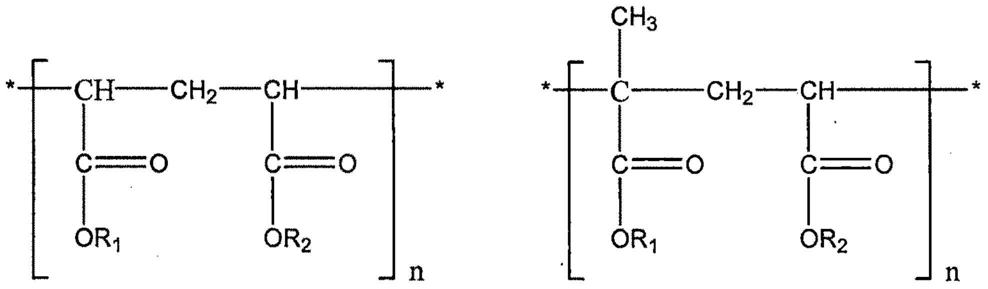
CHAPTER-II

PROCEDURE FOR LABORATORY PREPARATION OF POUR POINT DEPRESSANTS (CHEMICAL ADDITIVES)

2.1. General

In present oil industry variety of chemicals i.e polymers are used to eliminate different problems because these applications are easy and cost effective and the solution obtained for any problem is much better than any other method[129]. Use of additives to reduce the pour point is a well known art in the industry. One important feature of the additive is that it should be effective in small quantities. Another important feature is that the additive should not produce unwanted by-products with its use. An additive should be effective in all viscosities and being liquid for easy use are also desirable attributes in an additive. One of the structural characteristics of flow improver is linear polymer or copolymer with pendant side chains of specific length and nature. In copolymers, one of the comonomers may or may not contain a pendant side chain. The structural formula for copolymers of polyalkyl acrylates and polyalkyl methacrylates is shown in Figure 26.



polyalkyl acrylate polyalkyl methacrylate

Figure:27 Structure of polyalkyl acrylates and polyalkyl methacrylates

Depending upon the nature of R_1, R_2, a lot of products are possible. It is preferred that the alkyl group be a straight chain alkyl group of carbon number 10 to 30. The study from Gandhar and Nada waxes GC it has been revealed that main distribution of carbon number is from C_{13} to C_{32} and concentration is mainly distributed from 16 to 24 carbon numbers.

The present invention is directed to flow improving additive composition having low temperature characteristics. The composition comprises a major proportion of liquid hydrocarbyl distillate and a minor proportion of the flow improving additive. The composition comprised of an esterified fatty acid ester-maleic anhydride copolymer. The preferred esterified fatty acid ester and maleic anhydride copolymer having general structure as follows in Figure 28.

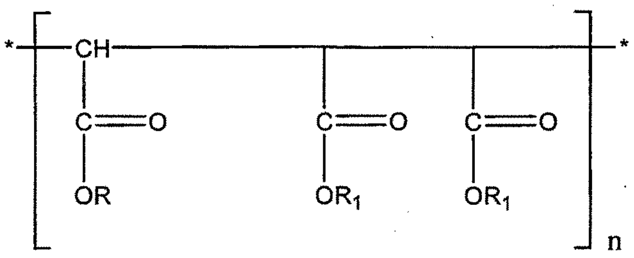


Figure:28 Structure of esterified fatty acid ester and maleic anhydride copolymer

The R and R_1 being an independently selected alkyl group and the alkyl group is straight chain of 10 to 22 carbon chain alcohol and or benzyl (aromatic) alcohol. The preferred molecular weight of the composition is 10,000-30,000. More preferably the esterified fatty acid ester-maleic anhydride copolymer is a reaction product of fatty acid ester-maleic anhydride copolymer and straight chain fatty alcohols having carbon chain from 4 to 22 and or benzyl (aromatic) alcohol. The most preferred straight chain alcohols have 10 to 22 carbon chain.

As used herein, C_8-C_{22} alkyl acrylates, undecylenate, oleate, methacrylate means an alkyl ester of acrylic acid, oleic, undecylenic, methacrylic acid having a straight chain alkyl group of 8 to 22 carbon atoms per group and benzyl undecylenate means benzyl ester of undecylenic acid. These above stated monomers are generally prepared by standard esterification procedure using technical grade long chain aliphatic carboxylic acids and technical grade long chain aliphatic aromatic alcohols with elimination of water by azeotroping[130,131]. These commercially available alcohols are mixtures of alcohols of varying chain lengths in the alkyl groups. On esterification, excellent reviews are given by Goldsmith[132], Keys[133] and Reid[134].

Polymers can be synthesized via many pathways, but a clear distinction should be made between the polymerization mechanisms leading to these mechanisms leading to these compounds. Flory[135] made a useful distinction based on polymerization mechanisms and most polymerizations can be classified as step growth or chain growth polymerization. The most widely used process for polymer synthesis is free radical polymerization[136-139]. Free radical polymerization has a major advantage that it is much less sensitive to ionic or coordination polymerization. A wide range of vinyl monomers can be polymerized via free radical polymerization. The process involves the generation of free radicals from an initiator, which are then added to the monomer. Addition of monomer to the growing chain radical continues until either two growing chains get terminated by chain transfer or by termination produces dead chains. The growing polymer chain in free radical polymerization is in the order of seconds, as radicals are generated from the initiator continuously throughout the polymerization, new chains are initiated, grow and are terminated throughout the polymerization. The copolymers may be traces of impurities than other polymerization techniques like prepared by various polymerization techniques including free radical and anionic polymerization[140,141].

Conventional methods of free radical polymerization is used to prepare the copolymers of the present work. Polymerization can be done under variety of conditions including bulk polymerization, solution polymerization (in organic solvent). Solution polymerization is preferred using suitable catalyst, preferably a free radical initiator and more preferably a peroxide catalyst such as benzoyl peroxide, tertiarybutyl hydroperoxide or di-t-butyl peroxide. The most preferred catalyst is benzoyl peroxide. Appropriate diluents used in the reaction are heavy aromatic solvents like benzene, toluene and xylene because initiator efficiency is more in aromatic solvent[142,143,145]. The duration and temperature of the reaction depend upon the desired molecular weight. The fatty acid ester and maleic anhydride are used in equal molar proportions to get the alternating copolymer.

