RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Polymers and oligomers are an important area of research for the oil industry and many uses for them have been discovered over the years. One important application for polymers is in crankcase lubricants, in which various specialty polymers and copolymers are used as viscosity modifiers, and pour point depressants. These polymers give an oil all seasons properties and are the most effective additives in producing multigrade oils [Felix and Albert, 2002]. Accordingly, the present work is divided to:

1- Preparation of styrene-maleic anhydride copolymer and octadecene-maleic anhydride copolymer.

2- Esterification of two copolymers with a series of n-alkanols haveing different number of carbon atoms.

3- Reaction of the prepared two copolymers with a series of amines.

4- Evaluation of the prepared copolymers as viscosity index improvers, pour point depressants and dispersants.

3.1. PREPARATION OF STYRENE-MALEIC ANHYDRIDE COPOLYMER

The copolymers of styrene-maleic anhydride is alternating copolymer i.e. each monomer be more reactive towards the other species than towards its own kind. The reaction is given in Fig. (3.1).

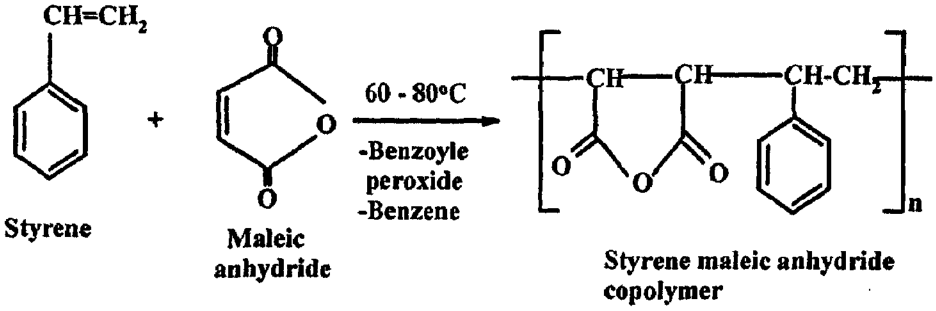


Fig. (3.1): Preparation of styrene-maleic anhydride copolymer

The I.R. spectra of styrene-maleic anhydride copolymer given in Fig. (3.2) which indicate the presence of the same two peaks of anhydride at 1773 cm^{-1} and at 1850 cm^{-1}, the presence of the peak at 710 ± 10 cm^{-1} characteristics of phenyl group .

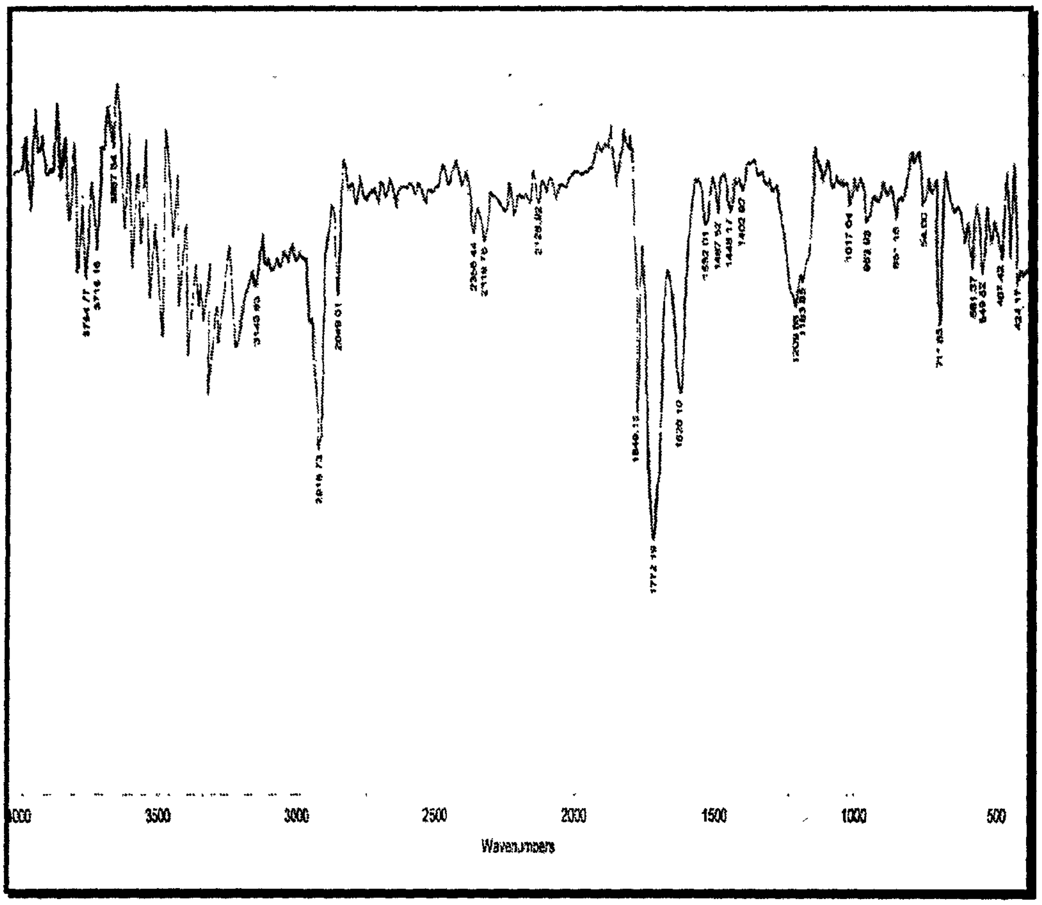
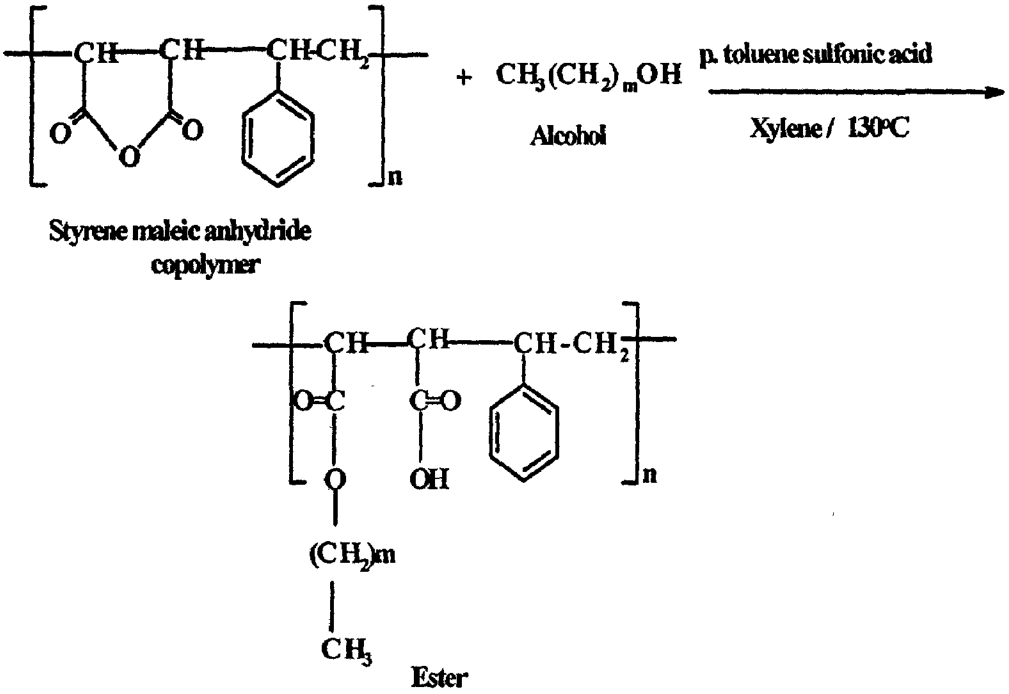


Fig. (3.2): I.R. Spectrum of the compound styrene-maleic anhydride copolymer

3.1.1. Esterification of Styrene-Maleic Anhydride Copolymer

Four different compounds were prepared by esterification of styrene maleic anhydride copolymer with different alcohols, the reaction is given in Fig. (3.3).



m =11, 15, 17 and 21.

Fig. (3.3): Esterification of styrene-maleic anhydride copolymer

The I.R. spectra of esters (A–D) are identical and given in Figs. (3.4) - (3.7); accordingly, the spectrum of compound (A) is represented in Fig. (3.4) which indicate the presence of the peak at 1730±10 cm^{-1} characteristics of C=O of the ester group and the presence of broad band at 3100-3500cm^{-1} characteristics of -OH group, presence of the peak at 2853cm^{-1} and at characteristics of CH_3CH_2- of used alcohols, presence of the peak at 1169±10 cm^{-1} characteristics of C-O group, presence of the peak at 700±10 cm^{-1} characteristics of phenyl group and disappear of two bands of anhydride which appear at 1790 cm^{-1} and 1870 cm^{-1}. This is indicating that the esterification reaction was carried out successfully.

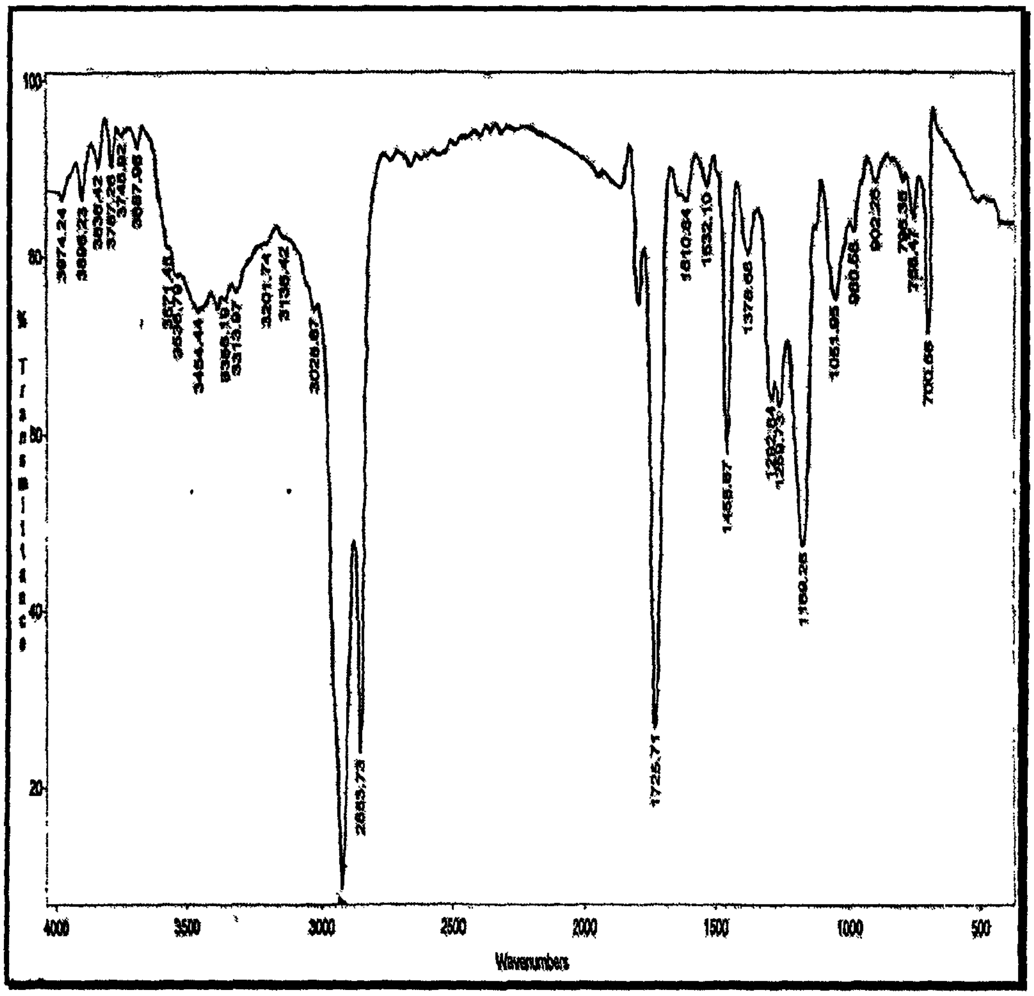


Fig. (3.4): I.R.Spectrum of the prepared compound (A)

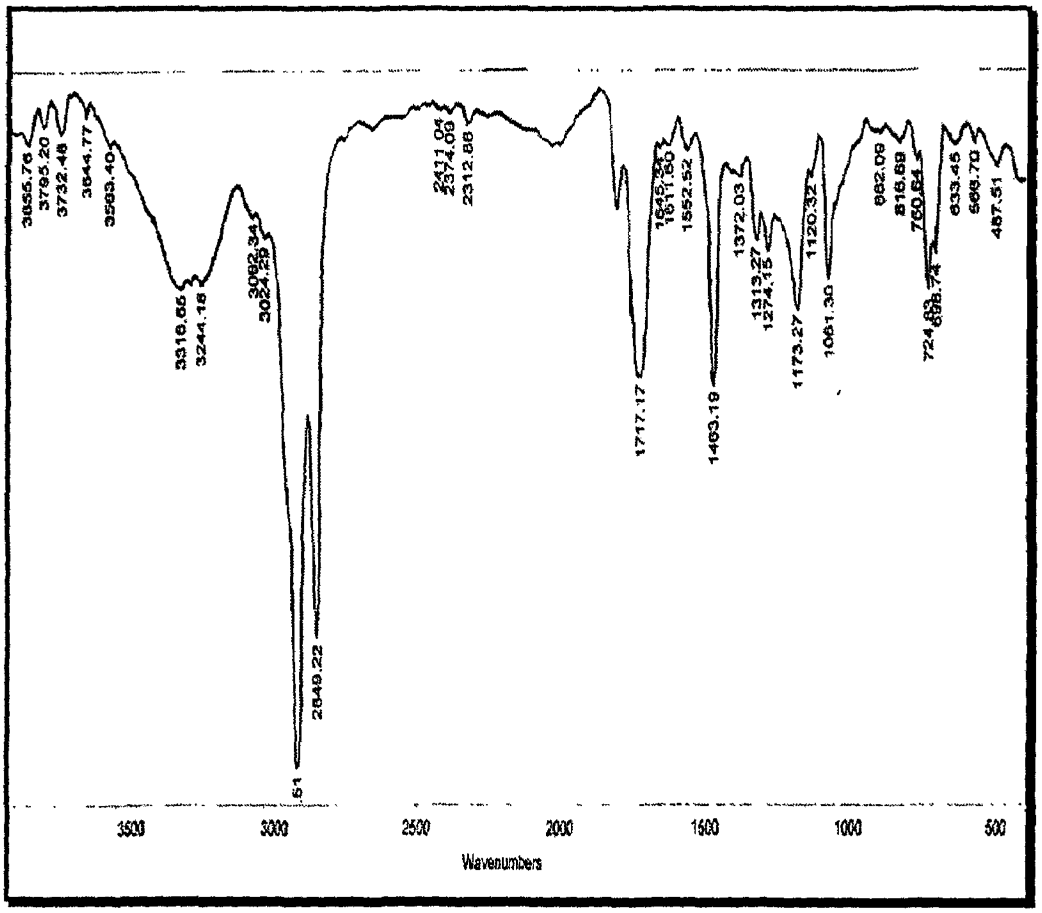


Fig. (3.5): I.R.Spectrum of the prepared compound (B)

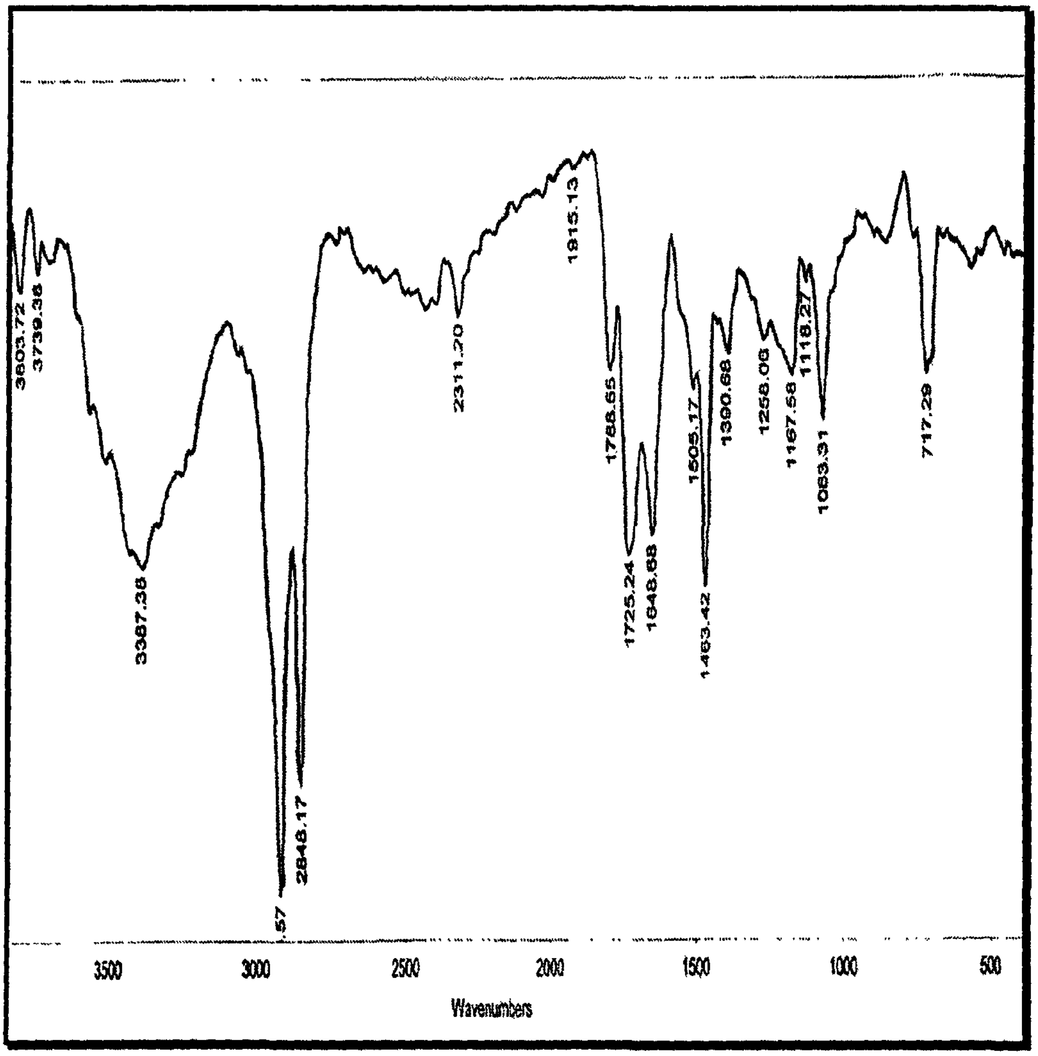


Fig. (3.6): I.R.Spectrum of the prepared compound (C)

