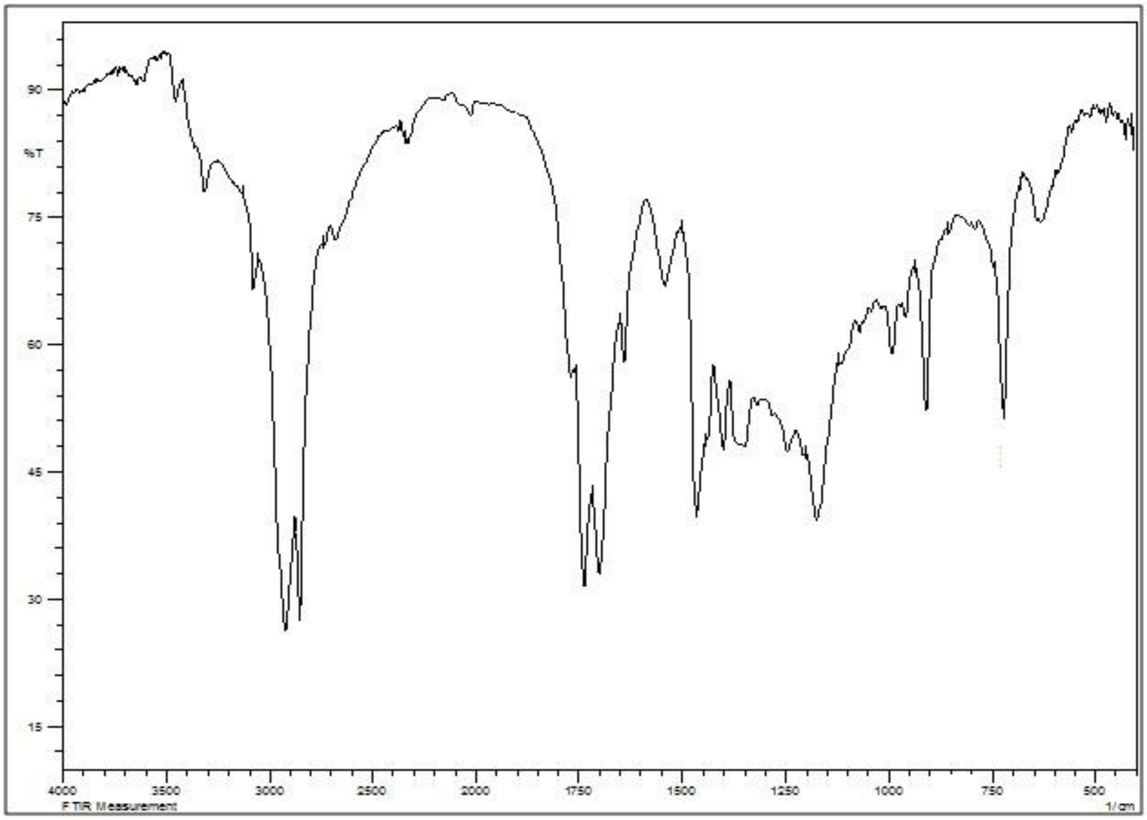


Fig 2.13 FTIR spectrum of 8-12CA18N

2.5.6.2 GPC results of poly(Octyl cinnamate-co-octadecyl maleimide-co-alkyl cinnamate) Polyimides

The synthesized polyimides were analyzed for their molecular weight and Polydispersity index using Gel Permeation Chromatography Technique. Polystyrene was used as molecular weight standards. The GPC apparatus used was of Perkin Elmer make having Model No. Turbo Matrix-40. The HPLC grade THF solvent was used with stayragel HR4 column, and 1ml/min flow rate at 25^{o}C. Molecular weights of polyimides are as shown in the Table 2.3.