The molecular weight of polymer is of prime importance in its synthesis and application. Since molecular weight of the polymer produced at any instant varies with the overall percent conversion due to changes in monomer and catalyst concentrations, temperature and the propagation and the termination rate constants. Maleic anhydride does not homopoloymerize but readily forms alternating copolymers with electron donor monomers such as styrene, vinyl ethers, and n-vinylcarbazole[146,147]. The molecular weight of alternating copolymer depends upon the concentration of activated complex. Higher the temperature lower is the complex concentration and lower is the molecular weight of the copolymer[148]. The effect of solvent on the rate of polymerization has been attributed to complex formation[149]. Gel effect is the "normal" behaviour for most of the polymerizations. The gel effect is observed under isothermal reaction conditions. Due to this there is marked increase in the average molecular weight of the polymer formed. The control of molecular weight in the free radical polymerization beyond the gel effect is achieved by various methods as,

1. Increase in polymerization temperature
2. Use of transfer agent
3. Method of weak inhibition[150-151]

The temperature imposition is not a universal method for controlling the molecular weight of the polymer formed. There are many polymers which are temperature sensitive and they alter their properties when exposed to high temperature. Particularly, for such polymers weak inhibition method is useful. Use of transfer agents in the polymerization system may cause low molecular weight polymers. Molecules of low molecular weight lead to increase in viscosity of reaction mass slowly than molecules of higher molecular weight. The method of weak inhibition and chain transfer with benzene is supposed to be involved in the control of molecular weight in these copolymers even though it is not specifically studied.

Further the copolymer of fatty acid ester-maleic anhydride is esterified with an appropriate alcohol. These alcohols are straight chain of 10-22 carbon atoms and or aromatic (benzyl alcohol). The alcohols used are in two moles for each mole of maleic anhydride. The esterification is well known to those skilled in the art. The reaction mixture of fatty acid ester and alcohols are reacted for 24 hours to a temperature of 140°C. Completion of the reaction can be monitored by conventional methods such as measuring the amount of water produced by the reaction and by infrared spectroscopy. To promote esterification reaction common catalyst can be added. Examples of common catalysts are methane sulfonic acids, acidic exchange resins[152,153] and sulfuric acid. A preferred catalyst is *p*-toluene sulfonic acid. The diluents such as heavy aromatic solvent are used like xylene.

General codes used for Diesters are summerised below:

A. Diester of Poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate	**(n ABA)**
B. Diester of Poly(n-alkyl oleate-co-maleic anhydride)dialkylate	**(n OA n)**
C. Diester of Poly(n-alkyl methacrylate-co-maleic anhydride)dibenzylate	**(n MBA)**
D. Diester of Poly(benzyl undecylenate-co-maleic anhydride)dialkylate	**(BAUn n)**

2.2 PROCEDURE-I

2.2.1.Synthesis of Diester of poly(n-alkyl acrylate-co-maleic anhydride) dibenzylate

Reagents

Chemical reagents used for the preparation of Diesters are fatty alcohols, toluene, benzene, xylene, Acrylic, Methacrylic acid, Oleic and Undecylenic acids Sulfuric acid and *p*-toluene sulfonic acid and Benzoyl peroxide were dried over the sodium wire.

2.2.2 Preparation of acrylic acid esters

All the acrylic acid esters were prepared by conventional acid catalyzed esterification method under azeotropic conditions using Dean and Stark apparatus. The alcohols were esterified with excess of acrylic acid (2 moles excess than required quantity) using sulfuric acid as a catalyst and toluene (depending upon total of reactants) as azeotroping agent with Hydroquinone as inhibitor. The progress of the reaction in all the cases was followed by the volume of water azeotroped in all cases. The time of esterification was varied from 8 hours to 12 hours. For higher alkyl esters time taken for the completion was relatively more

After completion of reaction, the crude esters in all cases were washed by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated dried over anhydrous sodium sulphate and the solvent was recovered by vacuum distillation. The ester analyzed by the infrared spectroscopy. Quantities of materials and analysis of the products are summarized in Table 1.

Sr. No.	Code	Acrylic acid mole	Alcohol mole	Toluene in ml
1	8 AE	0.094	0.092	44
2	10 AE	0.065	0.063	35
3	12 AE	0.050	0.048	35
4	14 AE	0.048	0.046	33
5	16 AE	0.043	0.041	33
6	18 AE	0.039	0.037	36

Table 1 Synthesis of n-alkyl acrylates

2.2.3. Analysis and Characterization[154-160]

One of the I.R. spectrums of ester is shown in Figure 29 and analysis of spectrum is shown in Table 2.

Sr. No.	Absorption At cm^{-1}	Assignment	Characteristic absorption cm^{-1}
1	1731	C=O stretching	1750-1735
2	2926 And 2854	C-H stretch	2962-2853
3	722	C-H bending	720

Table 2 IR spectral data of octadecyl acrylate

Infrared spectrophotometer IR Prestige-21 FT-IR Shimadzu spectrophotometer

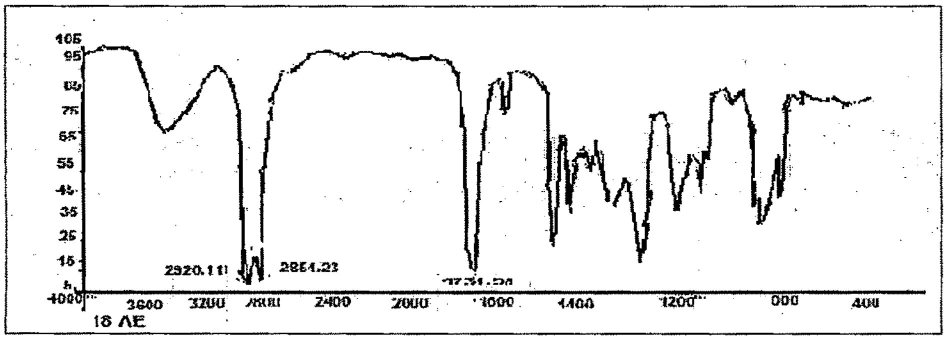


Figure:29 IR spestrum of octadecyl acrylate

2.2.4. Copolymerization of n-alkyl acrylate with maleic anhydride

The experimental assembly consists of four neck flask kept in thermostatically controlled oil bath. The center neck of the flask was fitted with the water condenser and the remaining two side neck possesses a thermometer pocket with a sensitive thermometer and a purger for nitrogen inlet. And the remaining neck was fitted with pressure equalizing dropping funnel.