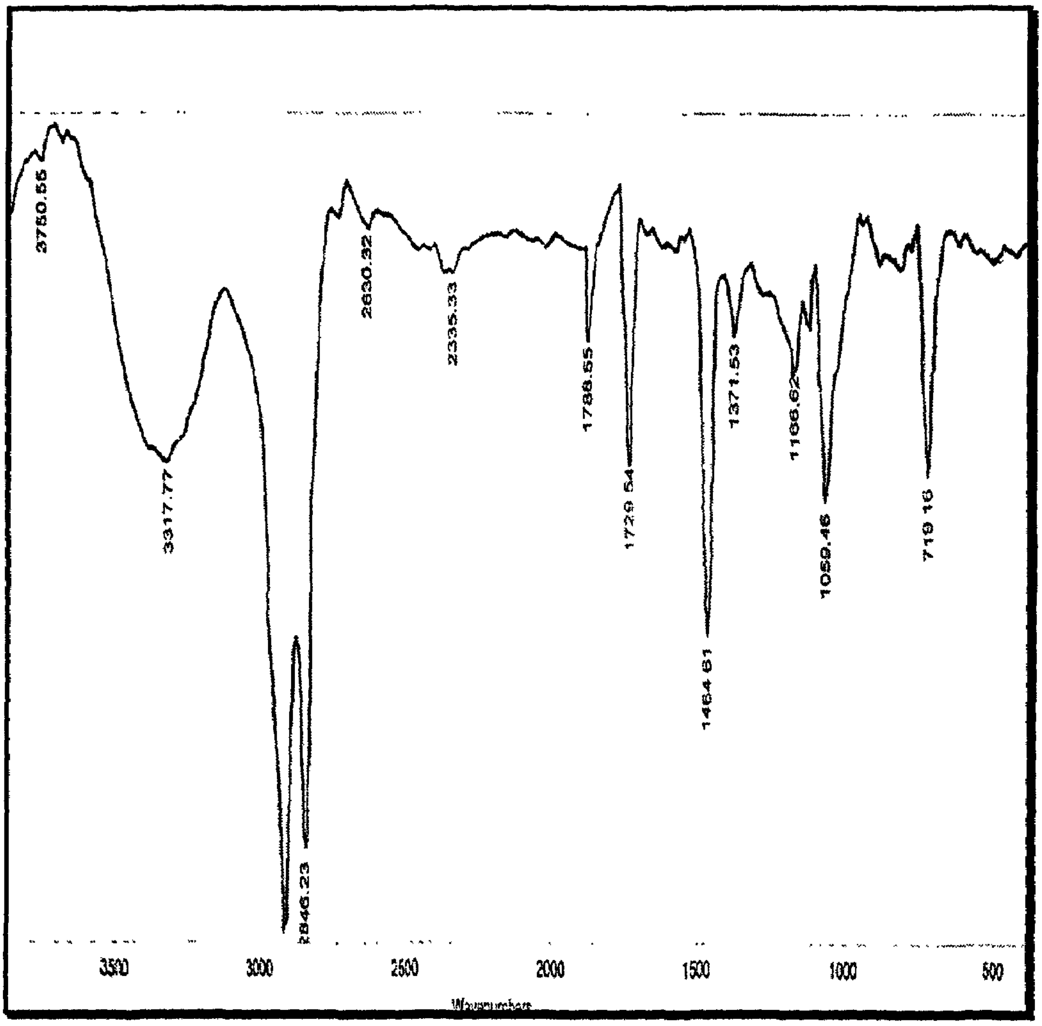


Fig. (3.7): I.R.Spectrum of the prepared compound (D)

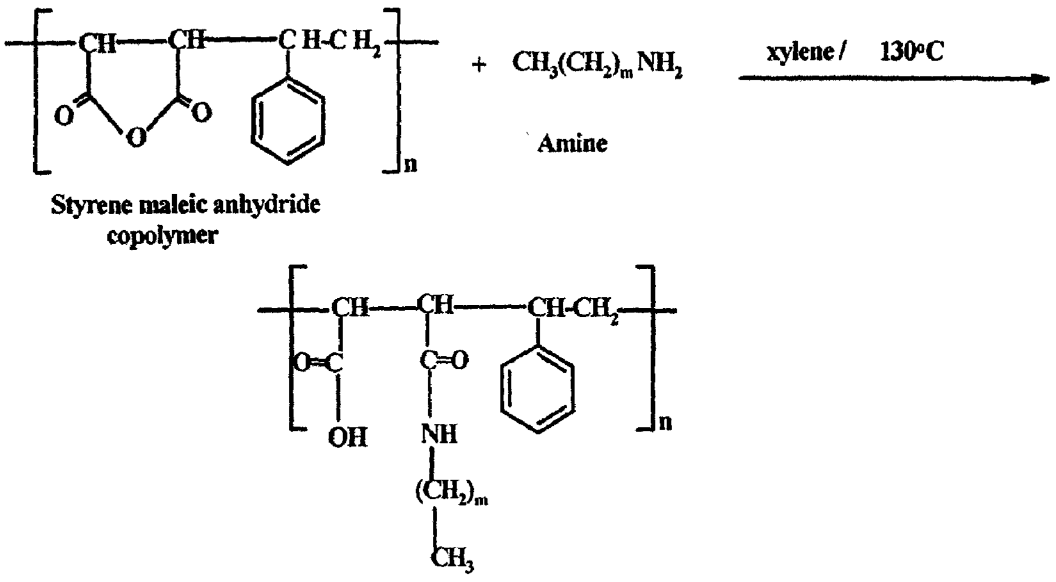
The mean molecular weights of the prepared copolymers were determined and given in Table (3.1) which indicate that the molecular weight increases by increasing the alkyl chain length of the alcohol used.

Table (3.1): The mean molecular weights of copolymers

Copolymer designation	**Mean molecular weight**	**Copolymer designation**	**Mean molecular weight**
Styrene-maleic anhydride copolymer	13 534	**A**	25 996
		B	29 748
		C	30 719
		D	32 133

3.1.2. The reaction of Styrene-Maleic Anhydride Copolymer with Different Amines

Three different compounds were prepared by the reaction of styrene- maleic anhydride copolymer with different amines, the reaction is given in Fig. (3.8).



m =11, 15 and 17.

Fig. (3.8): The reaction of styrene-maleic anhydride copolymer with different amines

The I.R. spectra of amide (E- G) are identical and given in Fig. (3.9)- (3.11), and the spectrum of (G) compound is represented in Fig. (3.11) which indicate the presence of C=O of amide at 1694 cm^{-1} , presence of abroad band at 3300-3500 cm^{-1} due to the presence of –NH and –OH group, presence of the peak at 2918 cm^{-1} characteristics of CH_3CH_2- of used amines, presence of the peak at 1148 ± 10 cm^{-1} characteristics of CO group , presence of the peak at 700±10 cm^{-1} characteristics of phenyl group and disappear of two bands of anhydride which appear at 1790 cm^{-1} and 1870 cm^{-1}. This indicates that the amidation was carried out.

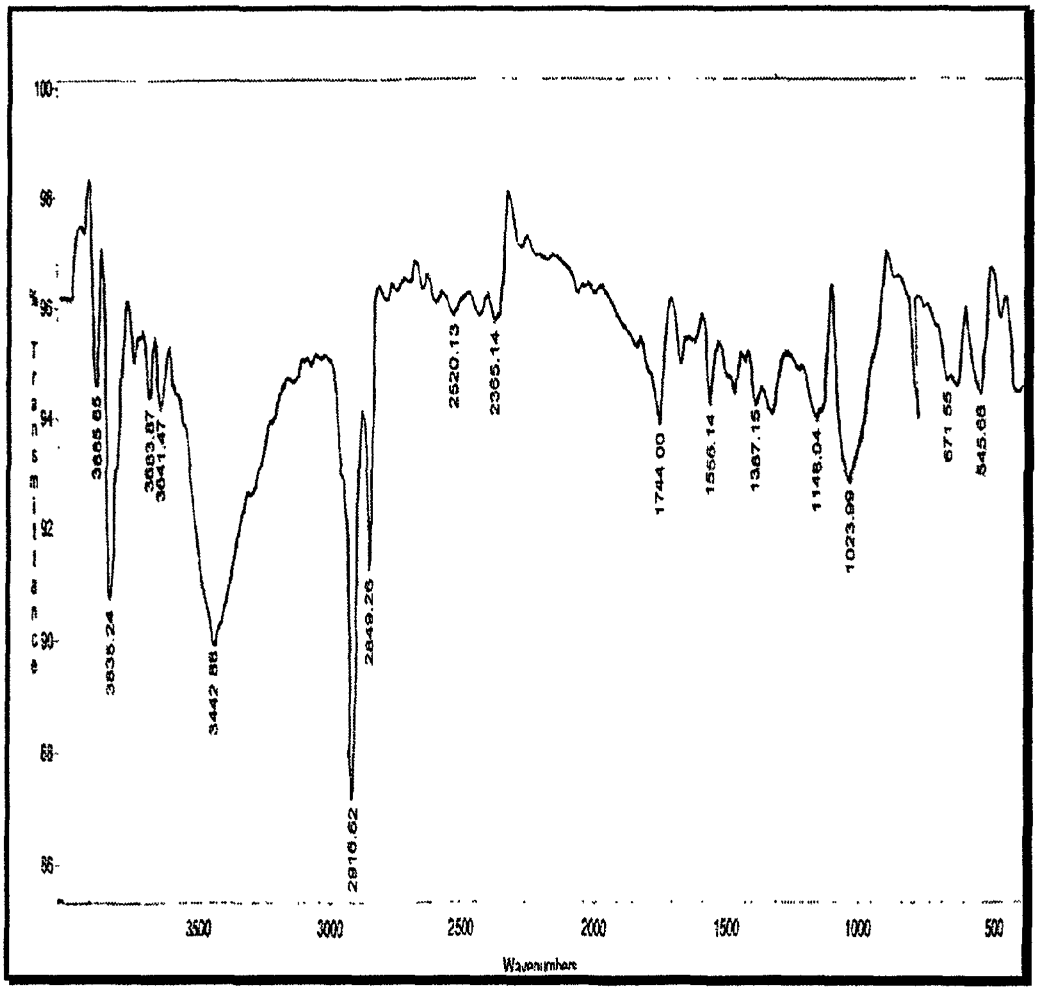


Fig. (3.9): I.R.Spectrum of the prepared compound (E)

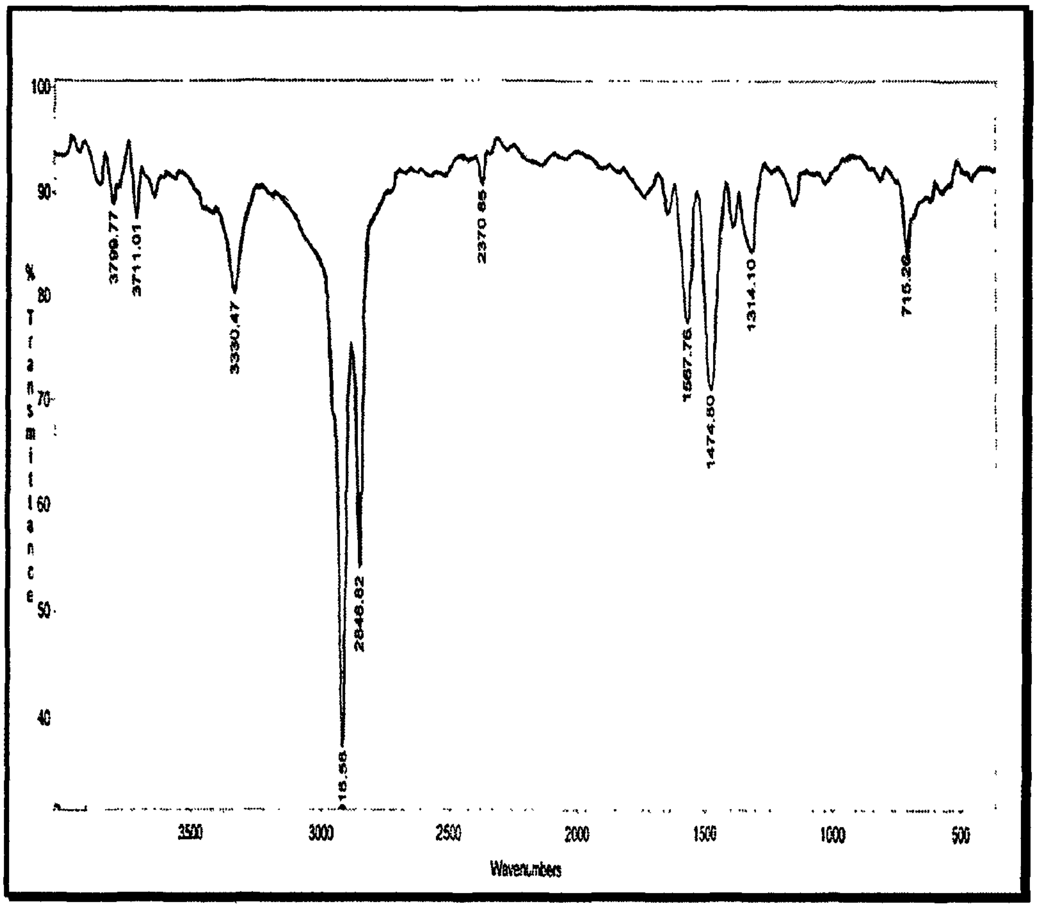


Fig. (3.10): I.R.Spectrum of the prepared compound (F)

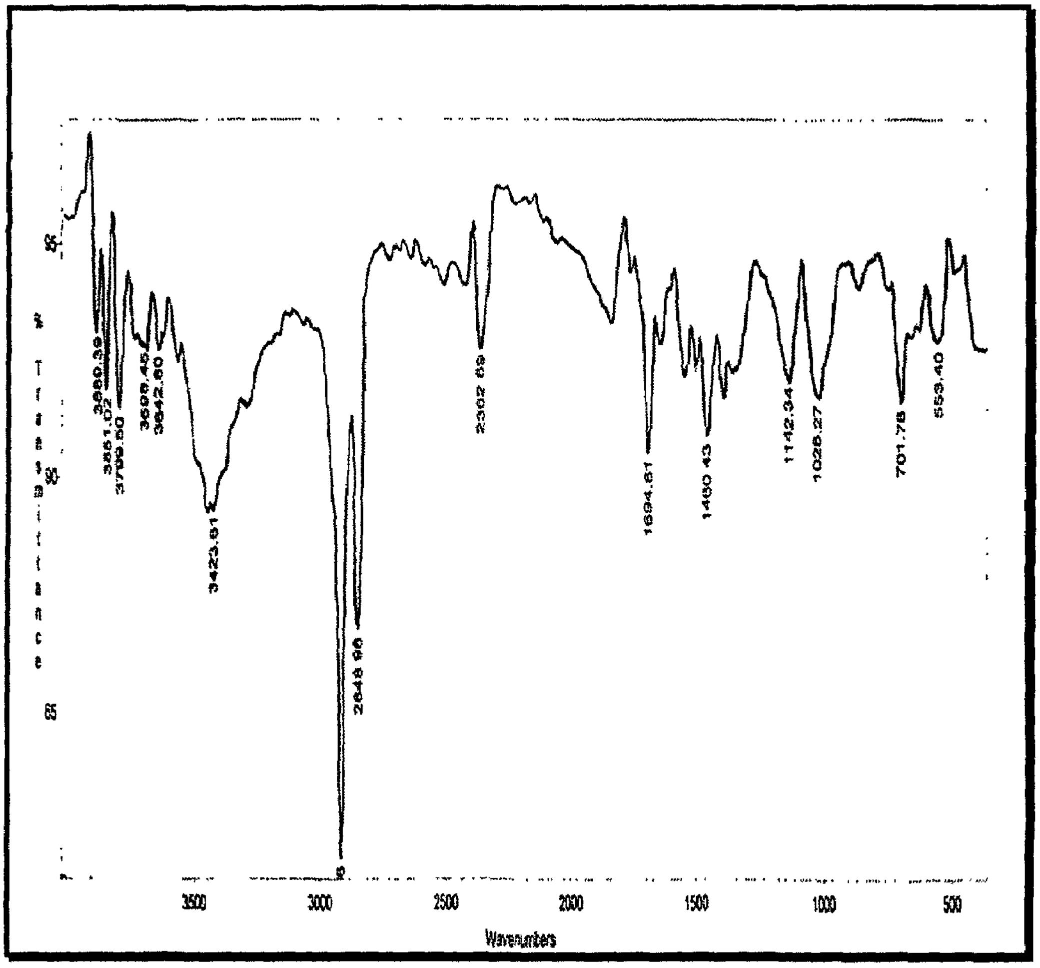


Fig. (3.11): I.R.Spectrum of the prepared compound (G)

The mean molecular weight of the prepared copolymers were determined and given in Table (3.2) which indicates that the molecular weight increases by increasing the alkyl chain length of the amine used.

Table (3.2): The mean molecular weights of copolymers

Copolymer designation	Mean molecular weight	Copolymer designation	Mean molecular weight
Styrene-maleic anhydride copolymer	13 534	**E**	25 952
		F	29 711
		G	31 557

The esterification and amidation percentage can be calculated from ^{1}HNMR analysis as Fig. (3.12) - (3.18). This was obtained by comparing the integration ratios of two signals. In this respect, the signal at 3.8 ppm (which assigned to O-CH_2 or N-CH groups) and the signal at 7.2 ppm (Which assigned to phenyl protons) were selected to determine the esterification and amidation of styrene-maleic anhydride copolymer. The integral values derived from these spectra were calculated and percentage of esterification and amidation given in Table (3.3).

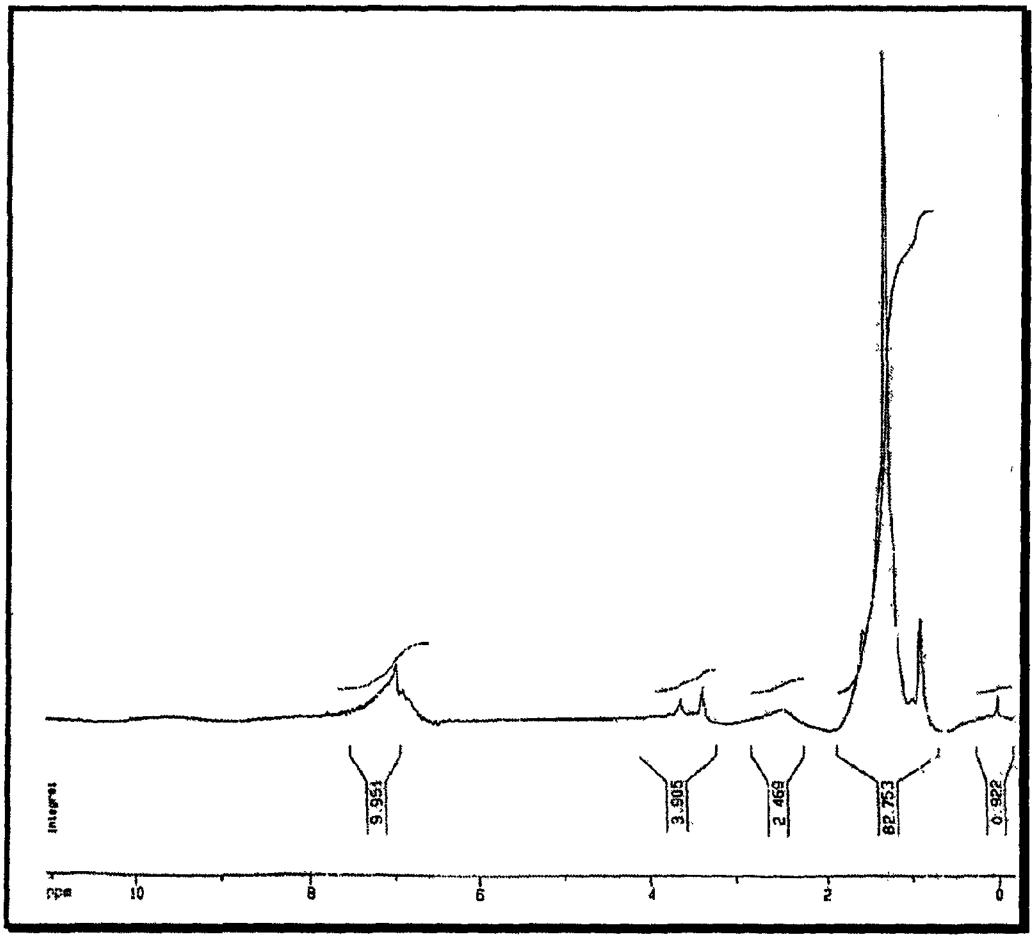


Fig. (3.12): ^{1}HNMR Spectrum of the prepared compound (A).