Table 2.3 Molecular Weights of poly (Octyl Cinnamate-co-octadecyl maleimide-co-alkyl Cinnamate)

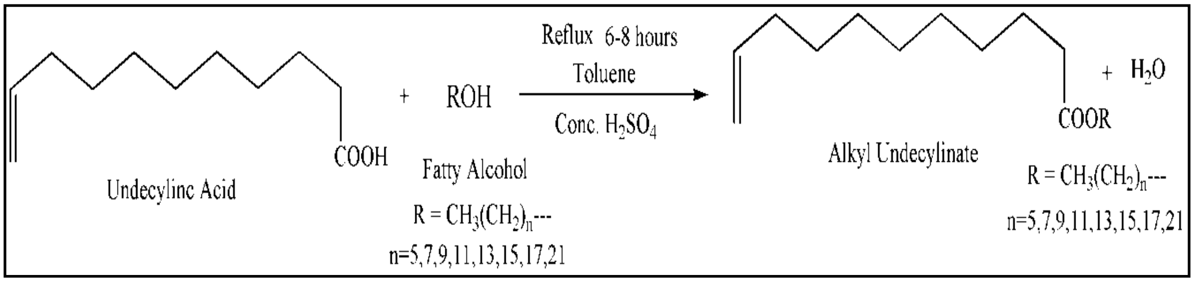
S. No.	Polymer Code	Weight Average Molecular Weight (M_w)	Number Average Molecular Weight (M_n)	Polydispersity Index (M_w/M_n)
1	8-6CA18N	22745	11788	1.9295
2	8-10CA18N	34174	15564	2.1957
3	8-12CA18N	30463	13943	2.1849
4	8-14CA18N	21731	11595	1.8742
5	8-16CA18N	30408	13126	2.3165
6	8-18CA18N	39814	17691	2.2505
7	8-22CA18N	33975	17174	1.9782

2.6 Synthesis of poly (octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate)

2.6.1 Synthesis of alkyl Undecylinate by esterification of Undecylinic acid with fatty alcohols

All esters of Undecylinic acid was prepared by traditional acid catalyzed esterification with n-alkyl alcohols (where C number = 6,8,10,12,14,16,18,22) by azeotropic distillation using Dean and Stark apparatus. The amount of toluene as azeotropic agent is taken as 60 to 80% of the total weight of the reactants. In all esterification conc. sulphuric acid was used as catalyst. 1ml of sulphuric acid per mole of Undecylinic acid was taken. Monitoring of esterification was done based on volume of water azeotrope collected in Dean and Stark apparatus. The duration of reaction was decided on the basis of volume of water separated in Dean and Stark apparatus where reaction was stopped when amount of water collected equaled theoretically calculated quantity of water separated during the entire reaction. Hence the total duration was found to be 6 to 8 hours based on batch size.

After completion of reaction the crude esters obtained were neutralized with 10% sodium bicarbonate solution to remove acidity due to catalyst used and unreacted Undecylinic acid. For esters of higher fatty alcohols like C_{16} to C_{22} dilution of crude esters with fresh toluene was needed to avoid crystallization and made work up easier. The neutralized crude solution was washed with D.M. water to remove impurities. The crude product was dried over anhydrous sodium sulphate and excess toluene was recovered by distillation under reduced pressure.



Scheme 2.10 Esterification of Undecylinic Acid with Fatty Alcohols

2.6.2 Characterization of Alkyl Oleate Esters

2.6.2.1 FTIR spectra of Alkyl Oleate Esters

The esters of Undecylinic acid with different fatty alcohols were characterized using Infrared spectroscopy technique. For this purpose Shimadzu FTIR-8400S spectrophotometer was used. Following figure shows a representative FTIR spectrum for all alkyl ricinolate having similar pattern.