First the assembly was dried under flame with flushing the nitrogen gas to replace the oxygen and moisture. The solvent benzene was charged into the polymerization flask with magnetic needle. Then the n-alkyl acrylate was charged along with recrystallized maleic anhydride in 1:1 mole ratio[161]. Pure dry nitrogen was introduced in the system from the bottom of the flask to replace the oxygen from the reaction mass. Nitrogen purging was continued to blanket the reactants with the nitrogen atmosphere and increased temperature upto 75°C and rate of nitrogen purging was increased with increasing stirring. Then the catalyst solution of benzoyl peroxide kept under nitrogen was introduced dropwise into the polymerization flask. Now slight exotherm was observed. The stage is lasting far half an hour to one hour. The temperature range was maintained in between 70°-75°C for 8 hours. After eight hours, the reaction mass was cooled to room temperature and further processed for the purification. The quantities of materials taken for synthesis are summarized in Table 3.

Above synthesized copolymer was purified by the solvent non-solvent method. The copolymer was precipitated by pouring the copolymer solution in 10-15 times volume of the non-solvent with agitation. The precipitant must be miscible with solvent and non-solvent for copolymer with solvent for initiator, oligomers and unreacted monomers. All the synthesized copolymers were purified by using benzene as a solvent and methanol as a non-solvent. The solvent non-solvent method was carried out for two to three times. Then the copolymer was separated and dried under vacuum at 50°C/25 mm Hg for 12 hours. Quantities taken for the reaction are shown in Table 3 as follows,

Sr. No.	**Code**	**Raw materials**			**Benzene ml**
		Alkyl acrylate (mole)	**Maleic anhydride (mole)**	**Benzoyl peroxide gm (% on wt. of total monomers)**	
1	8 AECO	0.062	0.062	0.160	25
2	10 AECO	0.047	0.047	0.146	22
3	12 AECO	0.041	0.041	0.140	25
4	14 AECO	0.037	0.037	0.136	22
5	16 AECO	0.033	0.033	0.133	24
6	18 AECO	0.031	0.031	0.130	22

Table 3 Synthesis of poly(n-alkyl acrylate-co-maleic anhydride)

2.2.5. Analysis and characterization

(1) Molecular weight:

The molecular weights of the copolymers were determined by gel permeation chromatography and are given in Table 4.

Sr. No.	Copolymer codes	Molecular weight
1	10 AECO	26612
2	12 AECO	25125
3	14 AE CO	28731
4	16 AECO	28231
5	18 AECO	39415

Table 4 Molecular weights of copolymers of n-alkyl acrylate and maleic anhydride

Gel Permeation Chromatography (GPC): Waters 510 pump connected through three series of Styragel HR columns (HT-3, HT-4, and HT-5) and Waters 410 differential refractometer

(2) One of the I.R. spectrums of copolymer is shown in Figure 30 and analysis of spectrum is shown in Table 5.

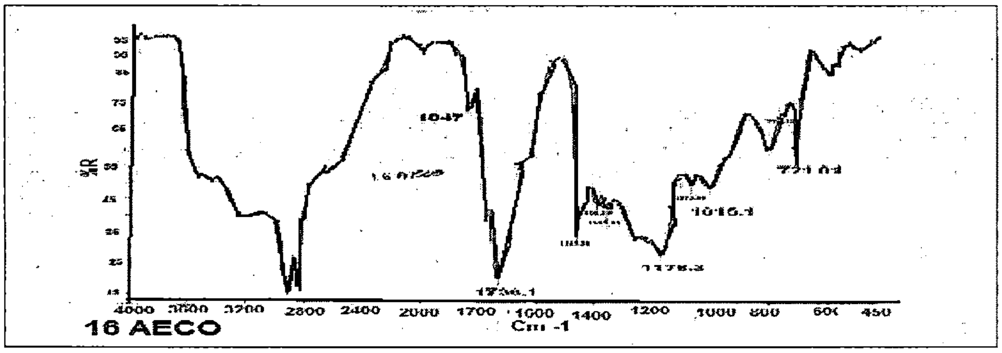


Figure 30 IR spectrum of poly(hexadecy acrylate-co-maleic anhydride)

Sr. No.	Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}
1	1847	Maleic anhydride unit C=O stretch	1830-1800 and 1775-1740
2	1015,1176,1075	C-O stretch	1300-900
3	1736	Ester	1735
4	721	C-H bend	720

Table 5 IR spectral data of Poly(hexadecylacrylate-co-maleic anhydride)

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.2.6 Diesterification of anhydride copolymer

The general methods of esterification of maleic anhydride copolymers were extensively studied by Cohen[162]. and Heller et al.[163]. Typical esterification methods under azeotropic conditions are mostly patented.

The experimental assembly consists of two neck flask kept in thermostatically controlled oil bath. The center neck of the flask was fitted with Dean and Stark apparatus connected to water condenser and the remaining side neck possesses a thermometer pocket with a thermometer.

All the esters were prepared by conventional acid catalyzed esterification method under azeotropic conditions using Dean and Stark apparatus. The fatty alcohols were esterified with copolymer in 2:1 molar proportion respectively. The molecular weight of copolymer was calculated as the sum of the molecular weights of alkyl acrylate and maleic anhydride since all of them are alternating copolymers. For the reaction, sulfuric acid and *p*-toluene sulfonic acid was used as a catalyst and xylene (80-90 % of total reactants) as azeotroping agent. The progress of the reaction in all the cases was followed by the volume of water azeotroped in all cases. The time of esterification was varied from 20 hours to 24 hours. For higher alkyl esters time requirement is more.