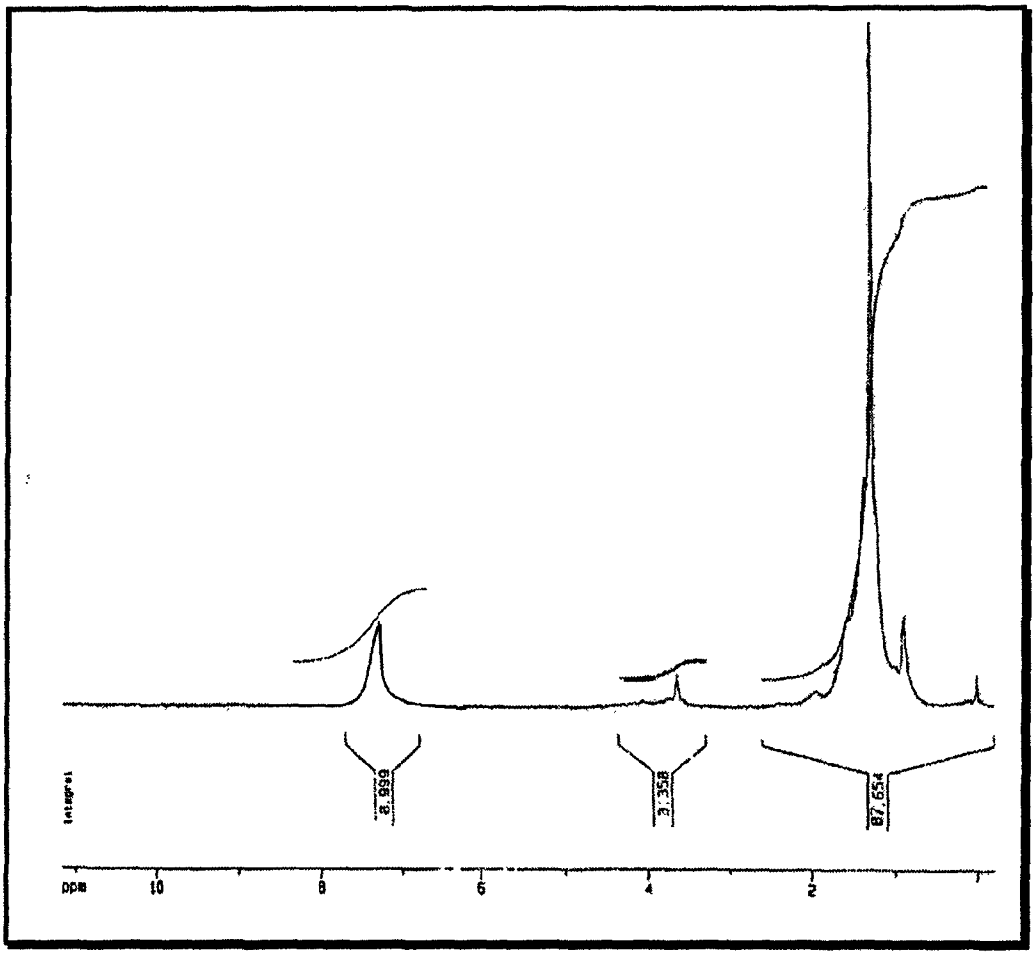


Fig.(3.13): ^{1}HNMR Spectrum of the prepared compound (B).

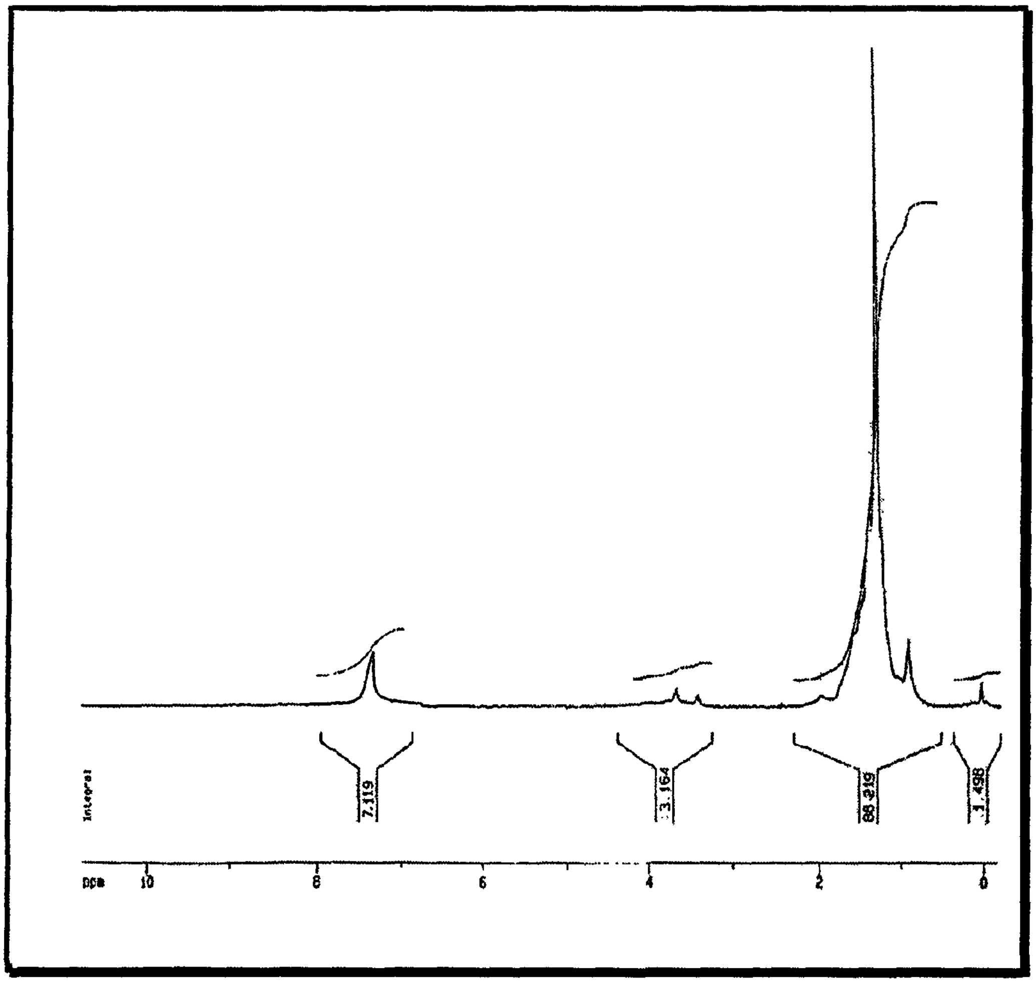


Fig.(3.14): ^{1}HNMR Spectrum of the prepared compound (C).

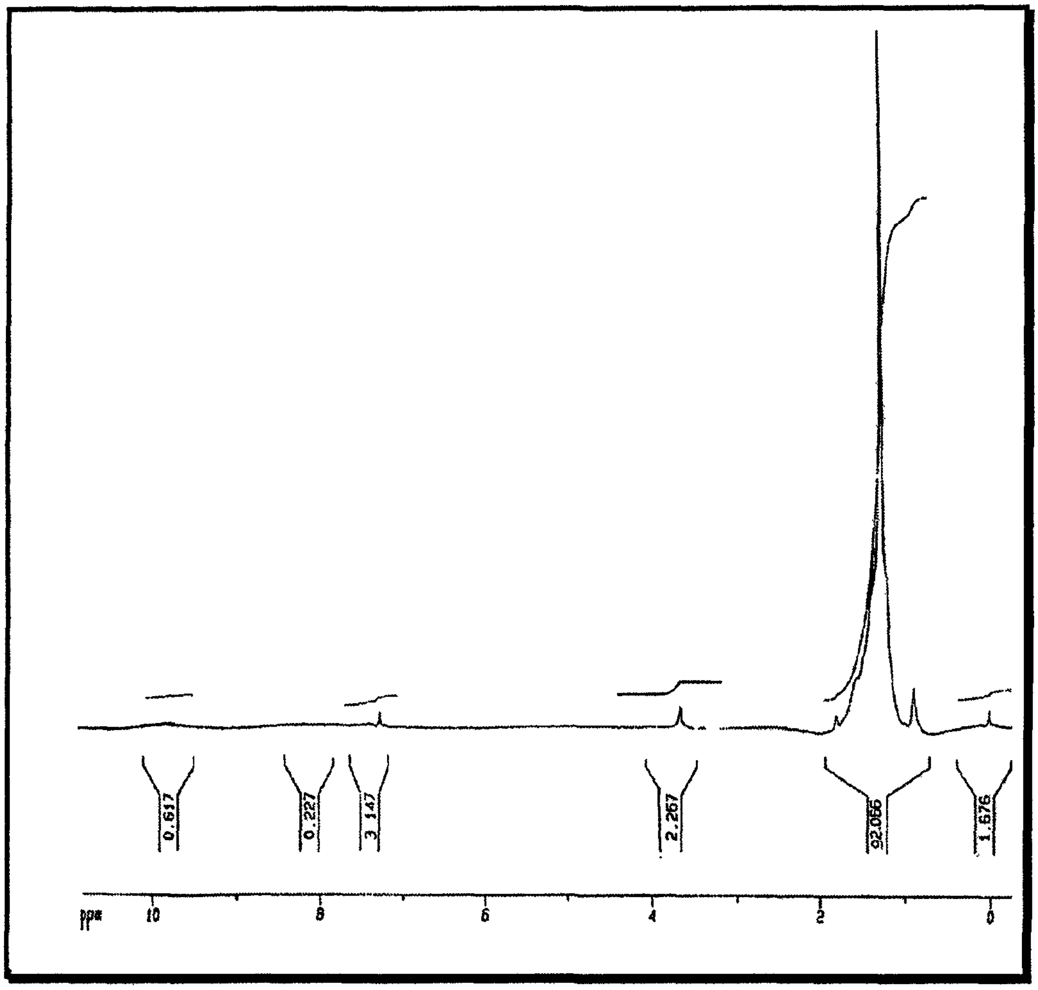


Fig.(3.15): ^{1}HNMR Spectrum of the prepared compound (D).

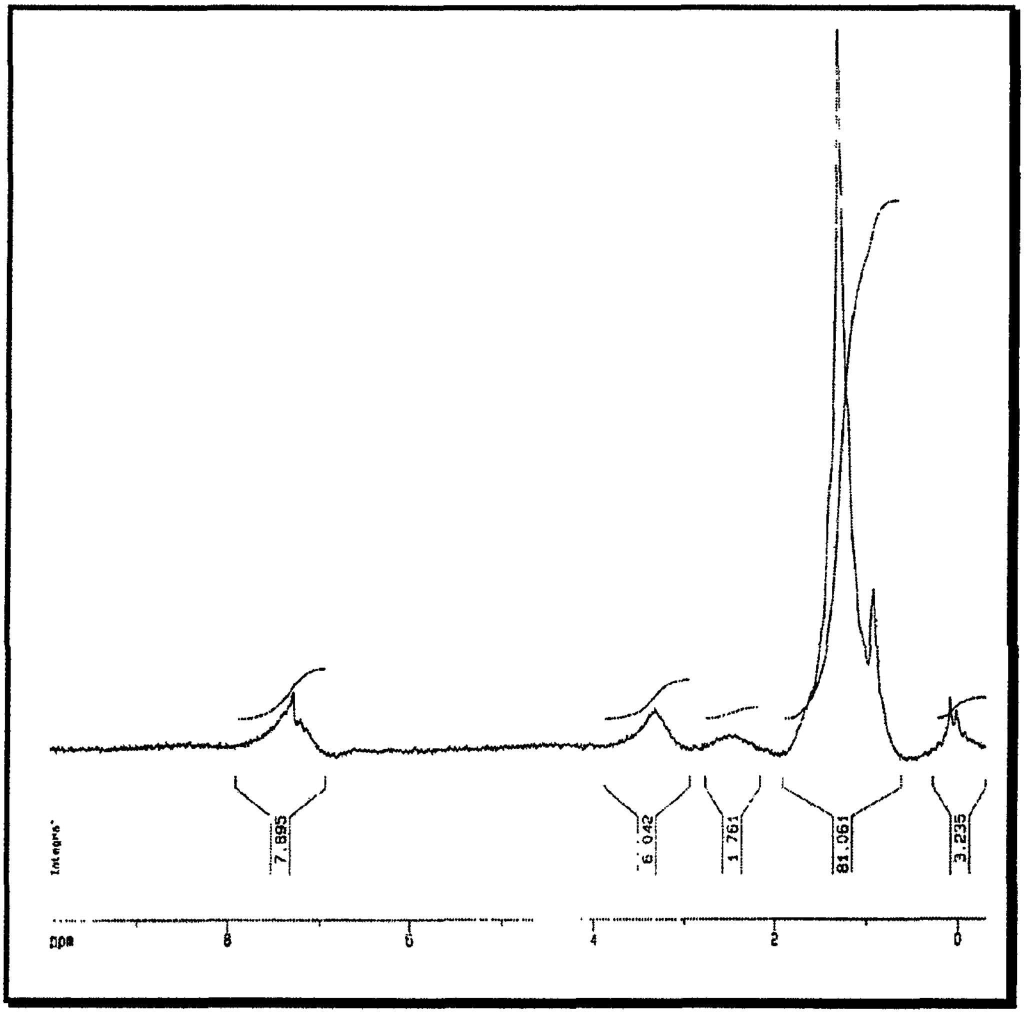


Fig.(3.16): ^{1}HNMR Spectrum of the prepared compound (E).

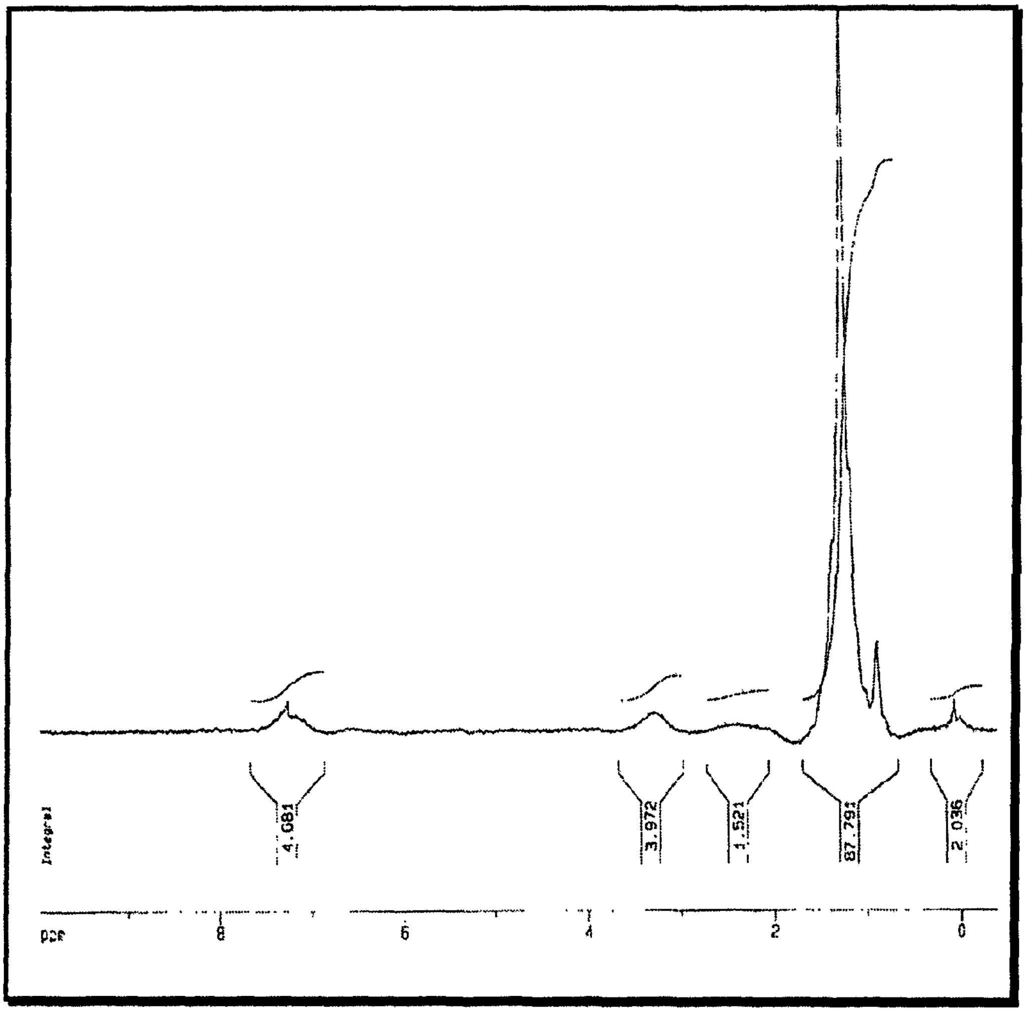


Fig.(3.17): ^{1}HNMR Spectrum of the prepared compound (F).