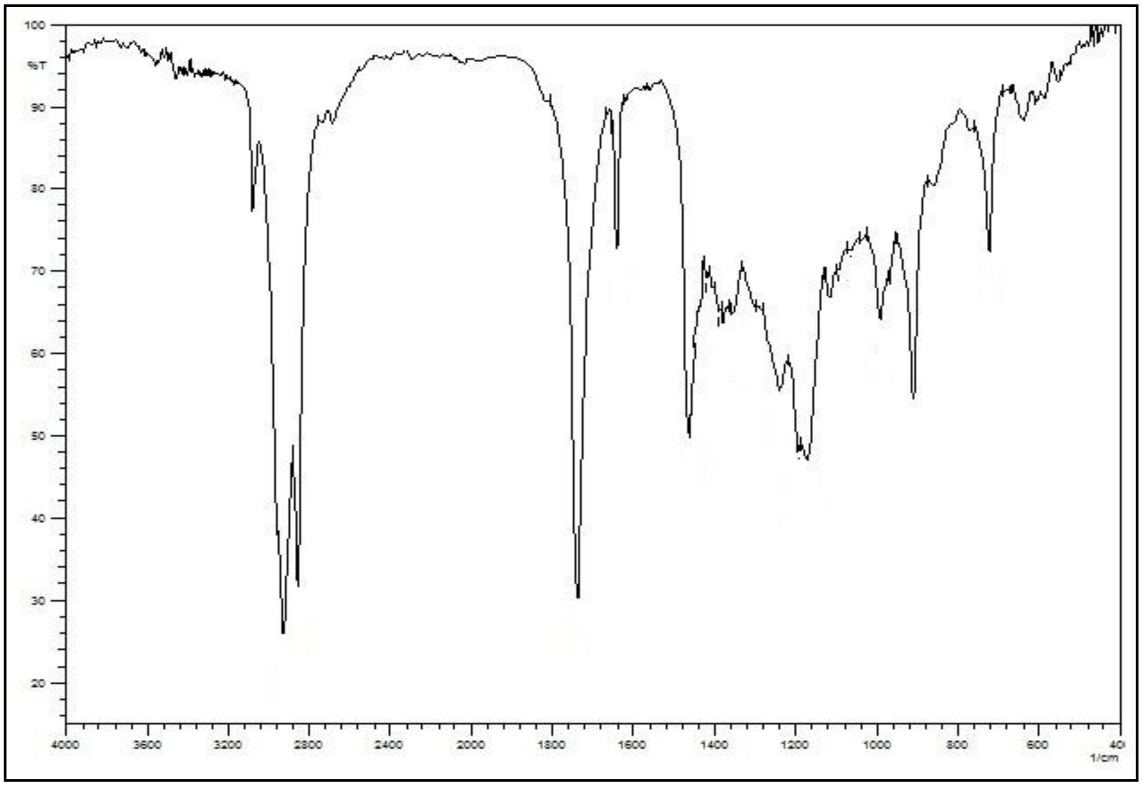


Fig. 2.14 FTIR spectrum of 10UA

In Fig. 2.8 the C-H stretching vibration of –CH_3- and –CH_2- groups absorbed strongly 2924.18 cm^{-1} & 2854.74 cm^{-1}. The C=O ester absorption appears as strong peak at

1739.85 cm^{-1}. The characteristics C=C is observed at 1641.48 cm^{-1}. The presence of ester functional group was confirmed by C-O stretching vibration at 1170.83 cm^{-1}. A strong absorption of bending vibration of C-(CH*)-C of long alkyl chain of ester found at 721.40 cm^{-1}.

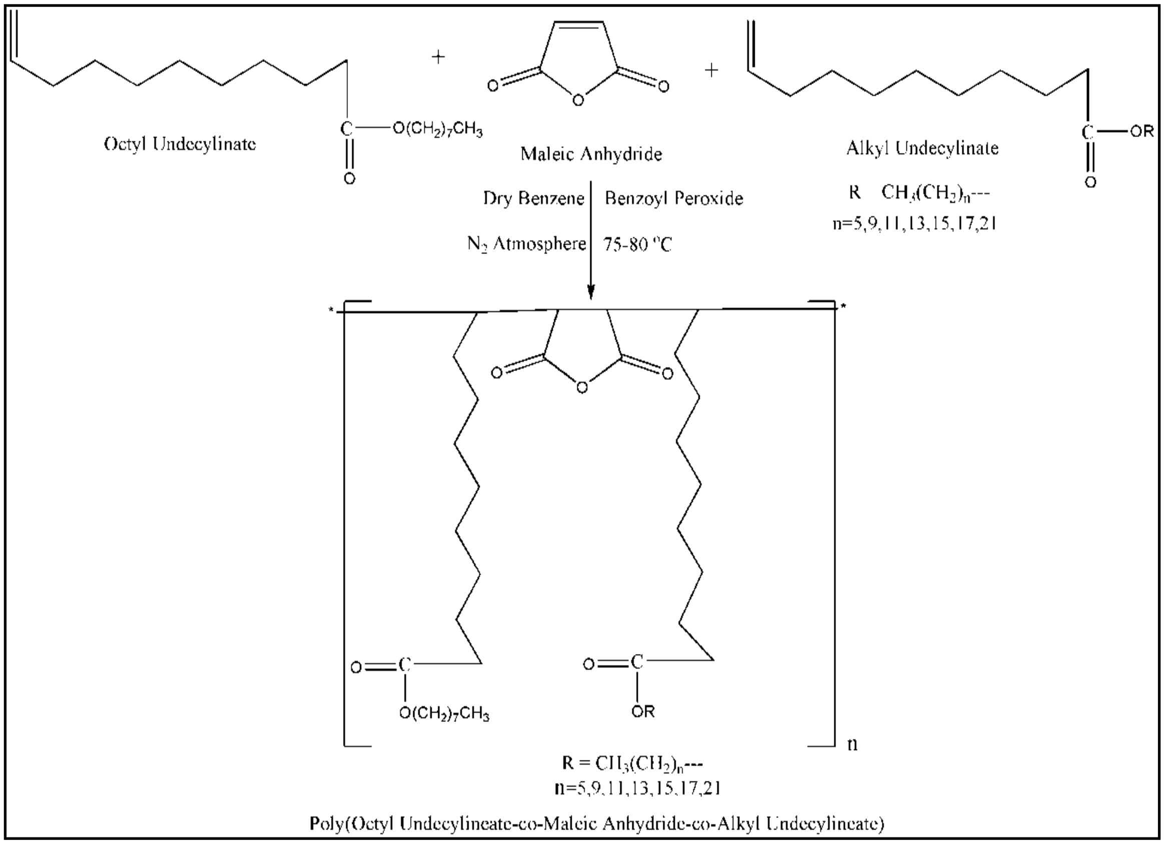
2.6.3 Synthesis of Poly (Octyl Undecylinate-co-maleic anhydride-co-alkyl Undecylinate) Terpolymer