After completion of reaction, the crude esters in all cases were neutralized by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated and dried over anhydrous sodium sulphate and the solvent was recovered by vacuum distillation to get the concentrated form of the product. Purification of the crude product was done by precipitation of the product in excess of the acetone. The unreacted fatty alcohol and copolymer went into acetone and the product was precipitated. Again the product was separated from acetone and dissolved in xylene and again precipitated into acetone. Further the product was dried under vacuum at 50°C/ 25 mm Hg for five hours. The ester analyzed by the infrared spectroscopy. Quantities of materials and analysis of the products are summarized in Table 6.

Sr. No.	Additive Code	Reactants			Xylene (ml)
		Copolymer (mole)	Alcohol (mole)	PTSA/H_2SO_4	
1	8 ABA	0.038	0.076	0.1/0.1	45
2	10 ABA	0.032	0.064	0.1/0.1	45
3	12 ABA	0.029	0.058	0.1/0.1	45
4	14 ABA	0.028	0.056	0.1/0.1	45
5	16 ABA	0.027	0.054	0.1/0.1	43
6	18 ABA	0.023	0.046	0.1/0.1	46

Table 6 Diesterification of poly(n-alkyl acrylate-co-maleic anhydride)

2.2.6. Analysis and characterization

One of the I.R. spectrums of diester is shown in Figure 31 and analysis of spectrum is shown in Table 7.

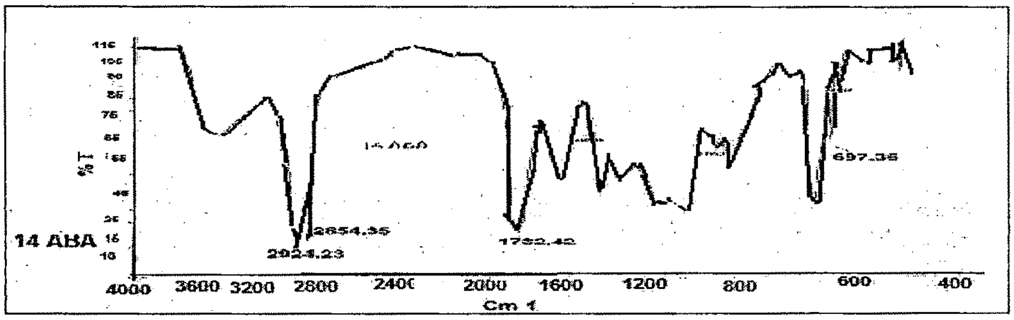


Figure 31 IR spectrum of poly(tetradecyl acrylate-co-maleic anhydride)dibenzylate

Sr. No.	Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}
1	1732	C=O stretching	1750-1735
2	2924 and 2854	C-H stretch	2962-2853
3	697	C-H bending	720

Table 7 IR spectral data of poly(tetradecyl acrylate-co-maleic anhydride)dibenzylate

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.3 PROCEDURE-II

Synthesis of Diester of poly(n-alkyl oleate-co-maleic anhydride) dialkylate

2.3.1 Preparation of Oleic acid ester:

n-alkyl oleate was prepared by reacting oleic acid and different aliphatic alcohol using sulfuric acid as a catalyst and toluene as a solvent. Water was separated azeotropically using Dean-Stark apparatus. After completion of reaction, the crude ester was neutralized by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated and dried over anhydrous sodium sulphate and the solvent was recovered by vacuum distillation. The ester analyzed by the infrared spectroscopy. Quantities of reactants are summarized in Table 8.

Code.	Oleic acid (mole)	Alkyl alcohol (mole)	Toluene ml
8 OE	0.094	0.092	46
10 OE	0.065	0.063	37
12 OE	0.055	0.053	37
14 OE	0.048	0.046	37
16 OE	0.043	0.041	35
18 OE	0.038	0.036	37
22 OE	0.032	0.030	38

Table 8 Synthesis of n-alkyl oleate

2.3.1.1 Analysis and characterization

The I.R. spectrum of ester is shown in Figure 32 and analysis of the spectrum is shown in Table 9.

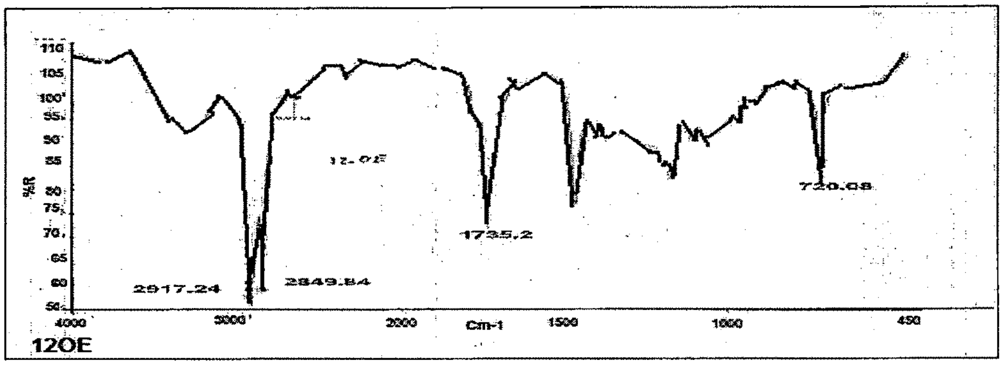


Figure 32 IR spectrum of dodecyl oleate

Sr. No.	Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}
1	1735	>C=Ostretching	1750-1735
2	2917 and 2849	C-H stretch	2962-2853
3	720	C-H bending	720

Table 9 IR spectral data of dodecyl oleate

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.3.2 Copolymerization of n-alkyl oleate with maleic anhydride

The above synthesized alkyl oleate was copolymerized with recrystallized maleic anhydride in 1:1 mole ratio in dry benzene under nitrogen atmosphere with benzoyl peroxide as an initiator (1 % by weight of total monomers) at 70°-75°C with constant stirring. After completion of reaction, excess benzene was distilled off under reduced pressure. Then, purification of copolymer was effected by repeated solvent non-solvent method (Benzene-methanol) and traces of solvent were removed by drying under reduced pressure at 50°C / 25 mm Hg for 12 hours. Quantities of reactants are summarized in Table 10.