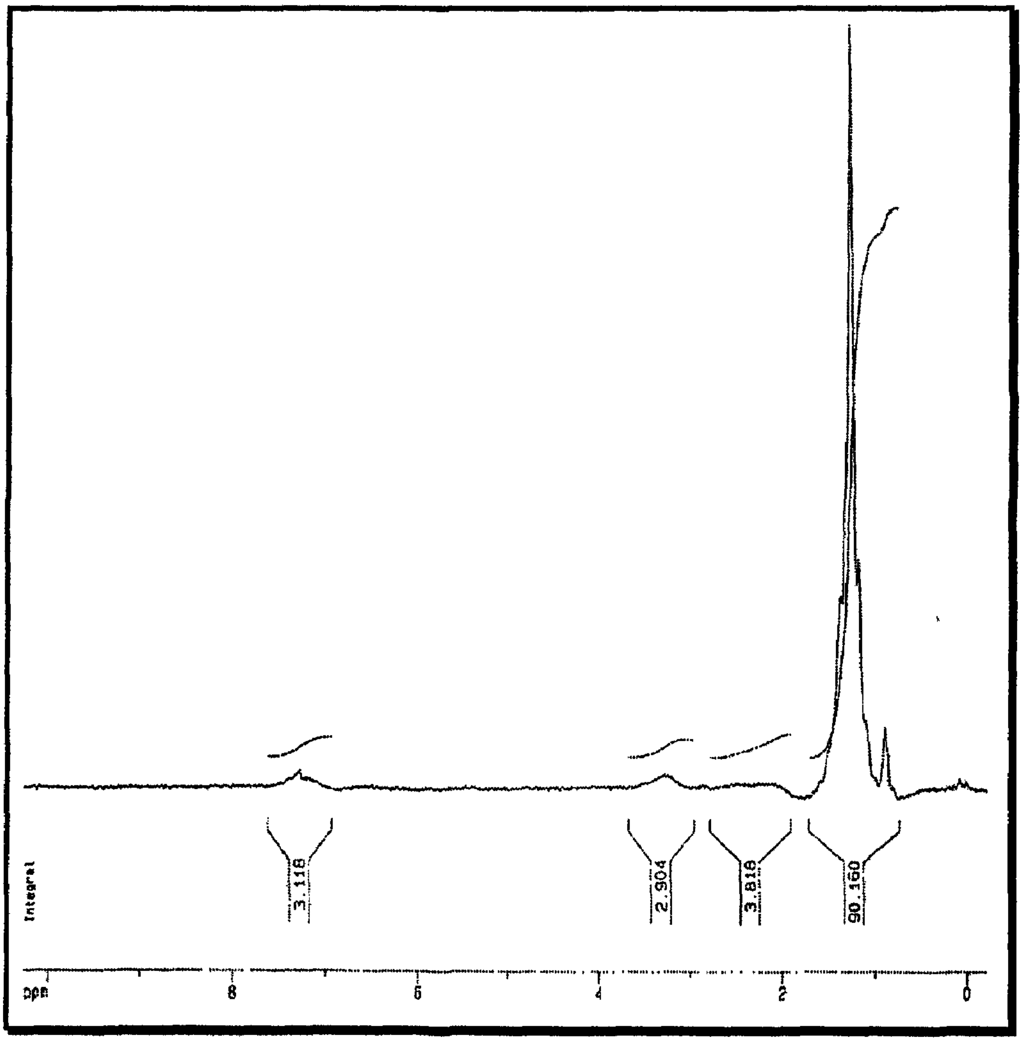


Fig.(3.18): ^{1}HNMR Spectrum of the prepared compound (G).

Table (3.3) Percentage of esterification and amidation of prepared copolymers:

Prepared Copolymer	**% Of Esterification**	**Prepared Copolymer**	**% Of Amidation**
A	93	**E**	100
B	100	**F**	100
C	93	**G**	100
D	60		

3.2. PREPARATION OF OCTADECENE-MALEIC ANHYDRIDE COPOLYMER

The copolymer of octadecene-maleic anhydride is alternating copolymer i.e. each monomer be more reactive towards the other species than towards its own kind. The reaction is given in Fig. (3.19).

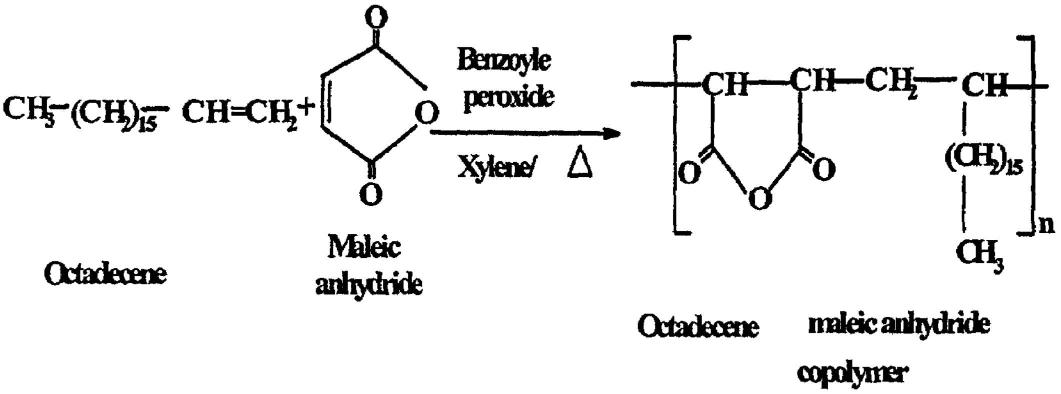


Fig. (3.19): Preparation of octadecene-maleic anhydride copolymer

The I.R. spectra of octadecene-maleic anhydride copolymer in Fig. (3.20) which indicate the presence of the same two peaks of anhydride at 1773 cm^{-1} and at 1850 cm^{-1}, octadecene-maleic anhydride copolymer indicates the presence of the peak at 2884 cm^{-1} characteristics of CH_3CH_2- group.

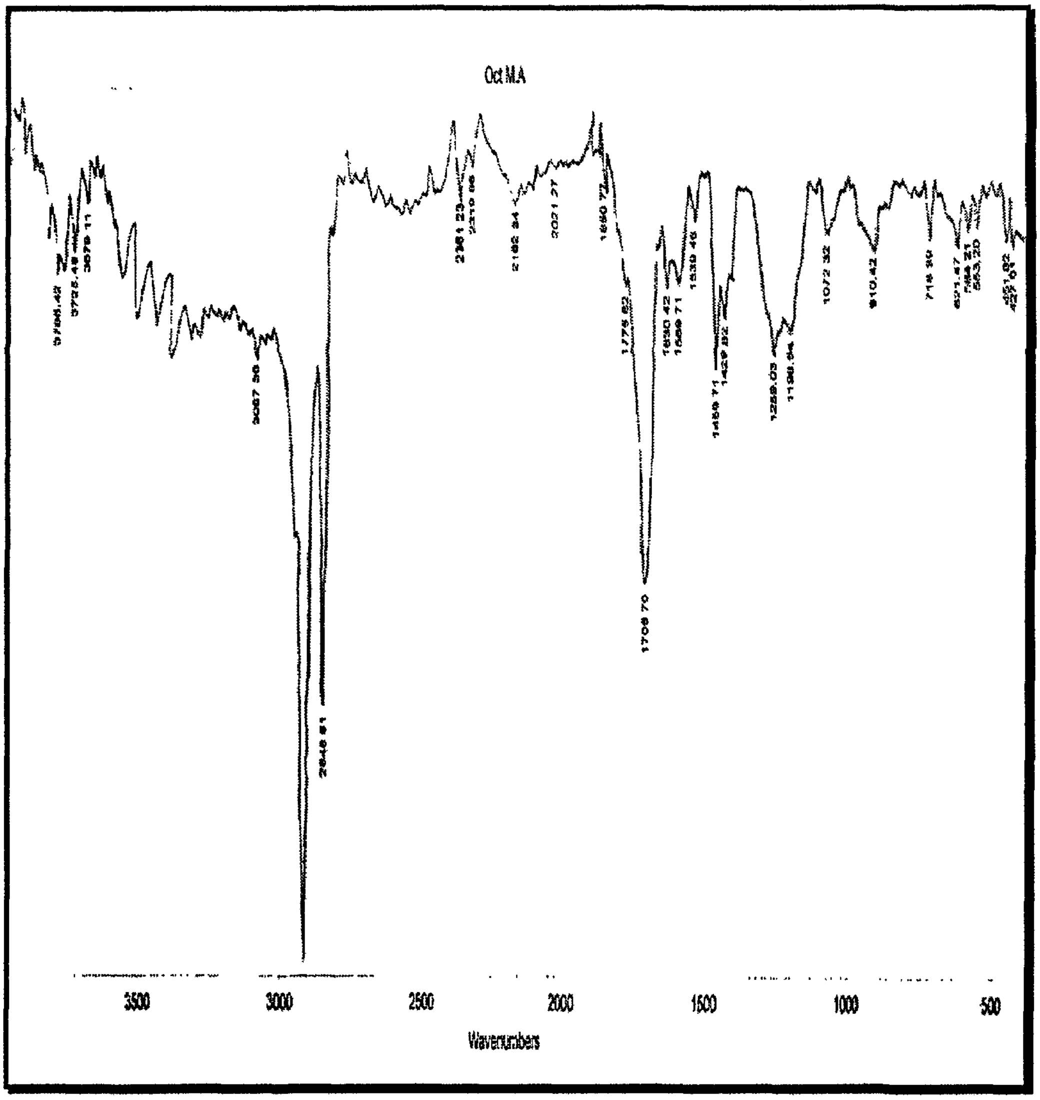
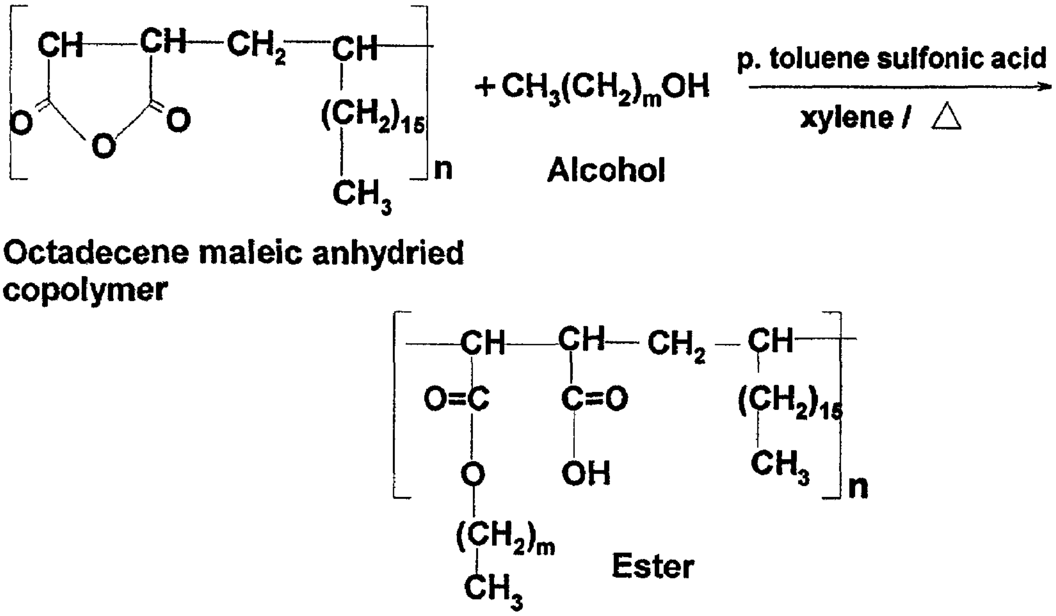


Fig. (3.20): I.R.Spectrum of the prepared compound octadecene-maleic anhydride copolymer

3.2.1. Esterification of Octadecene-Maleic Anhydride Copolymer

Four different compounds were prepared by esterification of octadecene-maleic anhydride copolymer with different alcohols, the reaction is given in Fig. (3.21).



m= 11, 15, 17 and 21.

Fig. (3.21): Esterification of octadecene-maleic anhydride copolymer

The I.R. spectra of esters (L–O) are identical; and given in Figs. (3.22) - (3.25), the spectrum of compound (L) is represented in Fig. (3.22) which indicate the presence of the peak at 1732 cm^{-1} characteristics of C=O of the ester group, the presence of broad band at 3404-3589 cm^{-1} characteristics of-OH ,the presence of peak at 2852 cm^{-1} and characteristics of CH_3CH_2- group, the presence of the peak at 1261 cm^{-1} characteristics of CO of acid group and disappear of two bands of anhydride which appear at 1790 cm^{-1} and 1870 cm^{-1}. This is indicating that the esterification reaction was carried out successfully.

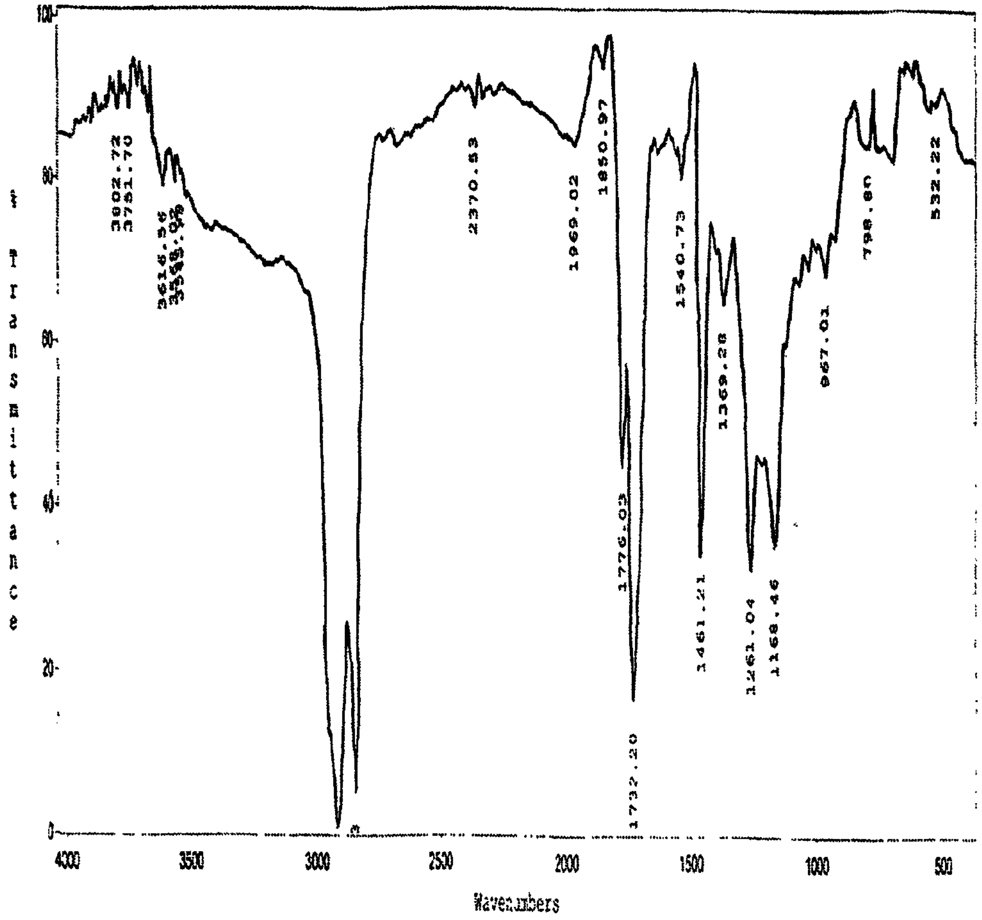


Fig. (3.22): I.R.Spectrum of the prepared compound (L).

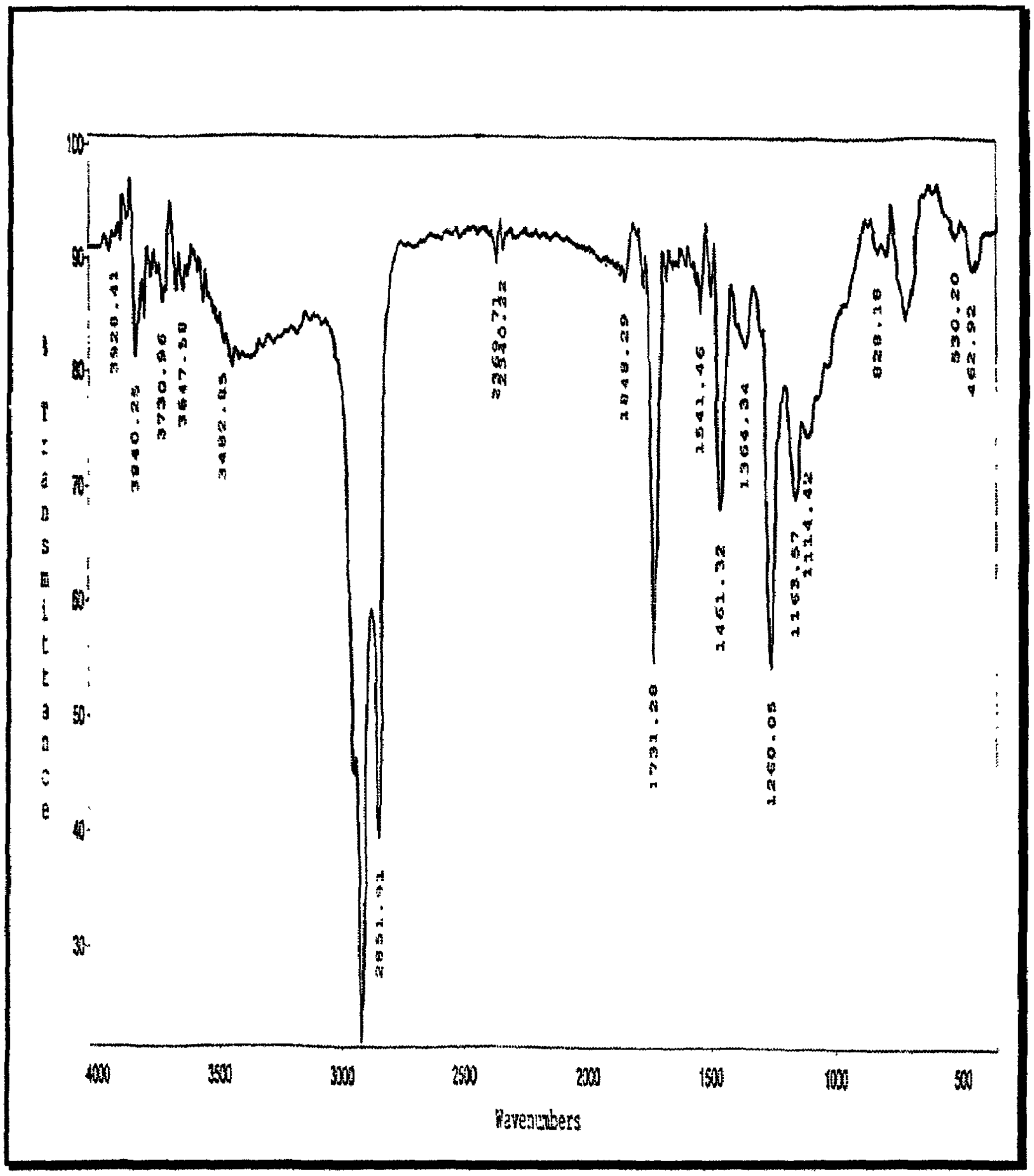


Fig.(3.23): I.R.Spectrum of the prepared compound (M).