Free radical solution polymerization was employed to synthesize all terpolymers. The laboratory set up consists of four necked round bottom flask kept in electrically controlled rotamantle. The centered neck is fitted with water condenser while the remaining two necks are fitted with thermometer pocket and a purger for nitrogen inlet. The last free neck was fitted with pressure equalizing funnel.

Firstly the round bottom flask was dried completely. The glassware assembly was set up and then nitrogen gas was passed continuously to replace the oxygen and moisture. The charging of solvent benzene under stirring of magnetic needle was done. Then the short chain alkyl ester octyl Undecylinate, long chain alkyl ester (carbon number ranging from 6 to 22) and re-crystallized maleic anhydride was charged in 1:1:1 mole ratio. The purging of nitrogen was continued to maintain inert atmosphere throughout the reaction time. Now the temperature was increased slowly by gradual heating till 75^{o}C and maintained throughout the reaction time. Then the initiator solution of 1 wt% of Benzoyl peroxide was added drop wise into the polymerization flask from pressure equalizing funnel at gap of every 15 minutes. Addition was completed in 2 hours time with slight exotherm noted. On completion of addition, the temperature of the reaction was maintained between 75 ^{o}C to 80 ^{o}C for 10 hours. On completion of time duration, the reaction mass was cooled to room temperature and used for further purification.

All the synthesized terpolymers were purified by solvent non-solvent method. The reaction mass containing excess benzene was removed by vacuum distillation using rotaevaporator.

The terpolymer precipitation was done by pouring polymeric reaction mass free of benzene into 10-15 times the volume of the non-solvent under stirring. The precipitant must be miscible with solvent and non-solvent for terpolymer with solvent for initiator, oligomers and unreacted monomers. In this process solvent used was benzene while methanol was a non-solvent. The method of solvent non-solvent was employed 2 to 3 times. Then the terpolymers were recovered and dried under vacuum at 50°C/25 mm Hg for 12 hours.



Scheme 2.11 Synthesis of poly (Octyl Undecylinate-co-maleic anhydride-co-alkyl Undecylinate) Terpolymer

The series represented by these terpolymers consists of seven polymers in which one monomer i.e. short chain ester octyl undecylinate was kept same while other long chain monomer of alkyl undecylinate was changed. The synthesized terpolymers were code named as 8-6UA, 8-10UA, 8-12UA, 8-14UA, 8-16UA, 8-18UA and 8-22UA. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. UA represents acid used was Undecylinic acid for ester synthesis.

2.6.4 Characterization of Poly (Octyl Undecylinate-co-maleic anhydride-co-alkyl Undecylinate) Terpolymer

2.6.4.1 FTIR spectra of poly (Octyl Undecylinate-co-maleic anhydride-co-alkyl Undecylinate) Terpolymer

Characterization of terpolymers was done using Shimadzu FTIR-8400S spectrophotometer. The FTIR spectrum of terpolymers representative for these polymers is shown in Fig. 2.15.