Sr. No.	Code	Raw materials			Benzene ml
		Alkyl Oleate (mole)	Maleic anhydride (mole)	Benzoyl peroxide gm (% on wt. of total monomers)	
1	8 OECO	0.026	0.026	0.126	25
2	10 OECO	0.023	0.023	0.123	22
3	12 OECO	0.022	0.022	0.121	25
4	14 OECO	0.020	0.020	0.120	22
5	16 OECO	0.019	0.019	0.119	24
6	18 OECO	0.018	0.018	0.118	22
7	22 OECO	0.016	0.016	0.116	19

Table 10 Synthesis of poly(n-alkyl oleate-co-maleic anhydride)

2.3.2.1 Analysis and characterization

(1) The molecular weight of copolymer were determined by gel permeation chromatography. Molecular weight is given in Table 11.

Sr. No.	Copolymer codes	Molecular weight
1	8 OECO	22138
2	10 OECO	28325
3	14 OECO	35367
4	16 OECO	35819
5	18 OECO	34315
6	22 OECO	40712

Table 11 Molecular weight of copolymer of n-alkyl oleate and maleic anhydride

Gel Permeation Chromatography (GPC): Waters 510 pump connected through three series of Styragel HR columns (HT-3, HT-4, and HT-5) and Waters 410 differential refractometer.

(2) One of the I.R. spectrums of copolymer is shown in Figure 33 and analysis of spectrum is shown in Table 12.

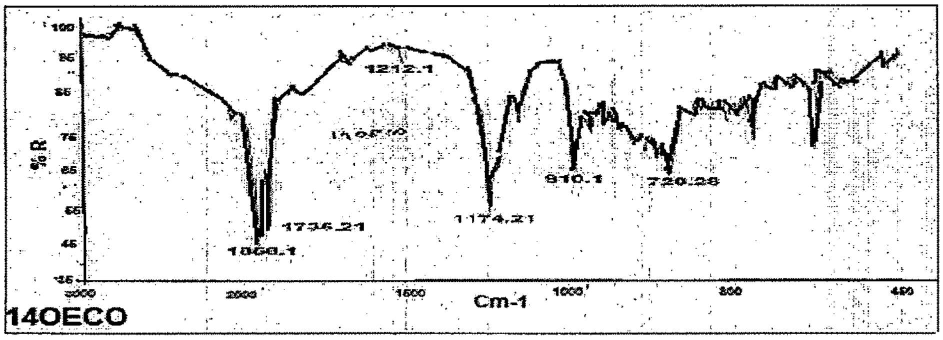


Figure 33 IR spectrum of poly(tetradecyl oleate-co-maleic anhydride)

Sr. No.	Absorption at cm^{-1}	Assignment
1	1856	Maleic anhydride unit C=O stretch
2	910, 1174, 1212	C-O stretch
3	1735	Ester
4	720	C-H bend

Table 12 IR spectral data of poly(tetradecyl oleate-co-maleic anhydride)

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.3.3 Diesterification of anhydride copolymer:

Previously synthesized copolymer were esterified with two moles of different fatty alcohols to produce diester. Traces of *P*-toluene sulfonic acid and sulfuric acid were used as catalyst with xylene as a solvent. Water was azeotropically distilled off. After completion of reaction, the crude esters in all cases were neutralized by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated and dried over anhydrous sodium sulphate and excess solvent was recovered by vacuum distillation. Crude product was purified by repeated precipitation in excess of the acetone. Further the product was dried under vacuum at 50°C/ 25 mm Hg for five hours. The ester analyzed by the infrared spectroscopy. Quantities of materials are summarized in Table 13.

Sr. No.	**Code**	**Reactants**			**Xylene (ml)**
		Copolymer (mole)	**Alcohol (mole)**	**PTSA/H_2SO_4**	
1	8 OA 8	0.021	0.042	0.1/0.1	47
2	10 OA10	0.019	0.038	0.1/0.1	47
3	12 OA 12	0.018	0.036	0.1/0.1	46
4	14 OA 14	0.017	0.034	0.1/0.1	47
5	16 OA 16	0.016	0.032	0.1/0.1	47
6	18 OA 18	0.015	0.030	0.1/0.1	48
7	22 OA 22	0.014	0.028	0.1/0.1	48

Table 13 Diesterification of poly(n-alkyl oleate-co-maleic anhydride)

2.3.3.1 Analysis and characterization

One of the I.R. spectrums of ester is shown in Figure 34 and analysis of spectrum is shown in Table 14.

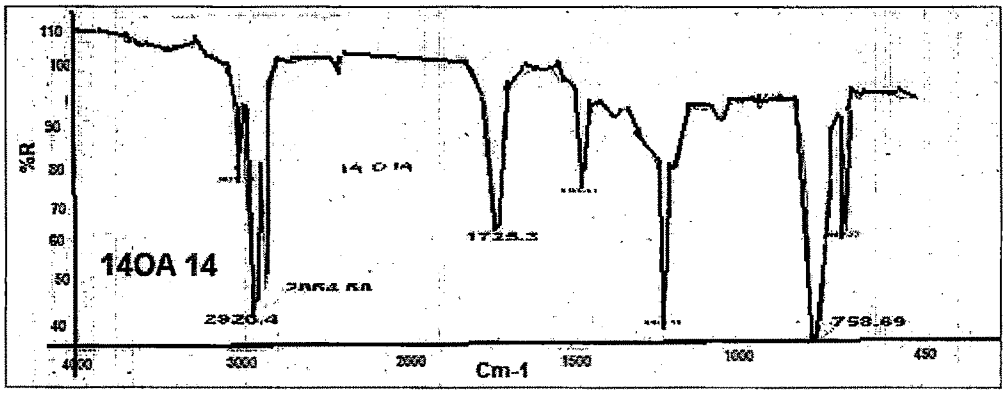


Figure 34 IR spectrum of poly(tetradecyl oleate-co-maleic anhydride)ditetradecylate

Sr. No.	Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}
1	1725	C=O stretching	1750-1735
2	2926 and 2854	C-H stretch	2962-2853
3	758	C-H bending	720

Table 14 IR spectral data of poly(alkyl oleate-co-maleic anhydride) ditetradecylate

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.4 PROCDURE- III

Synthesis of Diester of Poly(n-alkyl methacrylate-co-maleic anhydride)dibenzylate

2.4.1 Preparation of methacrylic acid ester:

Alkyl methacrylate was prepared by reacting methacrylic acid and alkyl alcohol using sulfuric acid as a catalyst, toluene as a solvent and hydroquinone as an inhibitor. Water was separated azeotropically using Dean-Stark apparatus. After completion of reaction, Inhibitor was removed by washing with 4% NaOH. The organic layer was separated and dried over anhydrous sodium sulphate and the solvent was recovered by vacuum distillation. The ester analyzed by the infrared spectroscopy. Quantities of materials are summarized in Table15.