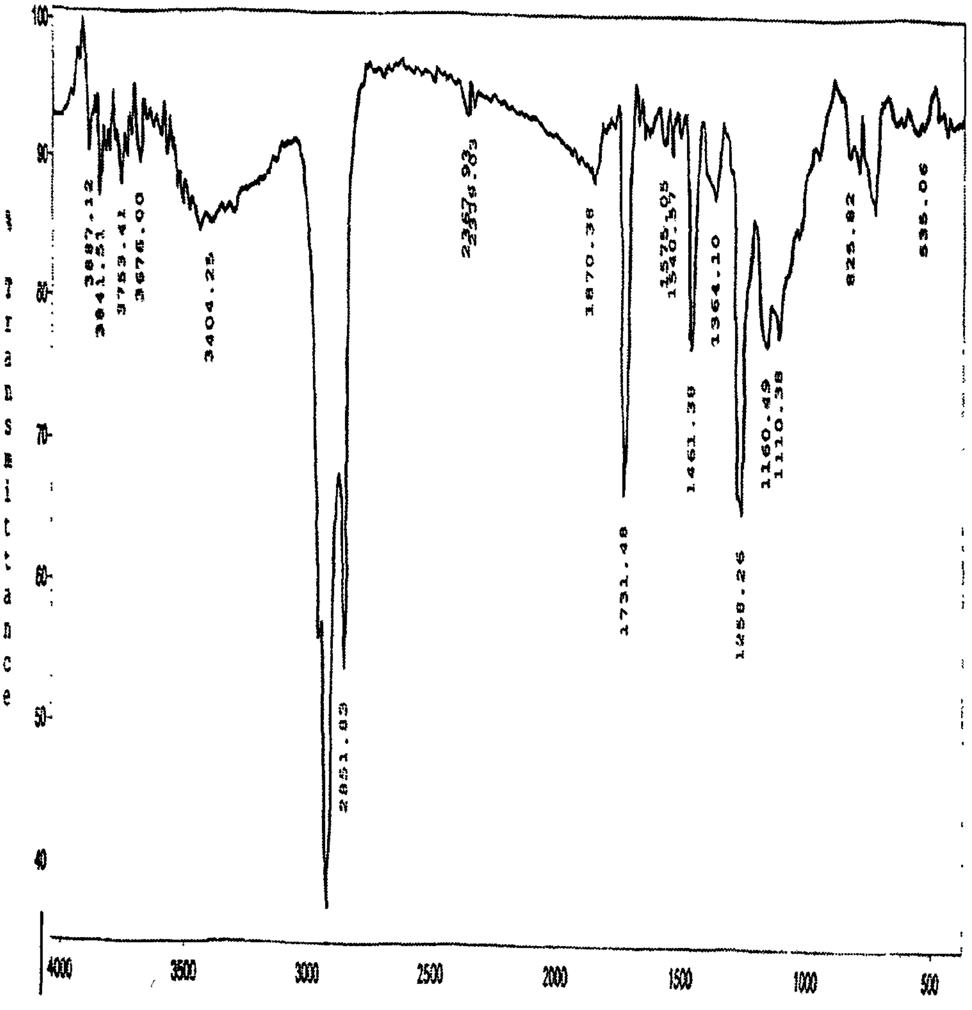


Fig.(3.24): I.R.Spectrum of the prepared compound (N).

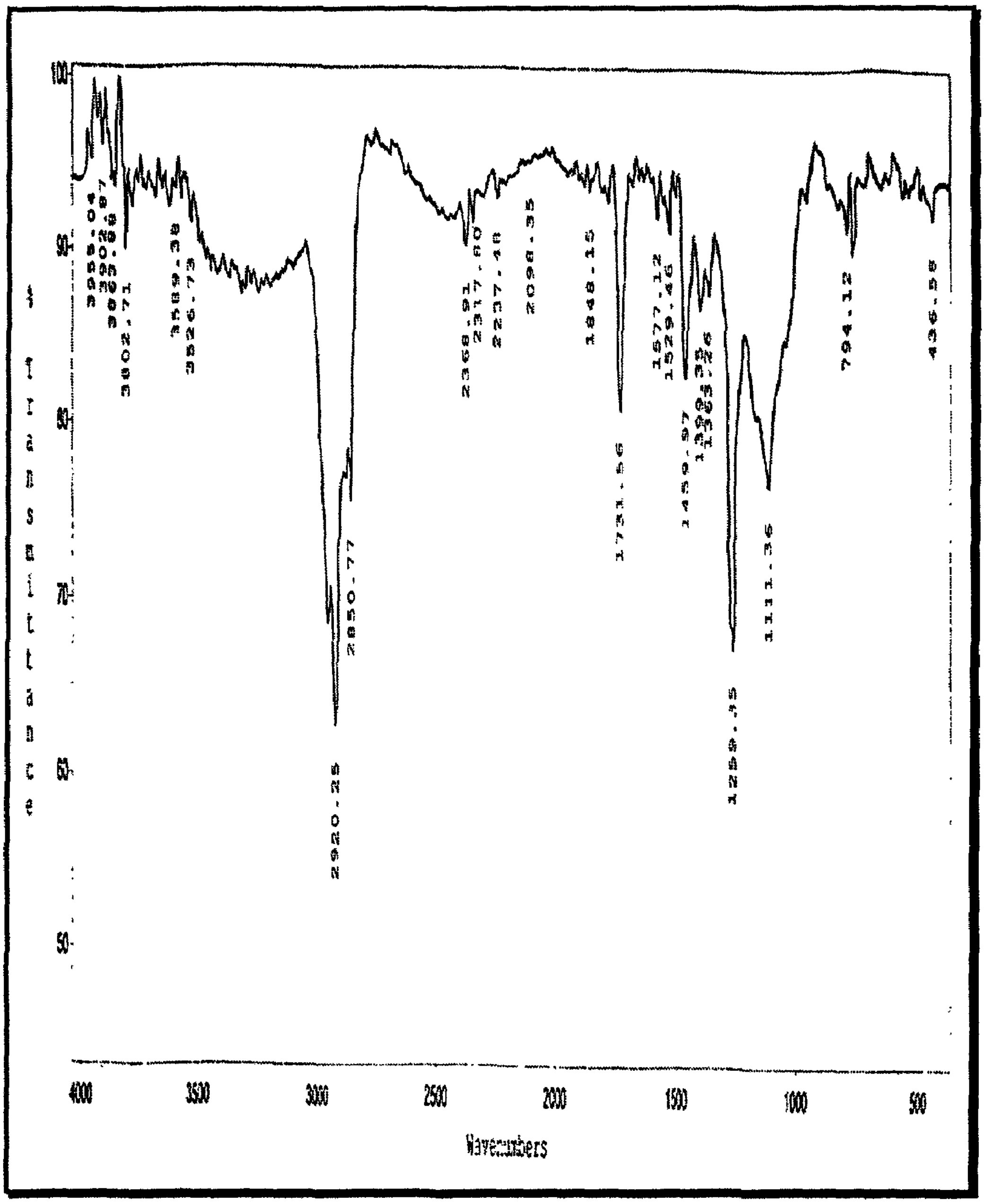


Fig.(3.25): I.R.Spectrum of the prepared compound (O).

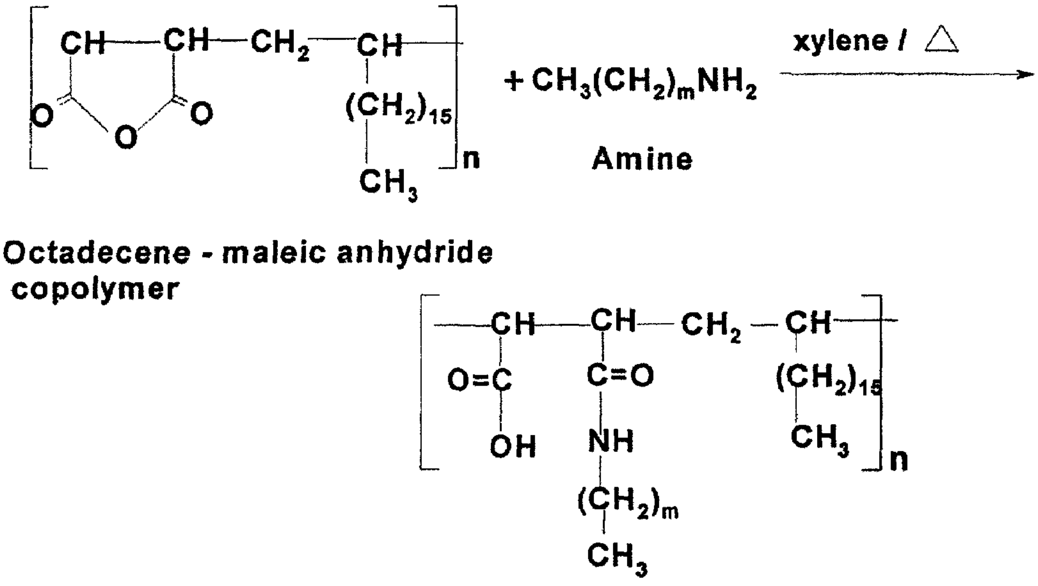
The mean molecular weight of the prepared copolymers were determined and given in Table (3.4)

Table (3.4): The mean molecular weights of copolymers

Copolymer designation	Mean molecular weight	Copolymer designation	Mean molecular weight
Octadecene-maleic anhydride copolymer	43 363	L	66 464
		M	55 056
		N	76 880
		O	55 883

3.2.2. The reaction of Octadecene-Maleic Anhydride Copolymer with Different Amines

Three different compounds were prepared by the reaction of octadecene-maleic anhydride copolymer with different amines, the reaction is given in Fig. (3.26).



m= 11, 15 and 21.

Fig. (3.26): The reaction of styrene-maleic anhydride copolymer with different amines

The I.R. spectra of amide (R-T) are identical are given in Figs. (3.27) - (3.30), and the spectrum of (R) is in Fig. (3.27) represented which indicate the presence of C=O of amide at 1640 cm^{-1}, the presence of two peaks at 2851 cm^{-1} characteristics of CH_3CH_2- group, the presence of the peak at 1261 cm^{-1} characteristics of CO of acid group ,the presence of abroad band at 3300-3500 cm^{-1} due to the presence of –NH and –OH group and disappear of two bands of anhydride which appear at 1790 cm^{-1} and 1870 cm^{-1} . This indicates that the amidation was carried out.

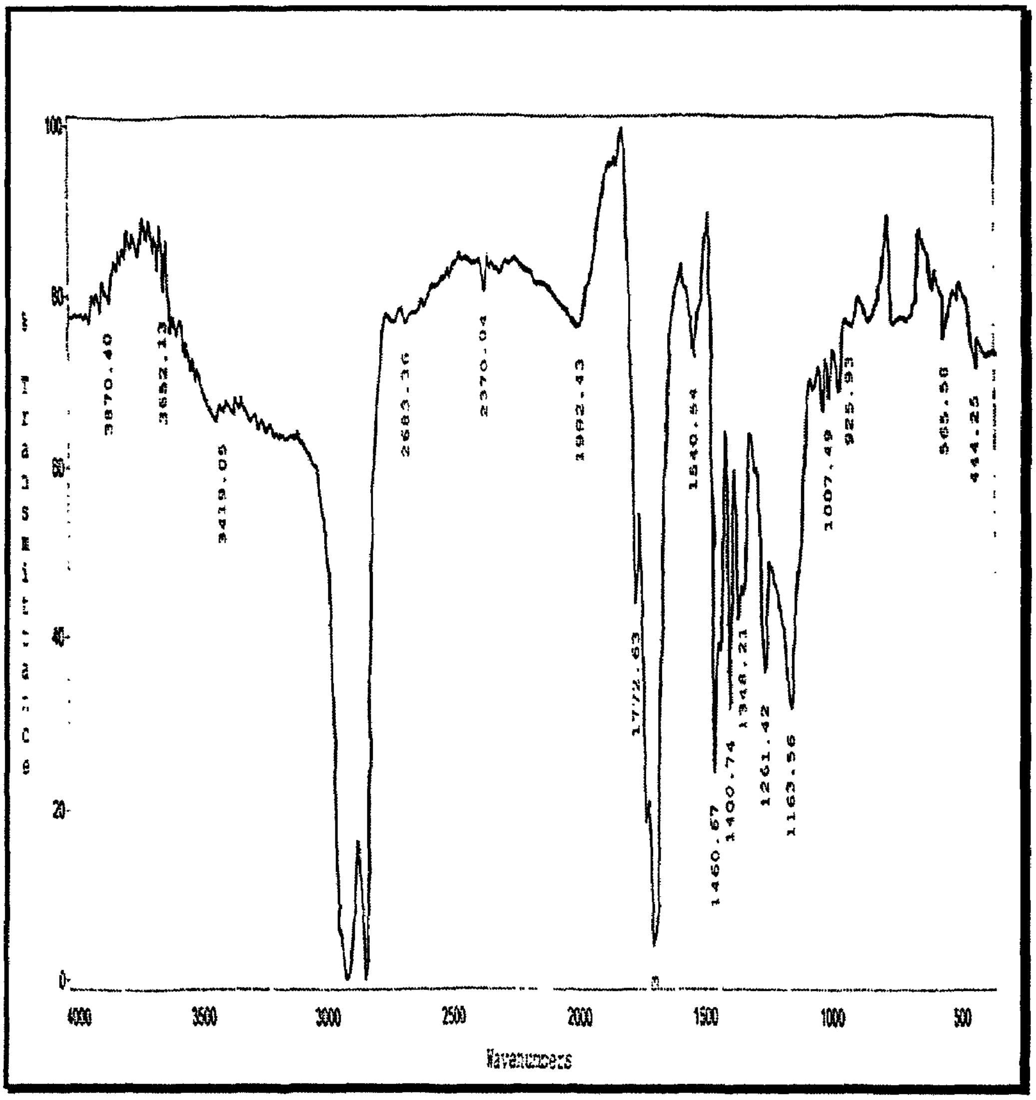


Fig. (3.27):I.R.Spectrum of the prepared compound (R).

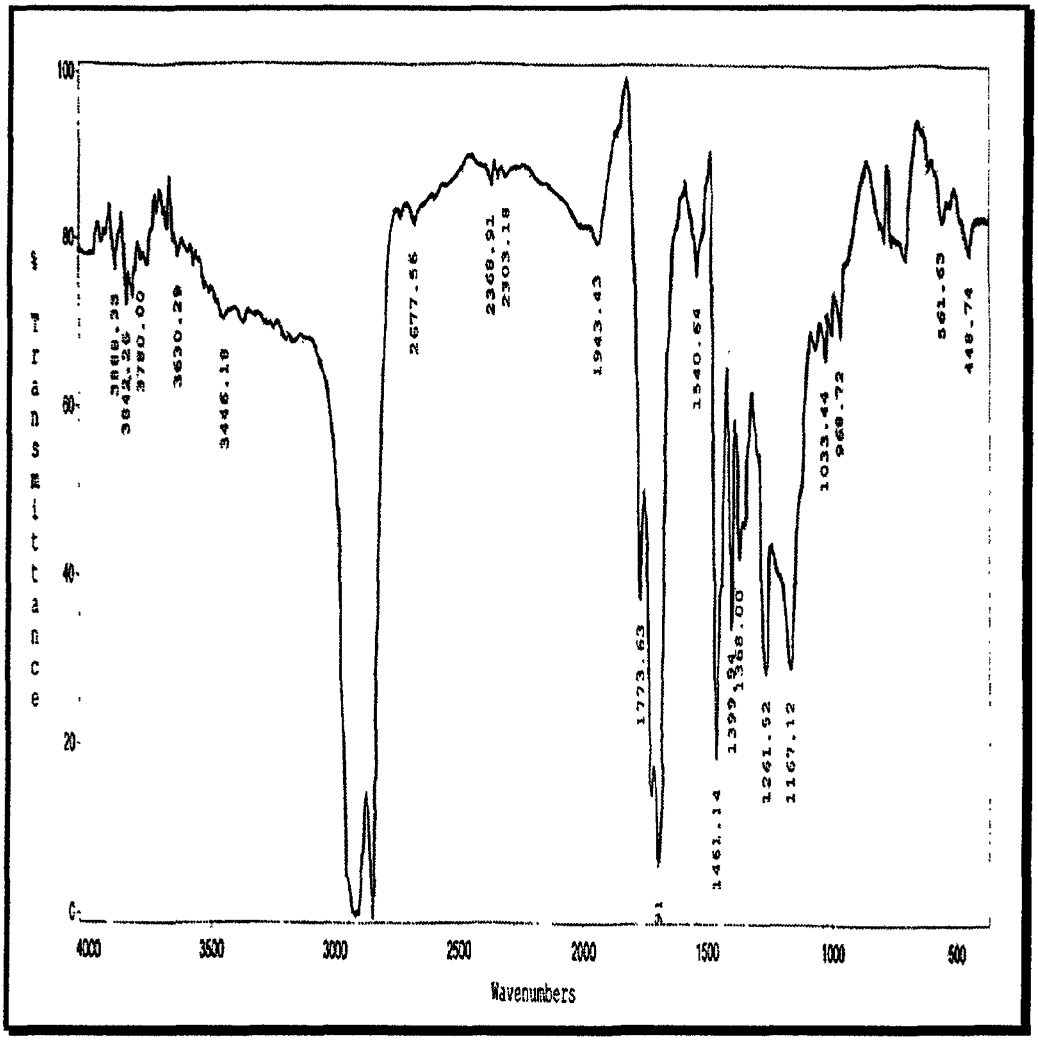


Fig. (3.28): I.R.Spectrum of the prepared compound (S).

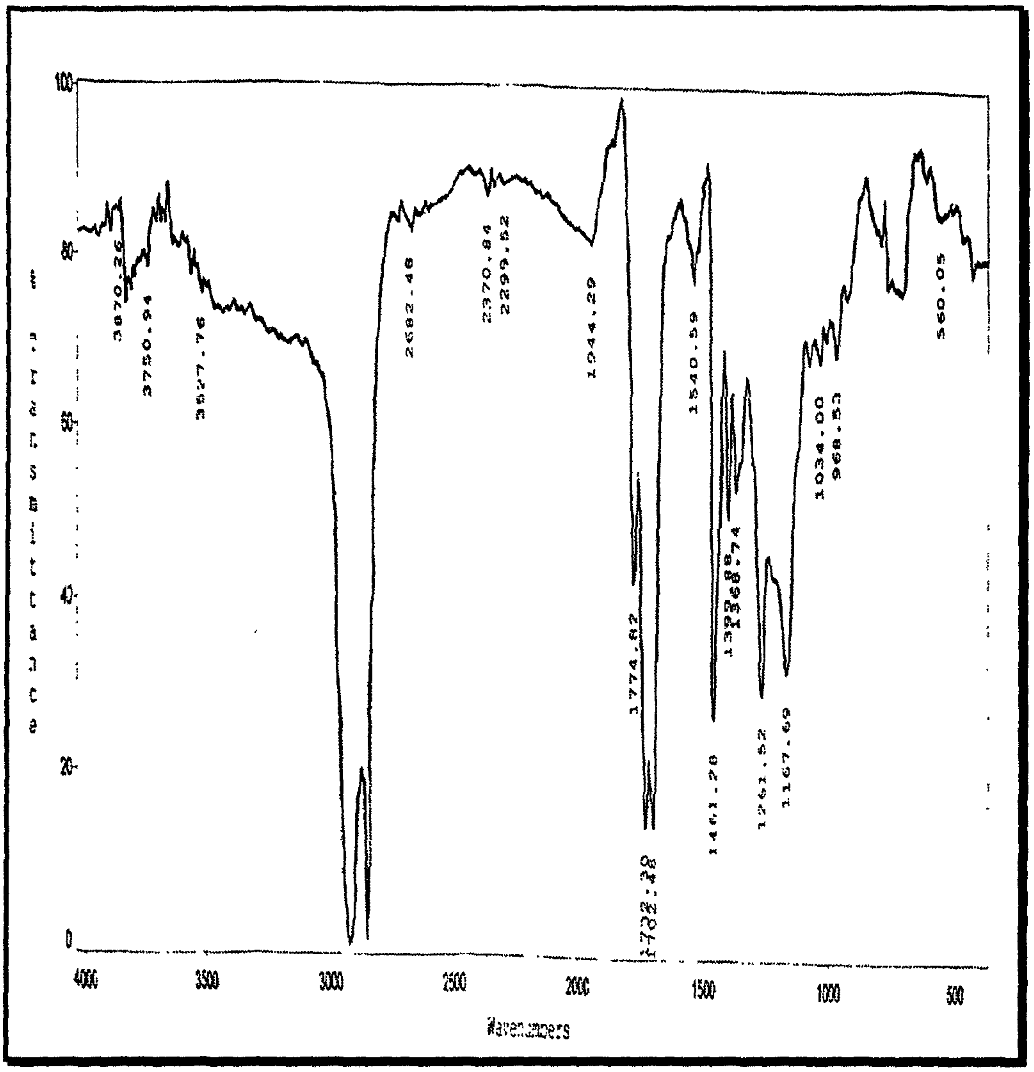


Fig.(3.29): I.R.Spectrum of the prepared compound (T).