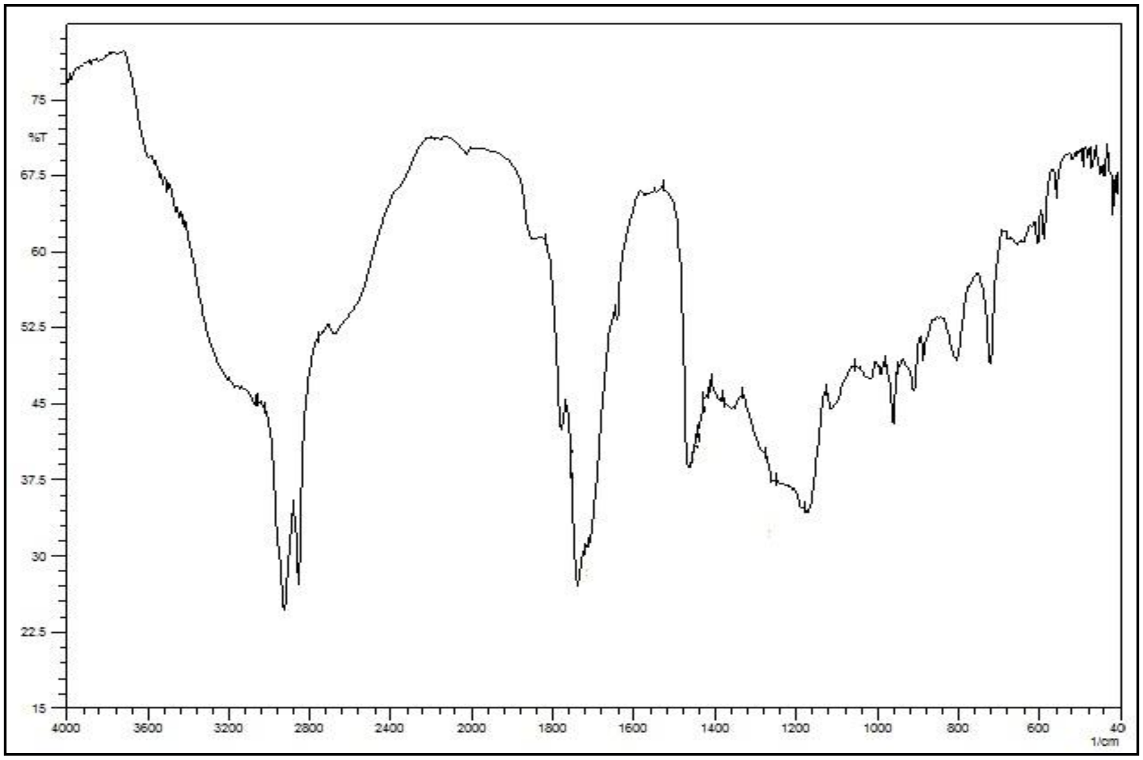
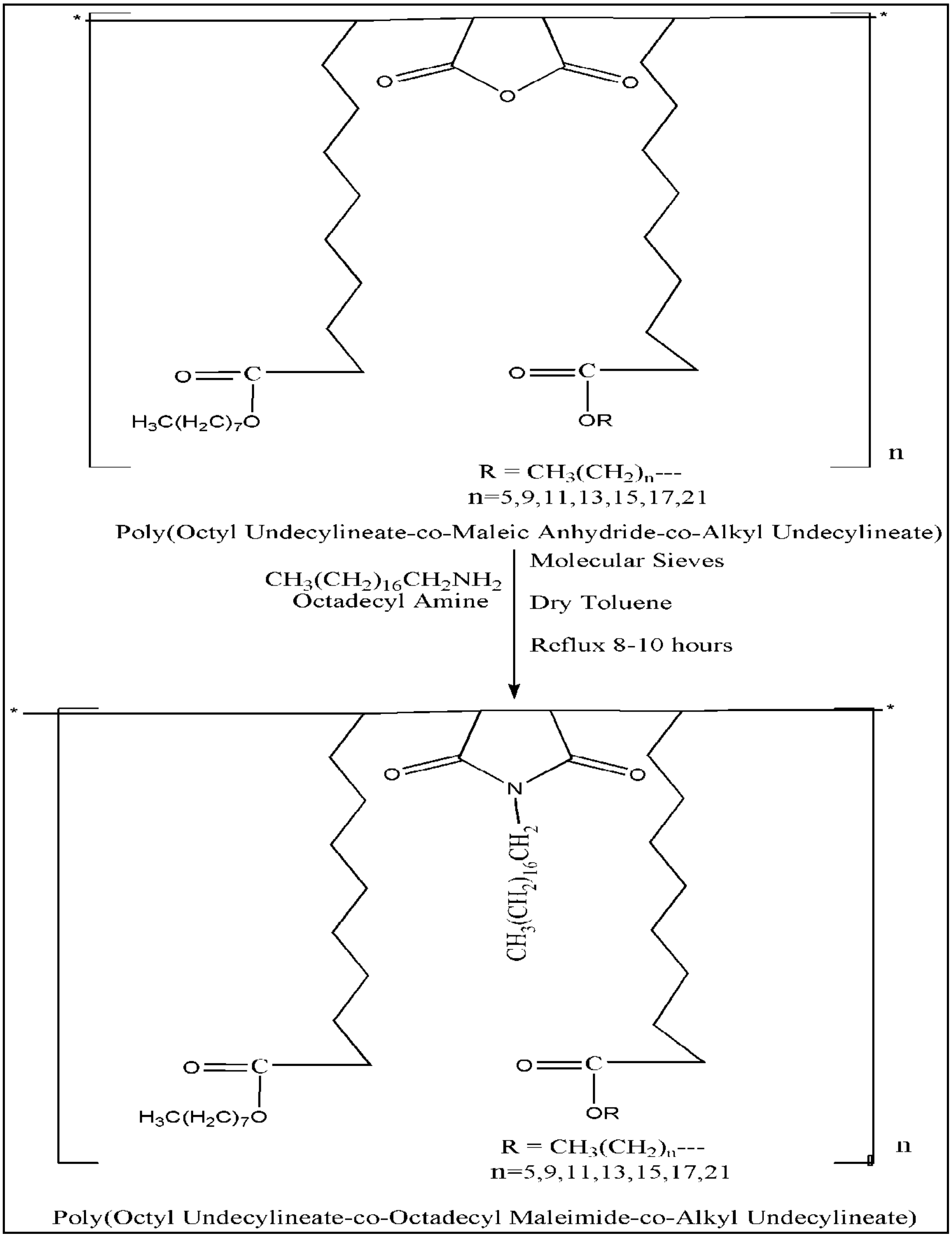