Sr. No.	Additive Code	Reactants		Toluene in ml
		Methacrylic acid (mole)	Fatty alcohol (mole)	
1	8 ME	0.065	0.063	45
2	10 ME	0.055	0.053	46
3	12 ME	0.048	0.046	47
4	14 ME	0.043	0.041	47
5	16 ME	0.038	0.036	47
6	18 ME	0.032	0.030	47

Table 15 Synthesis of n-alkyl methacrylate

2.4.1.1 Analysis and characterization

One of the I.R. spectrums of ester is shown in Figure 35 and analysis of spectrum is shown in Table 16.

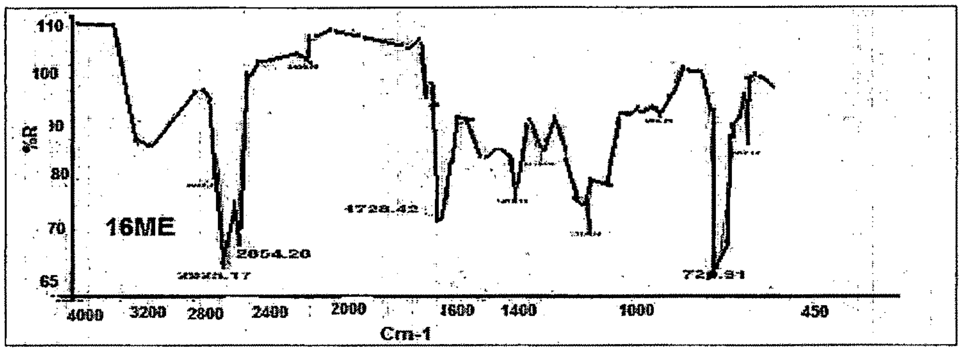


Figure 35 IR spectrum of poly(hexadecyl methacyrylate-co-maleic anhydride)

Sr. No.	Absorption at cm^{-1}	Assignment
1	1728	C=O stretching
2	2925 and 2854	C-H stretch
3	720	C-H bending

Table 16 IR spectral data poly(hexadecyl methacyrylate-co-maleic anhydride)

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.4.2 Copolymerization of n-alkyl methacrylate with maleic anhydride:

The above synthesized alkyl methacrylate was copolymerized with recrystallized maleic anhydride in 1:1 mole ratio in dry benzene under nitrogen atmosphere with benzoyl peroxide as an initiator (1 % by weight of total monomers) at 70°-75°C with constant stirring. After completion of reaction, excess benzene was distilled off under reduced pressure. Then, purification of copolymer was effected by repeated solvent non-solvent method (Benzene-methanol) and traces of solvent were removed by drying under reduced pressure at 50°C / 25 mm Hg for 12 hours. Quantities of materials are summarized in Table 17.

Sr. No.	Code	Reactants			Benzene ml
		Alkyl methacrylate (mole)	Maleic anhydride (mole)	Benzoyl peroxide gm (% on wt. of total monomers)	
1	8 MECO	0.038	0.038	0.137	13
2	10 MECO	0.034	0.034	0.133	13
3	12 MECO	0.031	0.031	0.130	13
4	14 MECO	0.029	0.029	0.128	13
5	16 MECO	0.026	0.026	0.126	12
6	18 MECO	0.024	0.024	0.124	12

Table 17 Synthesis of poly(n-alkyl methacrylate-co-maleic anhydride)

2.4.2.1 Analysis and characterization

(1) The molecular weights of copolymers were determined by gel permeation chromatography. Molecular weights are given in Table 18.

Sr. No.	Copolymer codes	Molecular weight
1	10MECO	20328
2	12 MECO	28719
3	14 MECO	25815
4	18 MECO	30325

Table 18 Molecular weights of copolymers of n-alkyl methacrylate and maleic anhydride

Gel Permeation Chromatography (GPC): Waters 510 pump connected through three series of Styragel HR columns (HT-3, HT-4, and HT-5) and Waters 410 differential refractometer

(2) One of the I.R. spectrums of copolymer is shown in Figure 36 and analysis of spectrum is shown in Table 19.

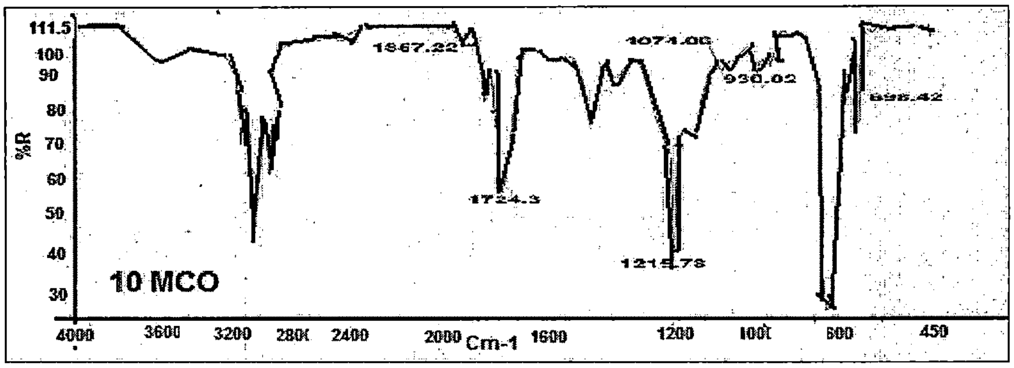


Figure 36 IR spectrum of poly(decyl methacrylate-co-maleic anhydride)

Sr. No.	Absorption at cm^{-1}	Assignment
1	1857	Maleic anhydride unit C=O stretch
2	930, 1074, 1215	C-O stretch
3	1724	Ester
4	698	C-H bend

Table 19 IR spectral data of poly(n-alkyl methacrylate-co-maleic anhydride)

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.4.3 Diesterification of anhydride copolymer:

Previously synthesized copolymer was diesterified with one mole of n-alkyl alcohol to produce diester. Traces of *P*-toluene sulfonic acid and sulfuric acid were used as catalyst with xylene as a solvent. Water was azeotropically distilled off. After completion of reaction, the crude esters in all cases were neutralized by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated and dried over anhydrous sodium sulphate and excess solvent was recovered by vacuum distillation. Crude product was purified by repeated precipitation in excess of the acetone. Further the product was dried under vacuum at 50°C/ 25 mm Hg for five hours. The ester analyzed by the infrared spectroscopy. Quantities of materials are summarized in Table 20.