The mean molecular weights of the prepared copolymers were determined and given in Table (3.5) which indicates that the molecular weight increases by increasing the alkyl chain length of the amine used.

Table (3.5): The mean molecular weights of copolymers

Copolymer designation	**Mean molecular weight**	**Copolymer designation**	**Mean molecular weight**
Octadecene -maleic anhydride copolymer	43 363	**R** **S** **T**	66 340 73 284 76 756

The esterification and amidation percentage can be calculated from ^{1}HNMR analysis as Figs. (3.30) - (3.36). This was obtained by comparing the integration ratios of two signals. In this respect, the signal at 3.8 ppm (which assigned to O-CH_2 or N-CH groups) and the signal at 1.5-2 ppm (Which assigned to aliphatic protons) were selected to determine the esterification and amidation of octadecene-maleic anhydride copolymer.

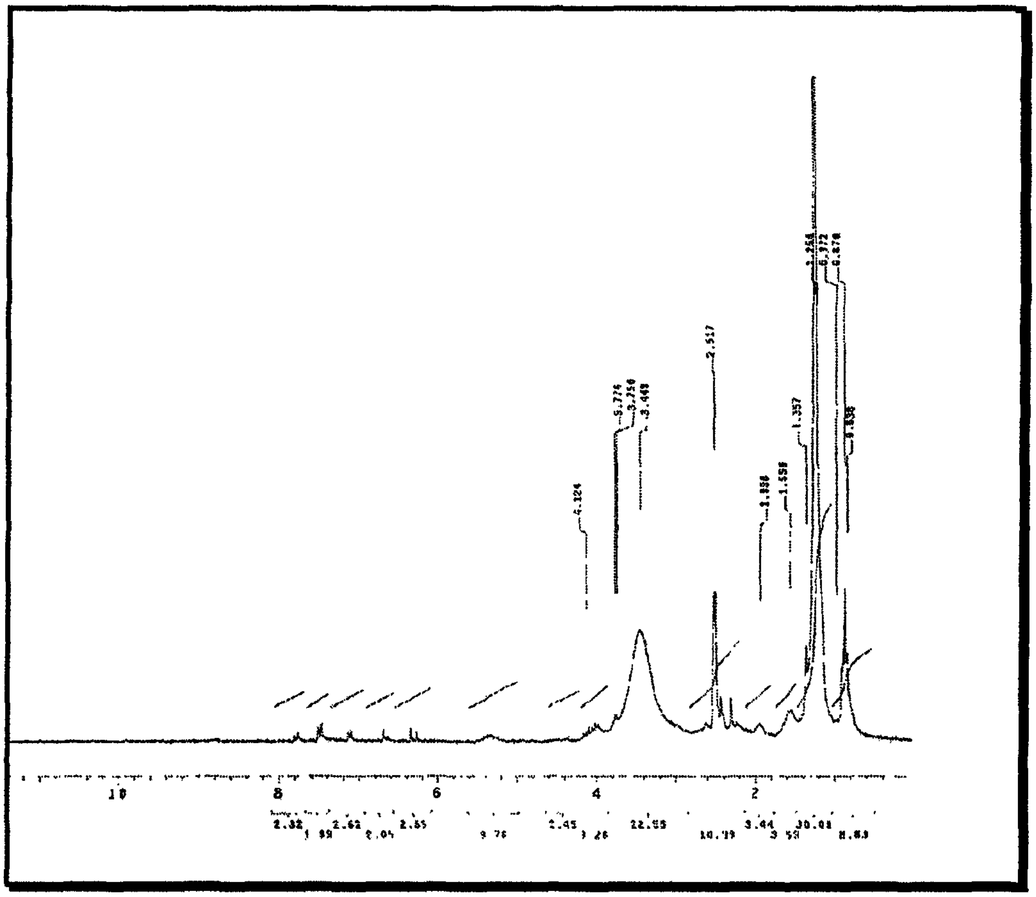


Fig.(3.30): ^{1}HNMR Spectrum of the prepared compound (L).

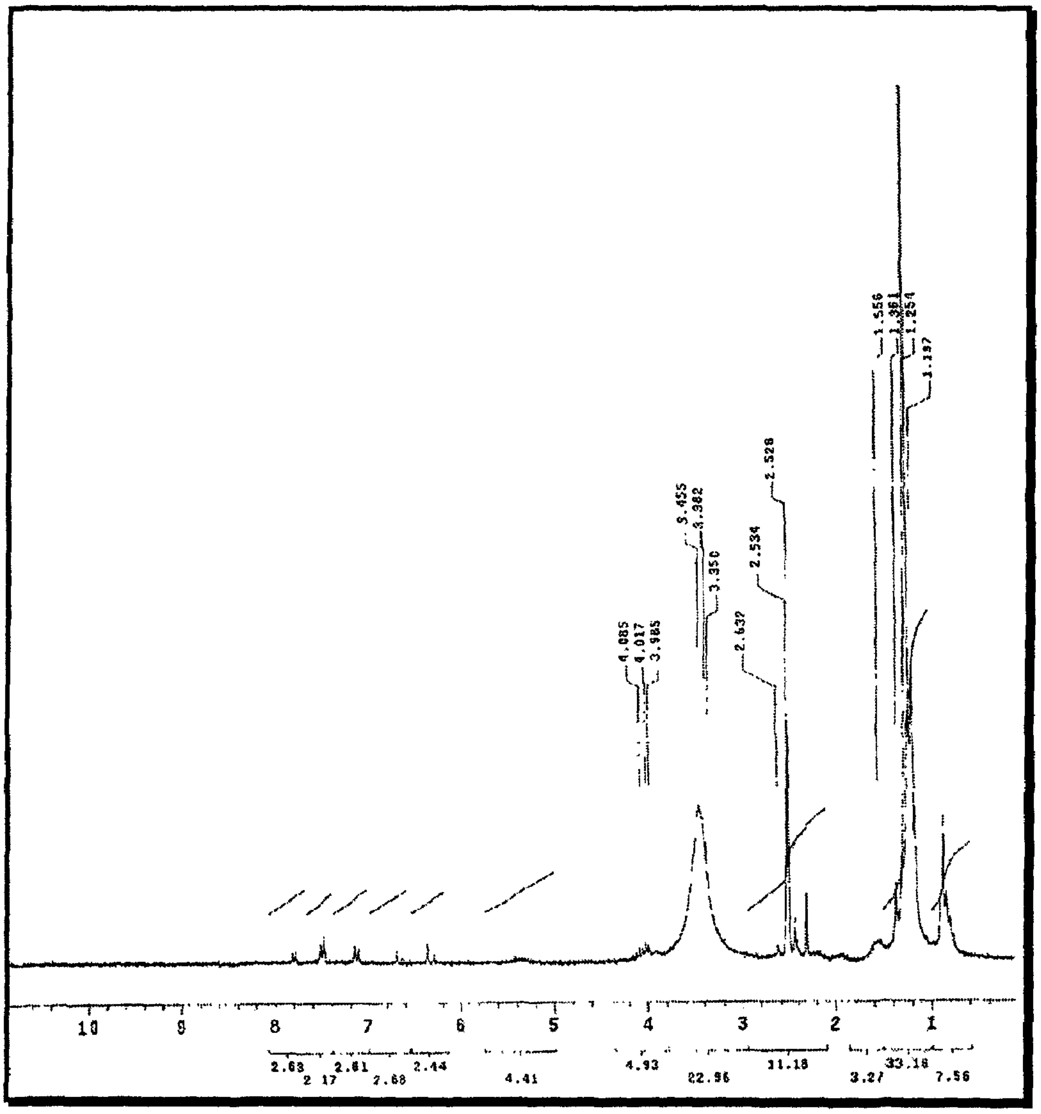


Fig.(3.31): ^{1}HNMR Spectrum of the prepared compound (M).

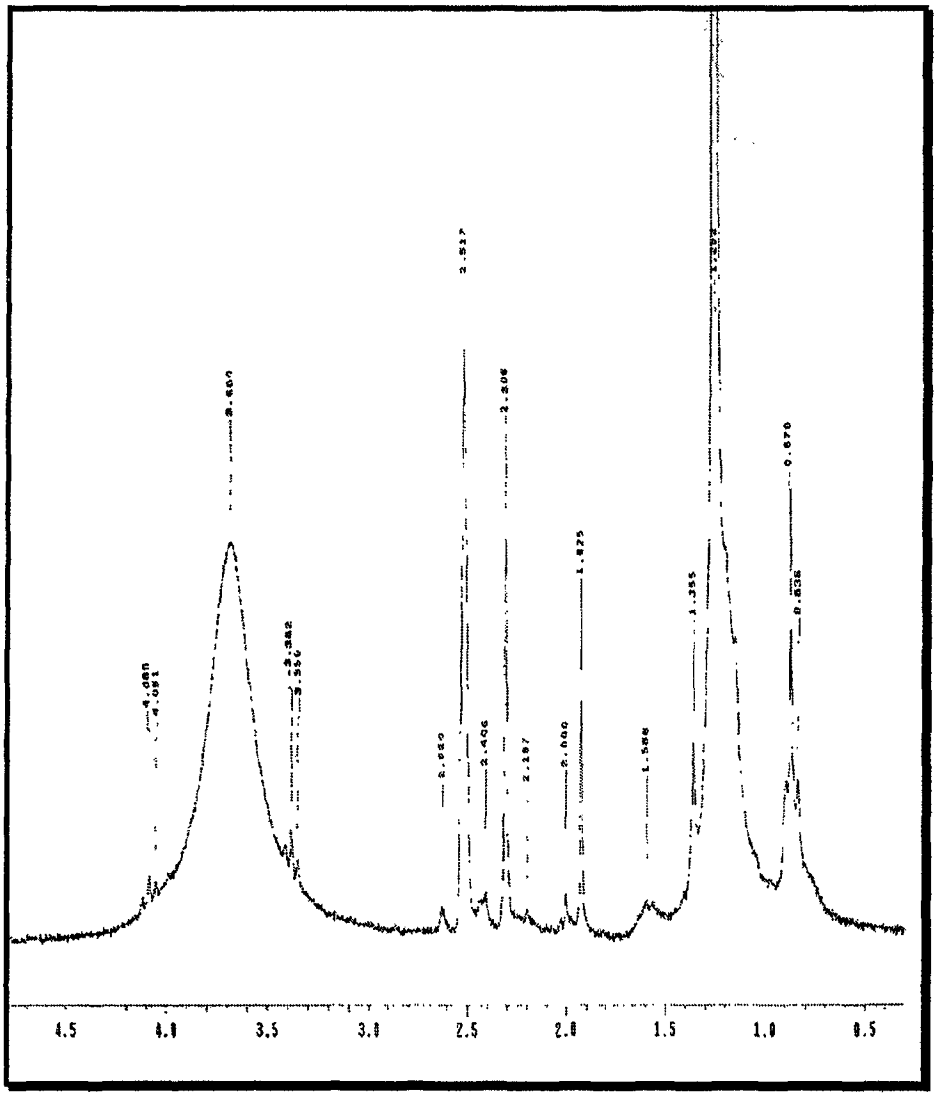


Fig.(3.32): ^{1}HNMR Spectrum of the prepared compound (N).

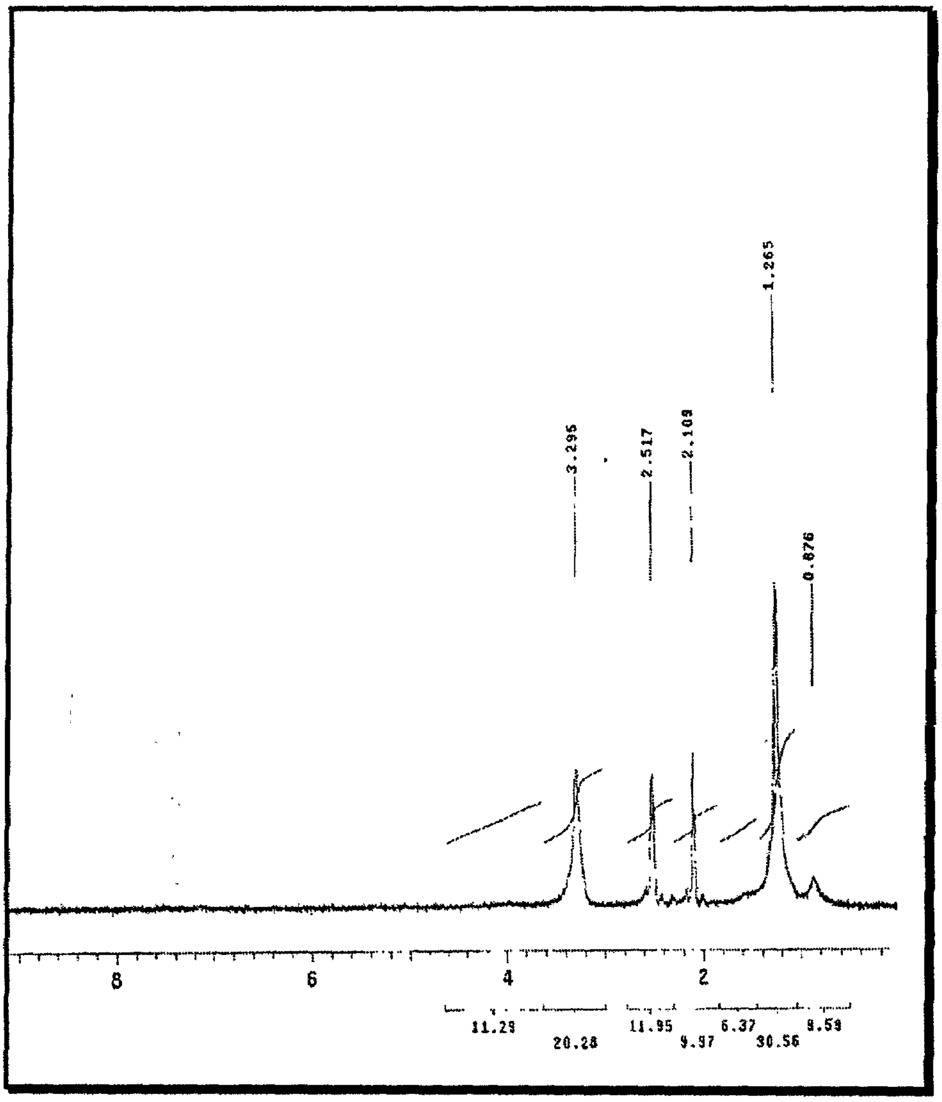


Fig.(3.33): ^{1}HNMR Spectrum of the prepared compound (O).

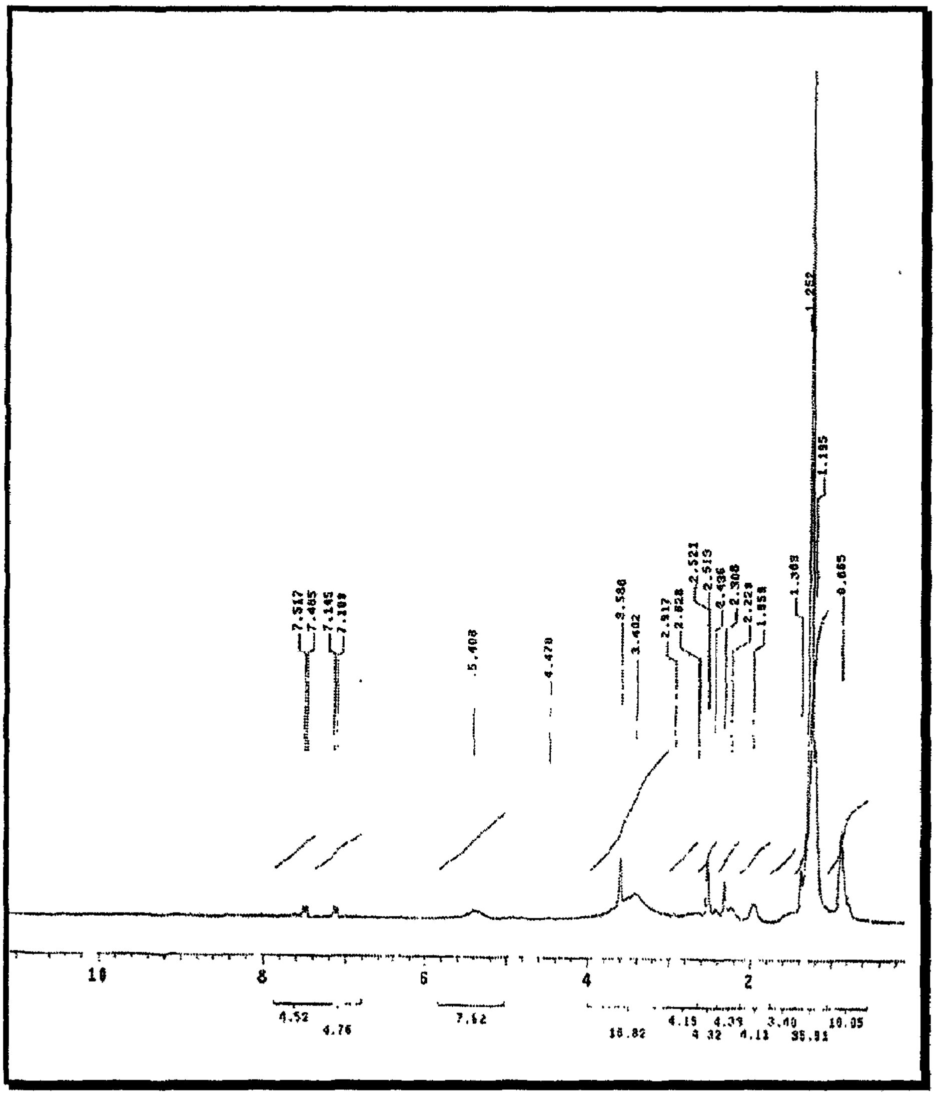


Fig.(3.34): ^{1}HNMR Spectrum of the prepared compound (R).