Fig. 2.15 FTIR spectrum of 8-10UA (Terpolymer)

The above figure shows FTIR spectrum of 8-10UA having appearance of two characteristics peaks of C=O stretching of maleic anhydride shifted under the impact of carbonyl group of Undecylinate ester to be found at 1778.43 $cm^{-1}$and 1737.92 cm^{-1} and the carbonyl group of Undecylinate ester at 1710.92 cm^{-1}.

2.6.5 Synthesis of poly(Octyl Undecylinate -co-octadecyl maleimide-co-alkyl Undecylinate)

In the final stage of synthesis all seven terpolymers were reacted with octadecyl amine to get polyimides. Solvent used was dry toluene. A round bottom flask completely clean and dried was used for this step where terpolymer and octadecyl amine was added in 1:1 mole ratio in presence of molecular sieves to trap water molecules. Dry toluene taken was 70 to 80 % of total volume of reactants. The time duration for reaction was 8-10 hours. On completion, the reaction mass was cooled to room temperature. Here also the product purification was done by solvent non-solvent method taking toluene as solvent and methanol non-solvent. The product obtained was vacuum dried for 6 to 7 hours. The obtained polyimides were code named as 8-6UA18N, 8-10UA18N, 8-12UA18N, 8-14UA18N, 8-16UA18N, 8-18UA18N and 8-22UA18N. The first digit in the code represents carbon number of short alkyl chain while 2nd and 3rd digit together represent carbon number of long chain esters. UA represents acid used was Undecylinic acid for ester synthesis. And 18N shows imide formed by octadecyl amine.



Scheme 2.12 Synthesis of poly (Octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate)

2.6.6 Characterization of poly(Octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate) Polyimides

2.6.6.1 FTIR spectra of poly(Octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate) Polyimides

Confirmation of Nitrogen incorporation in the copolymers was done through IR spectral analysis. Following figure shows representative FTIR spectrum of 8-10UA18N. The appearance of the characteristics peak for imide N-C stretching at 1701.27 cm^{-1} and C=O stretching at 1737.92 cm^{-1}.