Sr. No.	Code	Reactants			Xylene (ml)
		Copolymer (mole)	Alcohol (mole)	PTSA/H_2SO_4	
1	8 MBA	0.025	0.050	0.1/0.1	46
2	10 MBA	0.023	0.046	0.1/0.1	46
3	12 MBA	0.019	0.038	0.1/0.1	48
4	14 MBA	0.015	0.030	0.1/0.1	50
5	16 MBA	0.014	0.028	0.1/0.1	50
6	18 MBA	0.014	0.028	0.1/0.1	50

Table 20 Synthesis of poly(n-alkyl methacrylate-co-maleic anhydride) benzylate

2.4.3.1 Analysis and characterization

One of the I.R. spectrums of ester is shown in Figure 37 and analysis of spectrum is given in Table 21.

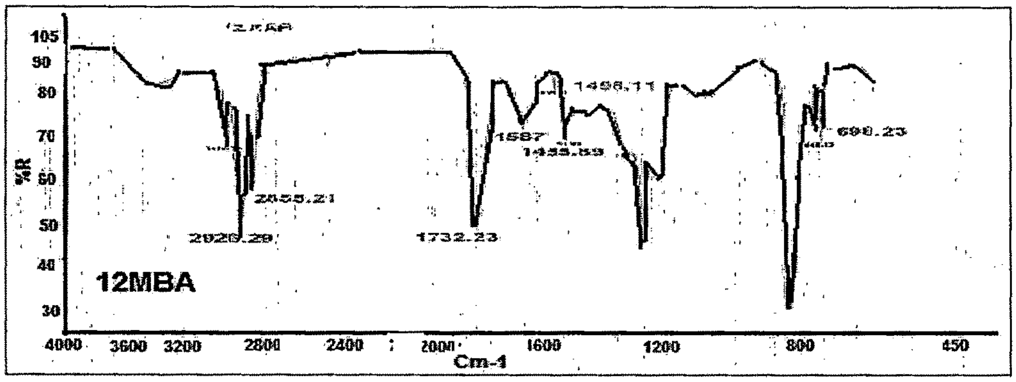


Figure 37 IR spectrum of poly(dodecyl methacrylate-co-maleic ahydride)dibenzylate

Sr. No.	Absorption at cm^{-1}	Assignment
1	1732	C=O stretching
2	2926 and 2855	C-H stretch
3	698	C-H bending
4	1587,1498,1455	Aromatic

Table 21 IR spectral data of poly(dodecyl methacrylate-co-maleic anhydride)dibenzylate

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.5 PROCEDURE IV

Synthesis of poly(benzyl undecylenate-co-maleic anhydride) dialkylate

2.5.1 Preparation of undecylenic acid ester:

Benzyl undecylenate was prepared by reacting undecylenic acid and benzyl alcohol using sulfuric acid as a catalyst and toluene as a solvent. Water was separated azeotropically using Dean-Stark apparatus. After completion of reaction, the crude ester was neutralized by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated and dried over anhydrous sodium sulphate and the solvent was recovered by vacuum distillation. The ester analyzed by the infrared spectroscopy. Quantities of materials are summarized in Table 22.

Sr. No.	Code	Reactants		
		Undecylenic acid (mole)	Fatty alcohol (mole)	Toluene in ml
1	BUnE	0.056	0.054	43

Table 22 Synthesis of Benzylate undecylenate

2.5.1.1 Analysis and characterization One of the I.R. spectrums of ester is shown in Figure 38 and analysis of spectrum is given in Table 23

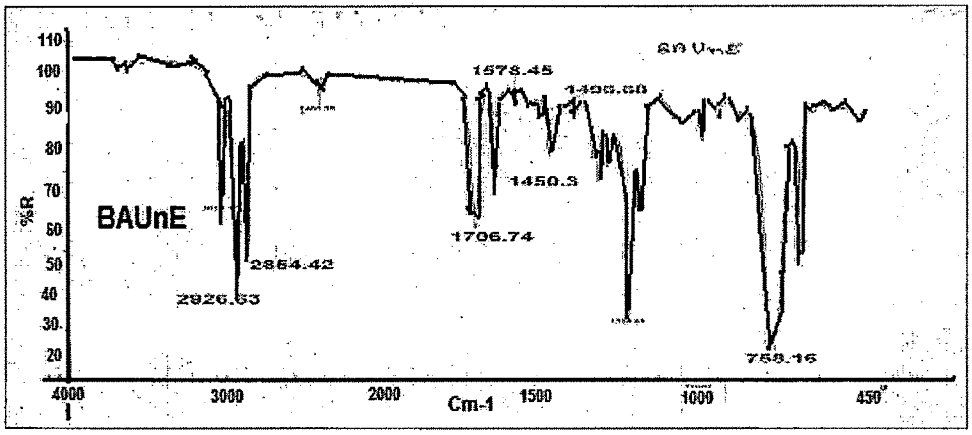


Figure 38 IR spectrum of Benzyl undecylenate

	Absorption at cm^{-1}	Assignment
1	1706	C=O stretching
2	2926 and 2854	C-H stretch
3	758	C-H bending
4	1578,1496,1450	Aromatic

Table 23 IR spectral data of Benzyl undecylenate

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.5.2 Copolymerization of Benzyl undecylenate with maleic anhydride:

The above synthesized benzyl undecylenate was copolymerized with recrystallized maleic anhydride in 1:1 mole ratio in dry benzene under nitrogen atmosphere with benzoyl peroxide as an initiator (1 % by weight of total monomers) at 70°-75°C with constant stirring. After completion of reaction, excess benzene was distilled off under reduced pressure. Then, purification of copolymer was effected by repeated solvent non-solvent method (Benzene-methanol) and traces of solvent were removed by drying under reduced pressure at 50°C / 25 mm Hg for 12 hours. Quantities of materials are summarized in Table 24.