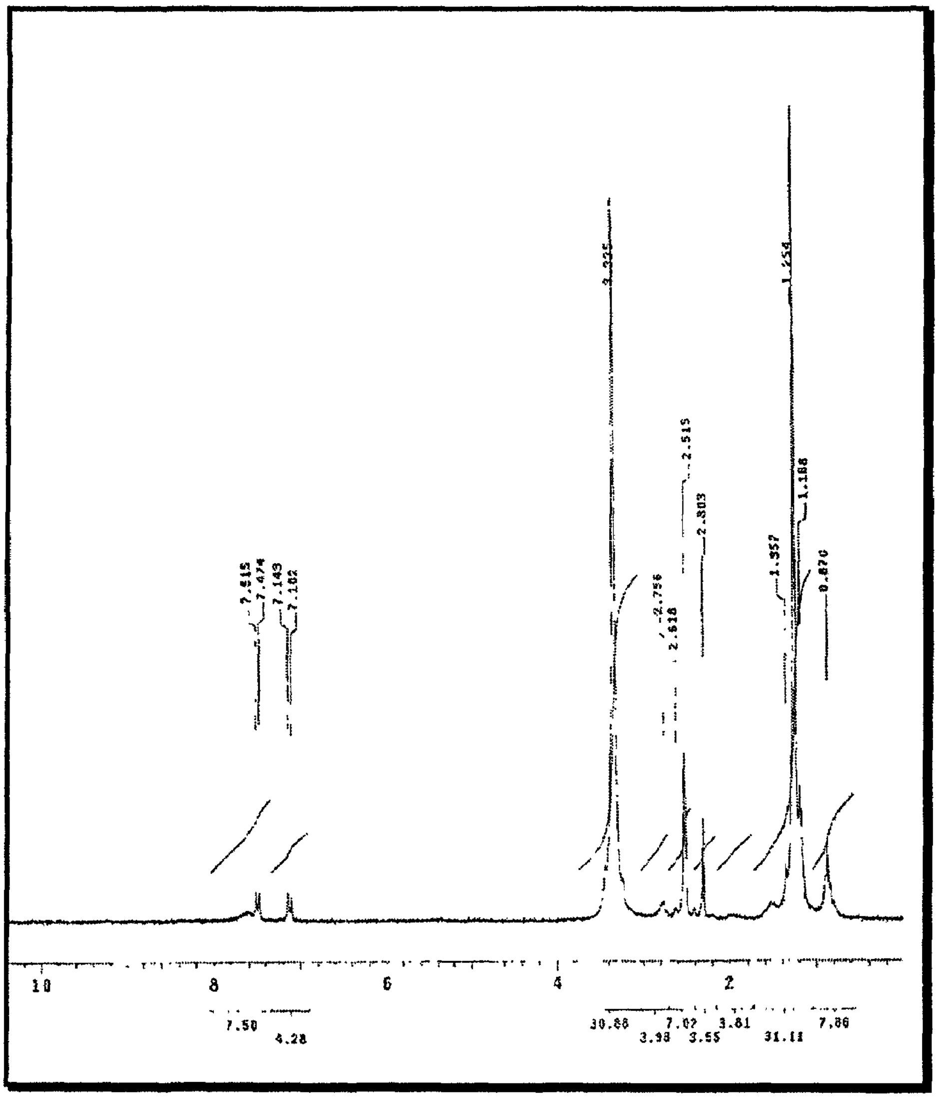


Fig.(3.35): ^{1}HNMR Spectrum of the prepared compound (S).

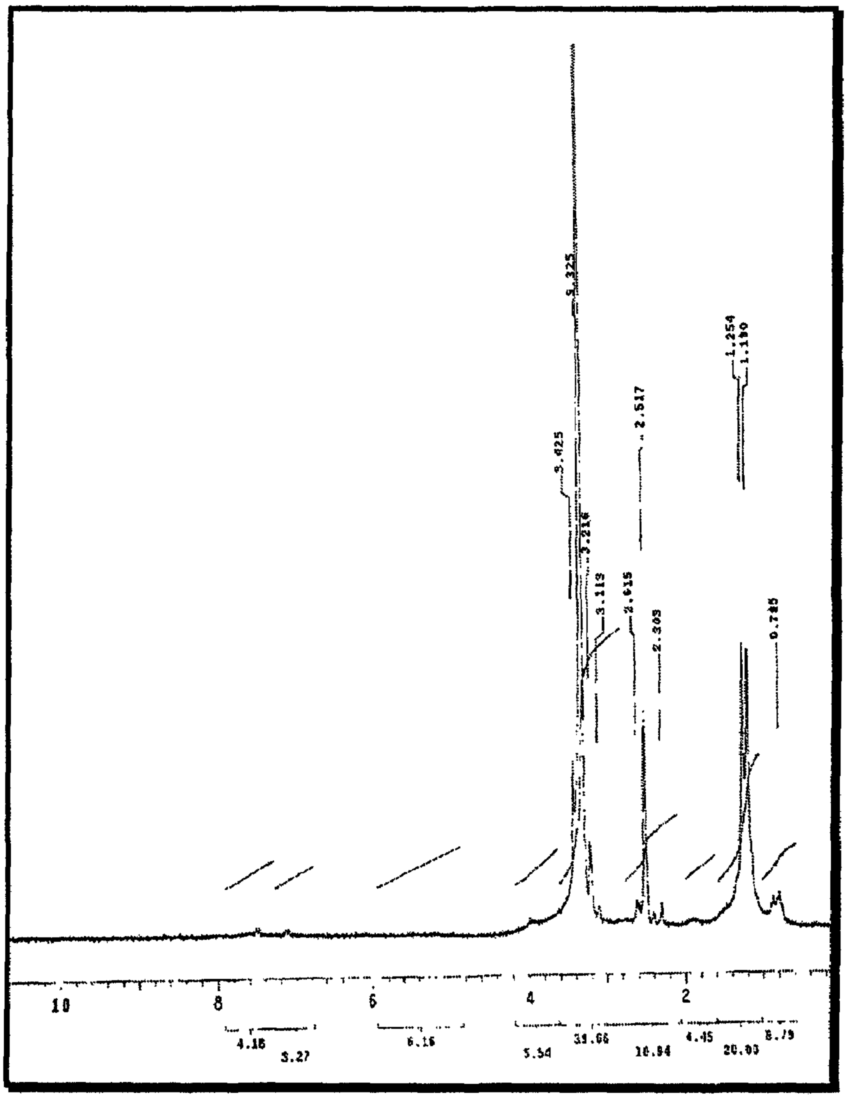


Fig.(3.36): ¹HNMR Spectrum of the prepared compound (T).

The integral values derived from these spectra were calculated and percentage of esterification and amidation given in Table (3.6).

Table (3.6) Percentage of esterification and amidation of prepared copolymers:

Prepared Copolymer	**% Of Esterification**	**Prepared Copolymer**	**% Of Amidation**
L	100	**R**	100
M	75	**S**	100
N	100	**T**	100
O	67		

3.3. SOLUBILITY OF THE COPOLYMERS IN THE SAE- 30 BASE OIL

The solubility of the prepared copolymers in the base oil was investigated according to the method described in chapter (II). The solubility test was carried out to determine which of the prepared copolymers will be tested as viscosity index improvers, pour point depressants and dispersants.

Dissolution is a particular case of dispersion of one component in another. With respect to dispersity, the true solutions are dispersed systems in which the components may be dispersed down to molecules, atoms or ions; hence, a true solution is molecularly dispersed system which has affinity between components, spontaneous formation, and constant concentration in time, homogeneity and thermodynamic stability.

Like low molecular- mass substances, polymers do not dissolve in all liquids. A given polymer will dissolve in some liquids when it comes in direct contact with them but shows no sign of dissolving in others. However, true solutions of polymers have their specific features [Gomez et. al., 1992], which distinguish them from true solutions of low molecular mass substances. These include swelling prior to dissolving, high viscosity, slow diffusion, and inability to pass through semi permeable membranes. These features are due to the great difference in size between the particles of the mixed components. The dissolution of a polymer is a slow process, which occurs in two stages, first, solvent molecules slowly diffuse into the polymer producing swollen gel, and the second stage of solution is the disintegration of the gel into a true solution due to the interaction between the polymer molecules and those of solvent.

The disintegration of the gel can be materially speeded by agitation. The solution process can be quite slow (days or weeks) for polymers of very high molecular mass. The solution process may be termined after the first stage, if the polymer intermolecular forces are high because of cross linking, crystallinity or strong hydrogen bonding.

The rate of dissolution of a polymer depends primarily on how rapidly the polymer and the solvent diffuse into one another. Solvent that promotes rapid solubility are usually small, compact molecules, but these kinetically good solvents need not be thermodynamically good as well. To test the homogeneity and thermodynamic stability the viscosity of five different samples from each solution was measured. For the true solutions, the viscosity test affords constant values and the copolymer was considered to be dissolved molecularly in the base oil. The dissolution results reveal that all the prepared copolymers are dissolved molecularly in the base oil to form true solutions. Accordingly, all the prepared copolymers were considered as VI, PP and dispersant evaluation.

3.4. FUNCTION AND EVALUATION OF THE PREPARED COPOLYMERS AS VISCOSITY INDEX IMPROVERS

Viscosity is one of the most important and visible properties of a fluid. Consumers initially judge the quality of motor oil by it. A proper viscosity is certainly important for motor oils, hydraulic fluids, automatic transmission fluids, gear oils and greases. Resistance to wear, deposit formation, pour ability and the ease of starting a cold engine are all influenced by the viscosity of the lubricant [Pourhossaini et. al., 2005].

Modern lubricants, especially motors oils, contain polymeric additives which modify the viscosity characteristics of the lubricants. These additives are called viscosity modifiers [Rundnick, 2003].

Viscosity modifiers, or viscosity index improvers as they are also known, provide an economical enhancement of lubricant performance benefiting engine life and fuel economy just to name a few of their many attributes. Without these specialized oil soluble polymers, today's high performance multigrade lubricants would not be possible. The majority of today's lubricants and certainly all of tomorrow's will be required to operate in a wide range of conditions that demand performance not possible without viscosity index improvers [Breon et. al., 1992].

When a high molecular weight compound (a polymer) is dissolved in a fluid, the viscosity of the fluid increases. The degree of increase, however, is greater at high temperatures than at low temperatures. Thus, the polymer minimizes the viscosity change caused by temperature. A polymer used for minimizing the viscosity change with temperature is called viscosity index improver or viscosity modifier [Stephen, 2004].

A polymer molecule is expressed schematically as a long piece of string which freely bends and stretches. In solution it exists as a random coil and is associated with solvent molecules. When a polymer is dissolved in a fluid, the viscosity of the fluid increases. The degree of the increases depends on the volume occupied by the polymer molecules and associated solvent in solution. This volume is known as the hydrodynamic volume of the polymer. Hydrodynamic volume is a function of (1) the size of polymer molecule, (2) the chemical structures of polymer and solvent molecules, (3) temperature, (4) the rate of shear and (5) pressure [Pawlak, 2001].

The hydrodynamic volume of a viscosity modifier in an oil increases with an increase in temperature because polymer molecules normally extend and associate more with the solvent molecules at high temperatures. Thus, the oil thickening ability of the polymer increases with increasing temperature. The viscosity of a fluid always decreases with increasing temperature and the polymer in the fluid compensates for a part of the viscosity decrease [Breon et. al., 1992]. A viscosity index improver must be able to increase the viscosity of base fluids at high temperatures. The current SAE specifications define the high temperature viscosity as the kinematic viscosity at 100°C.

The thickening power of a viscosity index improver commonly is expressed as the viscosity increase (in cSt) caused by the addition of one weight % of the polymer dissolved in a reference fluid. It should be noted that the relationship between polymer concentration and solution viscosity is not linear [Breon et. al., 1992].

The magnitude of the decrease in viscosity from low to high shear rate depends upon the molecular weight and the chemical structure of the polymer. The viscosity of a high molecular weight polymer decreases more than a low molecular weight homologue [Breon et. al., 1992]. Viscosity index improvers should increase low temperature viscosities as little as possible. There is no straight forward way to express the low temperature viscosity performance of a viscosity index improver. However, the low temperature viscosity performance of a viscosity index can be expressed indirectly by specifying a base fluid which is needed for formulating particular multigrade oil [Breon et. al., 1992].

Even though viscosity index is not required officially for the qualification of lubricants, it is being used extensively. Viscosity index increases with increasing concentration of a viscosity index and the molecular weight of the polymer. It is also affected by the chemical structure of polymer as well as that of the base fluid. When a viscosity modifying polymer in an oil is placed under shearing stress for a period of time, it degrades. The result is a viscosity loss. Since the degradation is chemically irreversible, the loss is permanent. The polymer degradation dependent up on shearing stress, time and temperature [Breon et. al., 1992]. A viscosity index improving polymer degrade most quickly at a high shear stress or shear rate. At a given shear stress, a high molecular weight polymer loses oil thickening ability more than a lower homologue [Breon et. al., 1992].

The prepared copolymers were tested for their effectiveness as viscosity index improvers for base oil (SAE 30) according to ASTMD-2270. In this respect, the kinematic viscosity of the oil contain different concentration of the tested additives was determined at 40°C and 100°C. The data are tabulated in Tables (3.7) – (3.12).

Table (3.7): Experimental viscosity data (in cSt) for the copolymers (A- D) at 40°C and 100°C.

Conc. x10^{-3} ppm	**A**		**B**		**C**		**D**	
	40°C	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**
30.00	87.8	10.2	91	10.5	90.5	10.5	100.5	13
20.00	91	10.3	88.7	10.2	91	10.5	93.3	12
10.00	91	10.3	88.7	10.2	87.8	10.2	94.2	11.4
5.00	93.7	10.4	93.3	10.5	92.8	10.4	96.9	11
2.50	95.6	10.5	93.7	10.5	93.3	10.5	96	10.7
0.00	95.6	10.5	95.6	10.5	95.6	10.5	95.6	10.5

Table (3.8): Experimental viscosity data (in cSt) for the copolymers (E- G) at 40°C and 100°C.

Conc. x 10^{-3} ppm	E		F		G	
	40°C	100°C	40°C	100°C	40°C	100°C
30.00	103.9	12.4	97.1	12.3	114.2	14.3
20.00	99.2	11.4	95.9	12.1	97.1	12.3
10.00	97.1	11.4	100.5	12	95.9	12.1
5.00	97.4	11.5	94.2	11.4	100.5	12
2.50	97.1	11.1	99.4	11.5	94.2	11.4
0.00	95.6	10.5	95.6	10.5	95.6	10.5

Table (3.9): Experimental viscosity data (in cSt) for the copolymers (L- O) at 40°C and 100°C.

Conc. x10^{-3} ppm	**L**		**M**		**N**		**O**	
	40°C	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**
30.00	99.4	11.3	100.5	11.6	97.1	11.9	98.2	13.4
20.00	97.1	11.1	99.4	11.3	95.9	11.1	97.1	12.3
10.00	97.1	11	97.1	11.1	99.4	11.3	95.9	12.1
5.00	95.9	10.9	95.8	10.9	95.9	11	95.9	12.1
2.50	95.8	10.7	95.9	10.8	95.9	11	95.9	11.6
0.00	95.6	10.5	95.6	10.5	95.6	10.5	95.6	10.5

Table (3.10) Experimental viscosity data (in cSt) for the copolymers (R- T) at 40°C and 100°C.

Conc. x 10^{-3} ppm	R		S		T	
	40°C	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**
30.00	97.1	12.3	134.8	16.8	182.7	21.9
20.00	97.1	11.9	117.6	14.4	132.5	17.2
10.00	99.4	11.3	103.9	12.4	110.8	113.6
5.00	96.9	10.9	99.4	11.4	99.4	11.5
2.50	96.5	10.8	97.1	11.2	98.2	11.2
0.00	95.6	10.5	95.6	10.5	95.6	10.5

Table (3.11) Experimental viscosity data (in cSt) for the blending copolymers [(D-S), (D-T), (C-S) and (C-T)] at 40°C and 100°C.

Conc. x 10^{-3} ppm	**D-S**		**D-T**		**C-S**		**C-T**	
	40°C	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**
30.00	95.9	10.9	134.8	16.8	67.1	11.5	132.5	17.2
20.00	114.2	14.3	95.9	10.9	98.2	13.4	67.1	11.5
10.00	97.1	12.3	117.6	14.4	95.9	10.9	134.8	16.8
5.00	97.1	11.9	95.9	12.1	114.2	14.3	73.1	11.1
2.50	97.1	11.1	100.5	12	95.9	12.1	97.1	12.3
0.00	95.6	10.5	95.6	10.5	95.6	10.5	95.6	10.5

Table (3.12) Experimental viscosity data (in cSt) for the blending copolymers [(O-F), (O-G), (N-F) and (N-G)] at 40°C and 100°C.

Conc. x 10^{-3} ppm	**O-F**		**O-G**		**N-F**		**N-G**	
	40°C	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**	**40°C**	**100°C**
30.00	95.9	10.9	72.3	11.1	73.1	11.1	72.3	11.1
20.00	114.2	14.3	97.1	12.3	95.9	12.1	97.1	12.3
10.00	97.1	12.3	95.9	12.1	97.1	11.9	97.1	11.9
5.00	97.1	11.1	99.4	11.5	97.4	11.5	97.1	11.1
2.50	90.5	10.5	91	10.5	87.8	10.2	90.5	10.5
0.00	95.6	10.5	95.6	10.5	95.6	10.5	95.6	10.5

3.4.1. Effect of Concentration of the Prepared Additive on VI

Different concentrations of the prepared additives ranging between 0.00 and 3.0 wt% were used to study the effect of the additive concentration on VI. The data tabulated in Tables (3.13) – (3.16) and Figs. (3.37) – (3.40) indicate that the viscosity index increases with increasing the concentration of the prepared additives in solution. As the temperature is raised the lube oil viscosity decreases meanwhile the polymer molecule expands, due to the increase in the solvation power, the size of the micelle increases. This increase in the micelle size counterbalances the reduction of the viscosity of the lube oil and hence decreases the changes of viscosity with temperature of the mixture [Eckert and Covey, 1988; Abdel-Azim and Malcolm, 1983; Abdel-Azim and Malcolm, 1984].

The increasing in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution. Consequently a high concentration of polymer will impart a high viscosity index than a low concentration of same polymer [Abdel-Azim and Malcolm, 1984].

Table (3.13): Dependence of VI on the concentration of additives (A, B, C and D).

Conc. x10^{-3} ppm	Viscosity index in presence of			
	A	**B**	**C**	**D**
30.00	96	97	98	126
20.00	94	95	97	116
10.00	94	95	96	108
5.00	92	94	95	98
2.50	91	93	94	94
0.00	91	91	91	91

Table (3.14): Dependence of VI on the concentration of additives (E, F and G).

Conc. $x10^{-3}$ ppm	**Viscosity index in presence of**		
	E	**F**	**G**
30.00	112	120	127
20.00	108	118	120
10.00	104	110	118
5.00	103	108	110
2.50	101	103	108
0.00	91	91	91

Table (3.15): Dependence of VI on the concentration of additives (L, M, N and O).