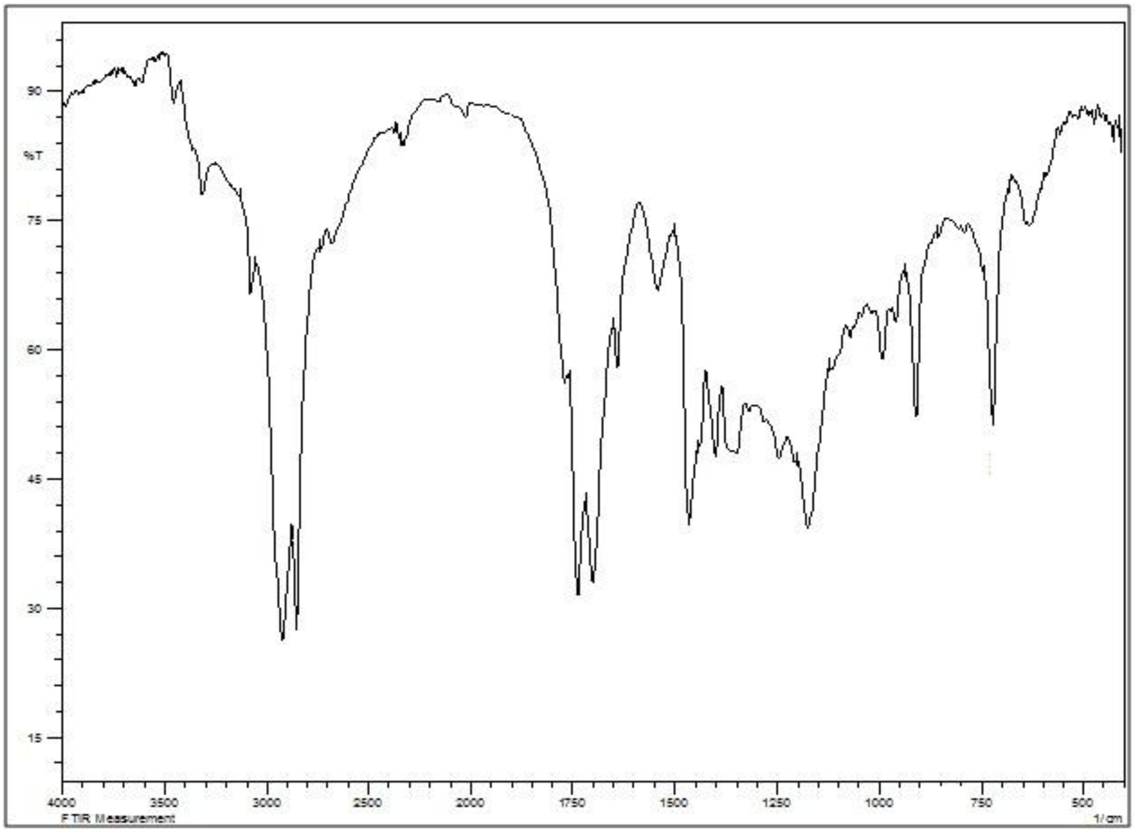


Fig. 2.16 FTIR spectrum of 8-10UA18N

2.6.6.2 GPC results of poly(Octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate) Polyimides

The synthesized polyimides were analyzed for their molecular weight and Polydispersity index using Gel Permeation Chromatography Technique. Polystyrene was used as molecular weight standard. The GPC apparatus used was of Perkin Elmer make having Model No. Turbo Matrix-40. The HPLC grade THF solvent was used with stayragel HR4 column, and 1 ml/min flow rate at 25^oC. Molecular weights of polyimides are as shown in the Table 2.4.

Table 2.4 Molecular Weights of poly (Octyl Undecylinate -co-octadecyl maleimide-co-alkyl Undecylinate)

S. No.	Polymer Code	Weight Average Molecular Weight (M_w)	Number Average Molecular Weight (M_n)	Polydispersity Index (M_w/M_n)
1	8-6UA18N	14488	8035	1.8030
2	8-10UA18N	15826	10235	1.5463
3	8-12UA18N	23576	12918	1.8250
4	8-14UA18N	25993	13798	1.8838
5	8-16UA18N	22105	12764	1.7317
6	8-18UA18N	25011	13756	1.8181
7	8-22UA18N	20904	13455	1.5536