Sr. No.	Code	Reactants			Benzene ml
		Benzyl undecylenate (mole)	Maleic anhydride (mole)	Benzoyl peroxide gm (% on wt. of total monomers)	
1	BUnCO	0.033	0.033	0.133	47

Table 24 Synthesis of poly(benzyl undecylenate-co-maleic anhydride)

2.5.2.1 Analysis and characterization

(1) The molecular weights of copolymers were determined by gel permeation chromatography. Molecular weights are given in Table 25.

Sr. No.	Copolymer codes	Molecular weight
1	BUnCO	37835

Table 25 Molecular weights of copolymers of benzyl undecylenate and maleic anhydride

Gel Permeation Chromatography (GPC): Waters 510 pump connected through three series of Styragel HR columns (HT-3, HT-4, and HT-5) and Waters 410 differential refractometer

(2) The analysis of one of the spectrum of copolymer is given in Table 26. Figure 39

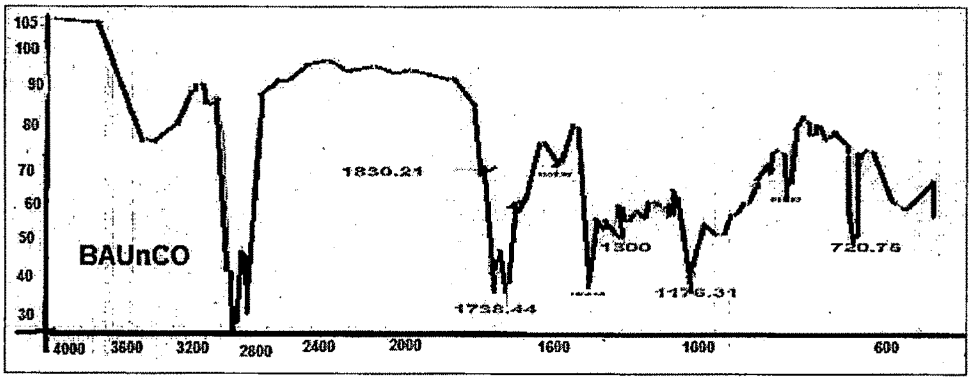


Figure 39 IR spectrum of Benzyl undecylenate-co-maleic-anhydride

Sr. No.	Absorption at cm^{-1}	Assignment
1	1830	Maleic anhydride
2	910, 1176, 1300	C-O stretch
3	1738	Ester
4	720	C-H bend

Table 26 IR spectral data of poly(benzyl undecylenate-co-maleic anhydride)

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer

2.5.3 Diesterification of anhydride copolymer:

Previously synthesized copolymer was esterified with two moles of different fatty alcohols to produce diester. Traces of *P*-toluene sulfonic acid and sulfuric acid were used as catalyst with xylene as a solvent. Water was azeotropically distilled off. After completion of reaction, the crude esters in all cases were neutralized by concentrated sodium bicarbonate solution to remove acidity. The organic layer was separated and dried over anhydrous sodium sulphate and excess solvent was recovered by vacuum distillation. Crude product was purified by repeated precipitation in excess of the acetone. Further the product was dried under vacuum at 50°C/ 25 mm Hg for five hours. The ester was analyzed by the infrared spectroscopy. Quantities of materials are summarized in Table 27.

Sr. No.	Code	Reactants			
		Copolymer (mole)	Alcohol (mole)	PTSA/H_2SO_4	Xylene (ml)
1	BAUn 8	0.022	0.044	0.1/0.1	47
2	BAUn 10	0.023	0.046	0.1/0.1	45
3	BAUn 12	0.019	0.038	0.1/0.1	47
4	BAUn 14	0.025	0.050	0.1/0.1	43
5	BAUn 16	0.015	0.030	0.1/0.1	49
6	BAUn 18	0.014	0.028	0.1/0.1	49

Table 27 Synthesis of poly(benzyl undecylenate-co-maleic anhydride) dialkylate

2.5.3.1 Analysis and characterization

One of the I.R. spectrums of ester is shown in Figure 40 and analysis of spectrum is shown in Table 28.

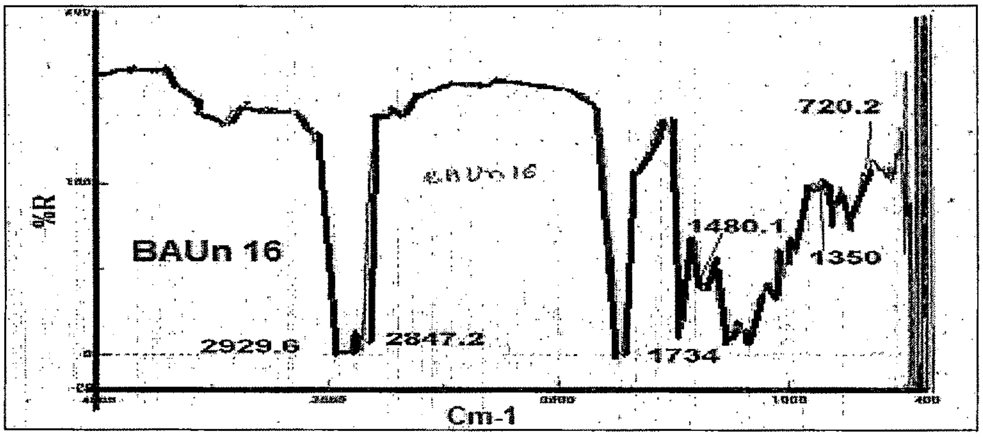


Figure 40 IR spectrum of poly(benzylate undecylenate-co-maleic anhydride) hexadecylate

Sr. No.	Absorption at cm^{-1}	Assignment
1	1734	C=O stretching
2	2929 and 2847	C-H stretch
3	720	C-H bending
4	1480, 1350	Aromatic

Table 28 IR spectral data of poly(benzyl undecylenate-co-maleic anhydride) hexadecylate

Infrared spectrophotometer: IR Prestige-21 FT-IR Shimadzu spectrophotometer