Conc. x10^{-3} ppm	**Viscosity index in presence of**			
	L	**M**	**N**	**O**
30.00	100	103	113	136
20.00	99	100	101	120
10.00	98	99	100	118
5.00	97	98	99	118
2.50	95	96	99	111
0.00	91	91	91	91

Table (3.16): Dependence of VI on the concentration of additives (R, S and T).

Conc. x10^{-3} ppm	**Viscosity index in presence of**		
	R	**S**	**T**
30.00	120	135	145
20.00	113	124	142
10.00	100	112	121
5.00	96	101	103
2.50	95	98	99
0.00	91	91	91

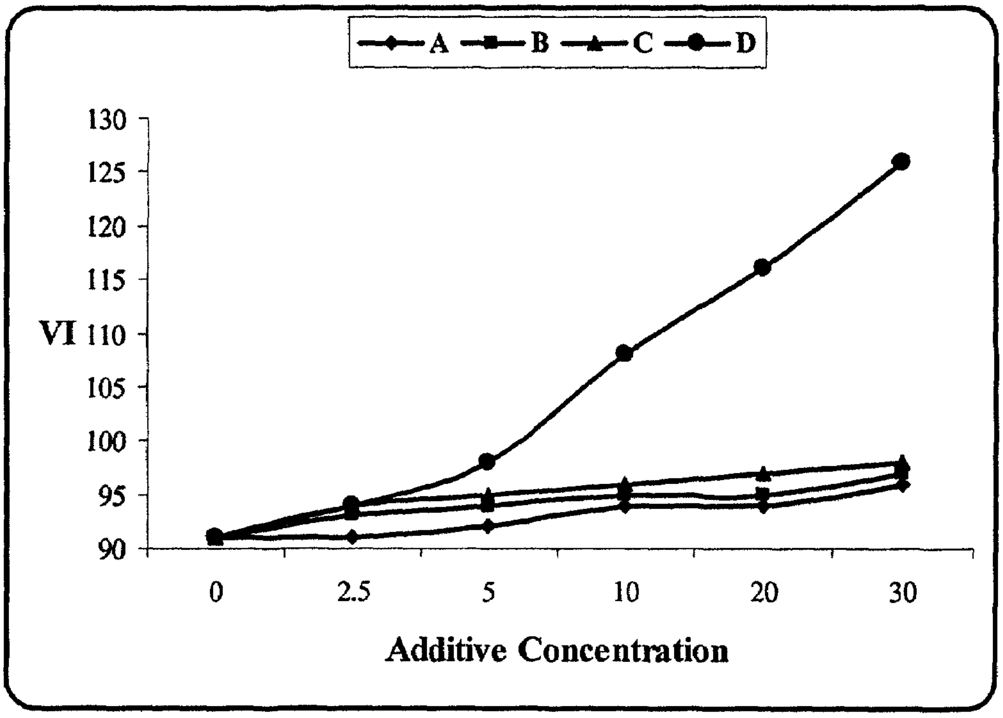


Fig. (3.37): Effect of concentration of VI for lube oil doped with (A, B, C and D) additives.

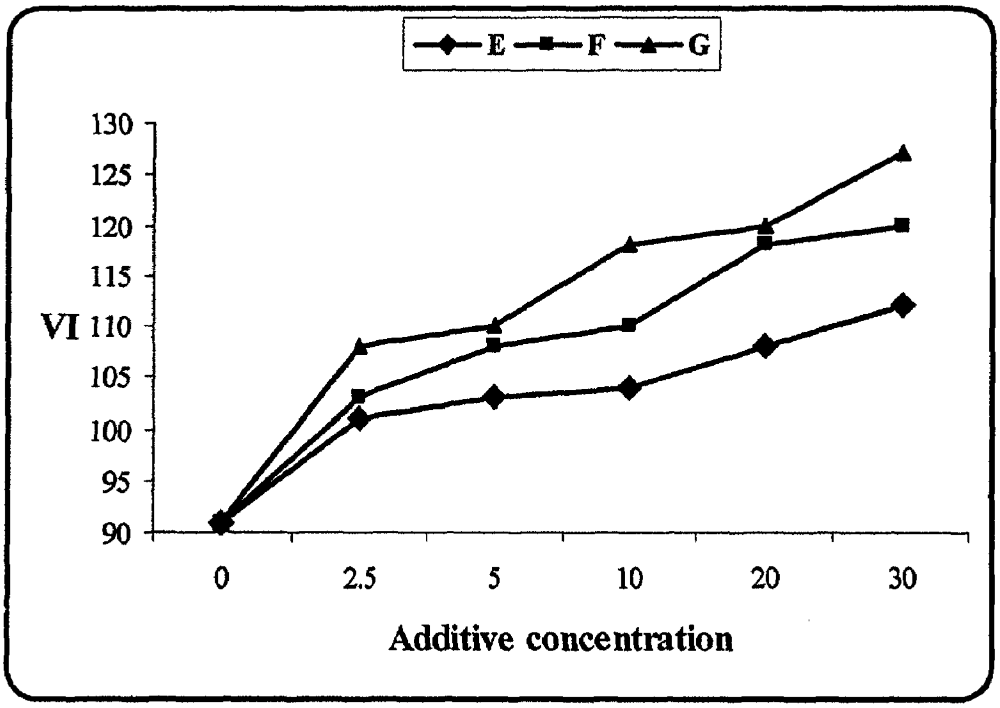


Fig. (3.38): Effect of concentration of VI for lube oil doped with (E, F and G) additives.

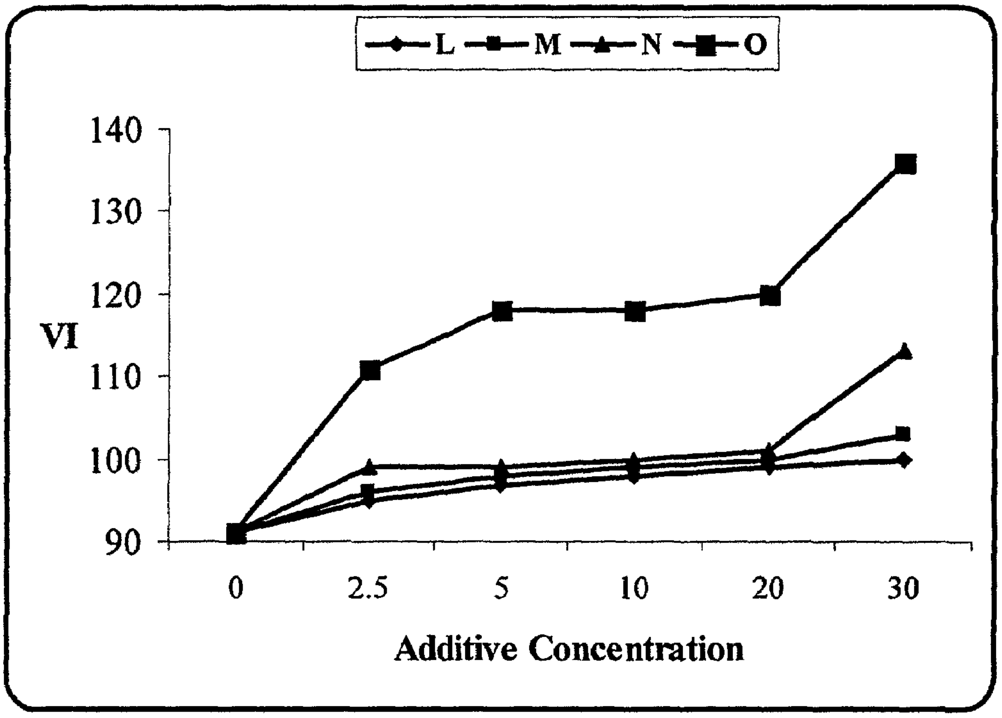


Fig. (3.39): Effect of concentration of VI for lube oil doped with (L, M, N and O) additives.

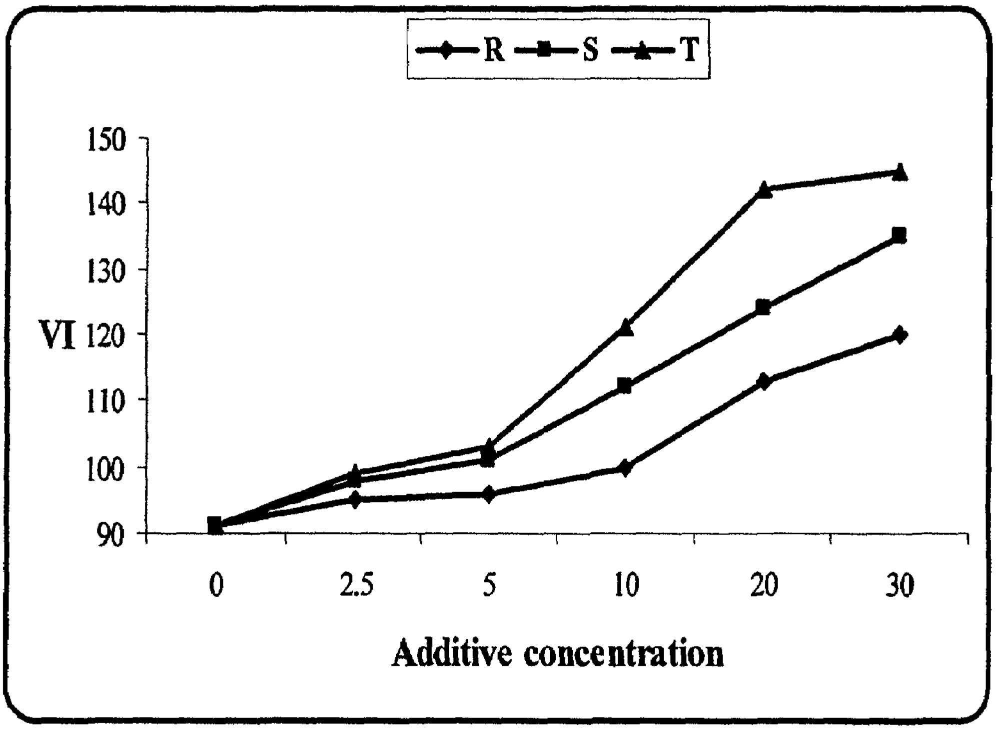


Fig. (3.40): Effect of concentration of VI for lube oil doped with (R, S and T) additives.

3.4.2. Effect of Alkyl Chain Length on VI

The effect of alkyl chain length on the prepared additives as viscosity index improvers as shown in Figs. (3.41) - (3.44) for additive concentration $30\text{x}10^{-3}$ ppm which indicate that the efficiency increases with increasing the alkyl chain length of the used alcohols and amines. This may be due to the effect of the molecular weight on the effective radius of polymers and hence on VI [Guangteng et. al., 1996; Abdel – Azim and Rasha , 2001; Amal, 2001].

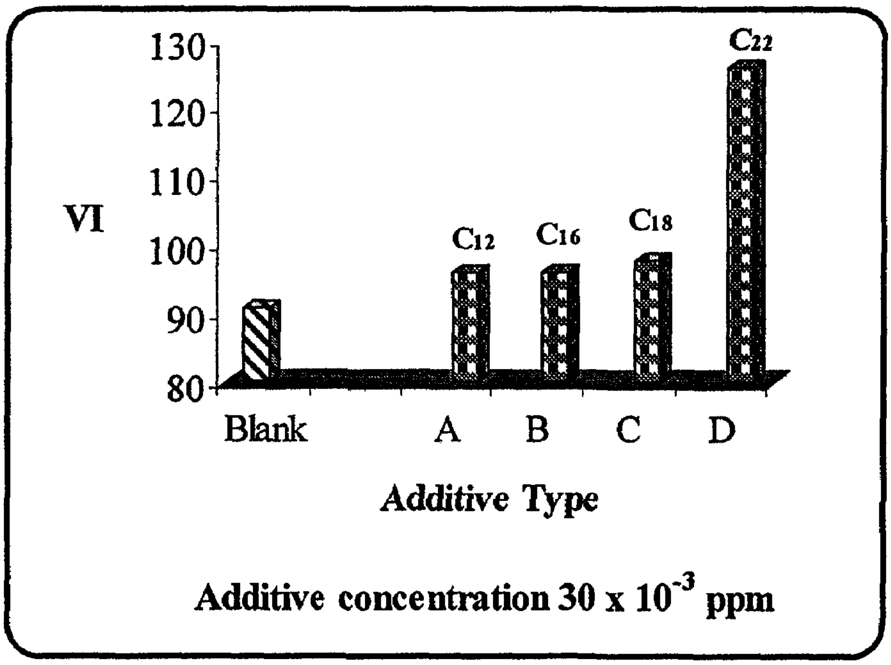


Fig. (3.41): Effect of Alkyl chain length of (A, B, C and D) additives on VI of lube oil.

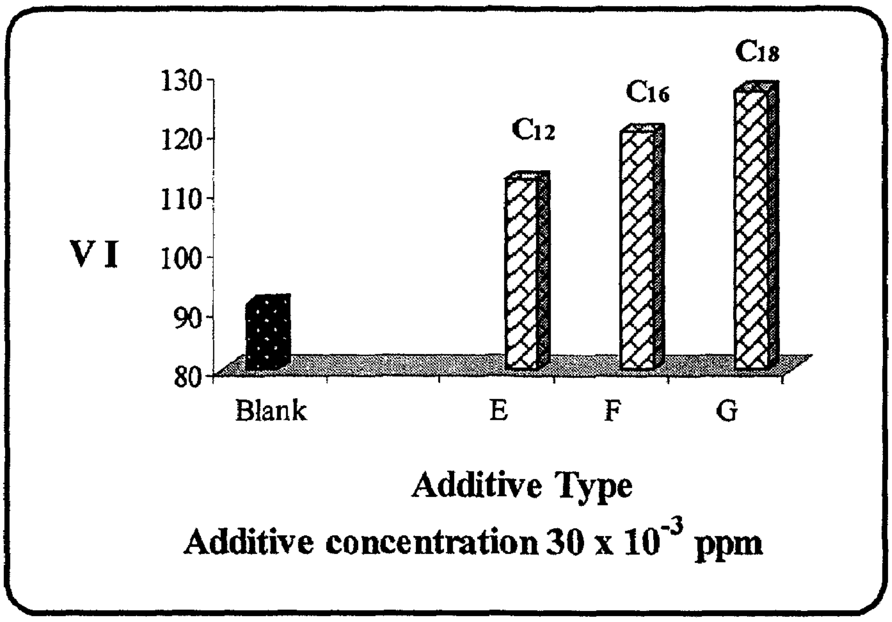


Fig. (3.42): Effect of Alkyl chain length of (E, F and G) additives on VI of lube oil.

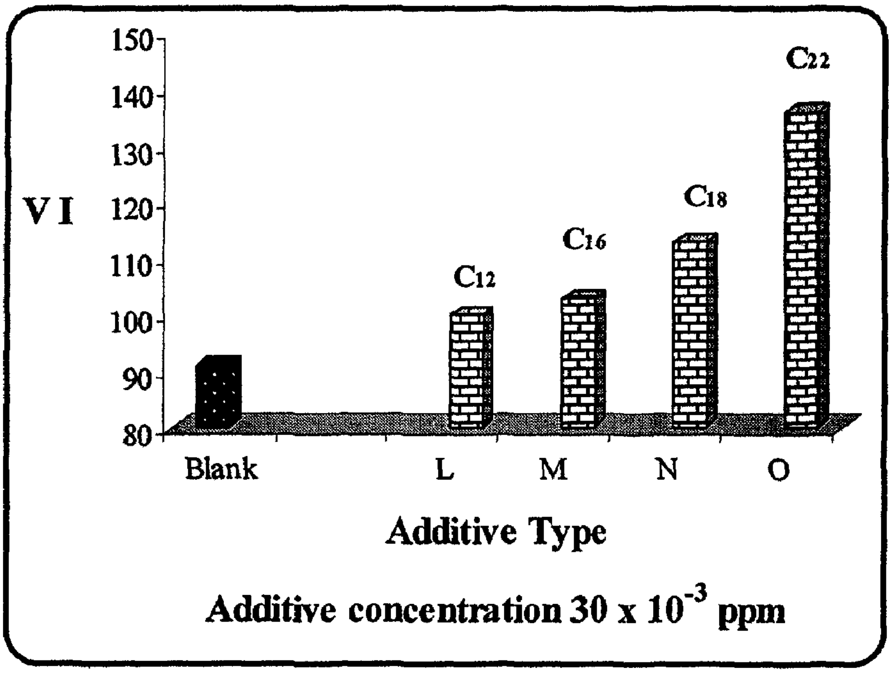
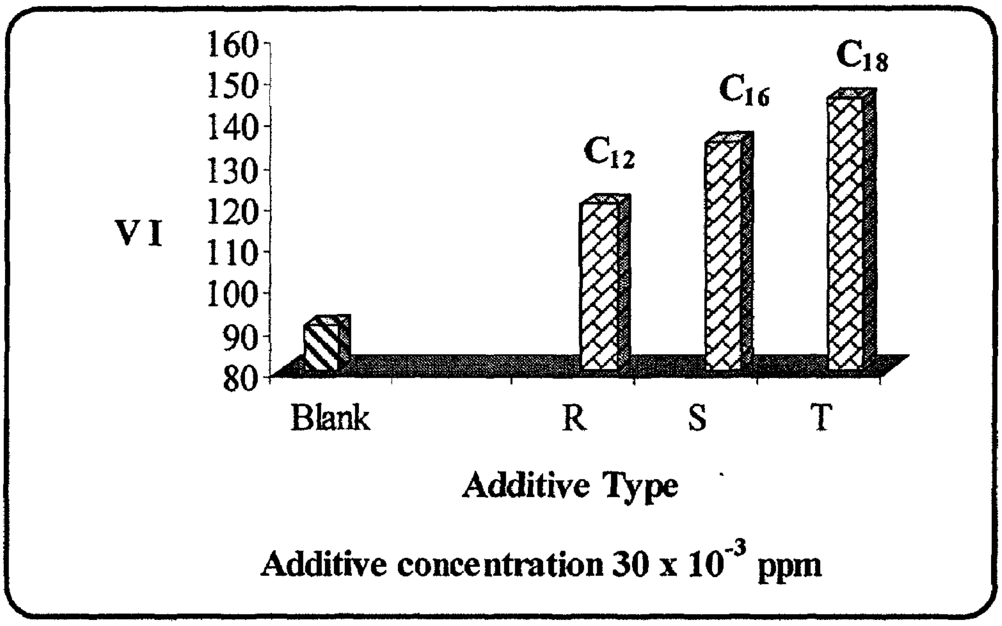


Fig. (3.43): Effect of Alkyl chain length of (L, M, N and O) additives on VI of lube oil.



Additive concentration 30 x 10^{-3} ppm

Fig. (3.44): Effect of Alkyl chain length of (R, S and T) additives on VI of lube oil.

3.4.3. Effect of Monomer Type on VI

The effect of monomer type used in the preparation of the polymeric additives on the viscosity index of the lube oil are given in Figs. (3.45) – (3.46) which indicate that the polymers prepared from octadecene-maleic anhydride esters copolymers attain high viscosity index than that of polymers prepared from styrene-maleic anhydride esters copolymers; this is may be due to the copolymers prepared from octadecene-maleic anhydride esters have higher molecular weight than that of styrene-maleic anhydride esters.

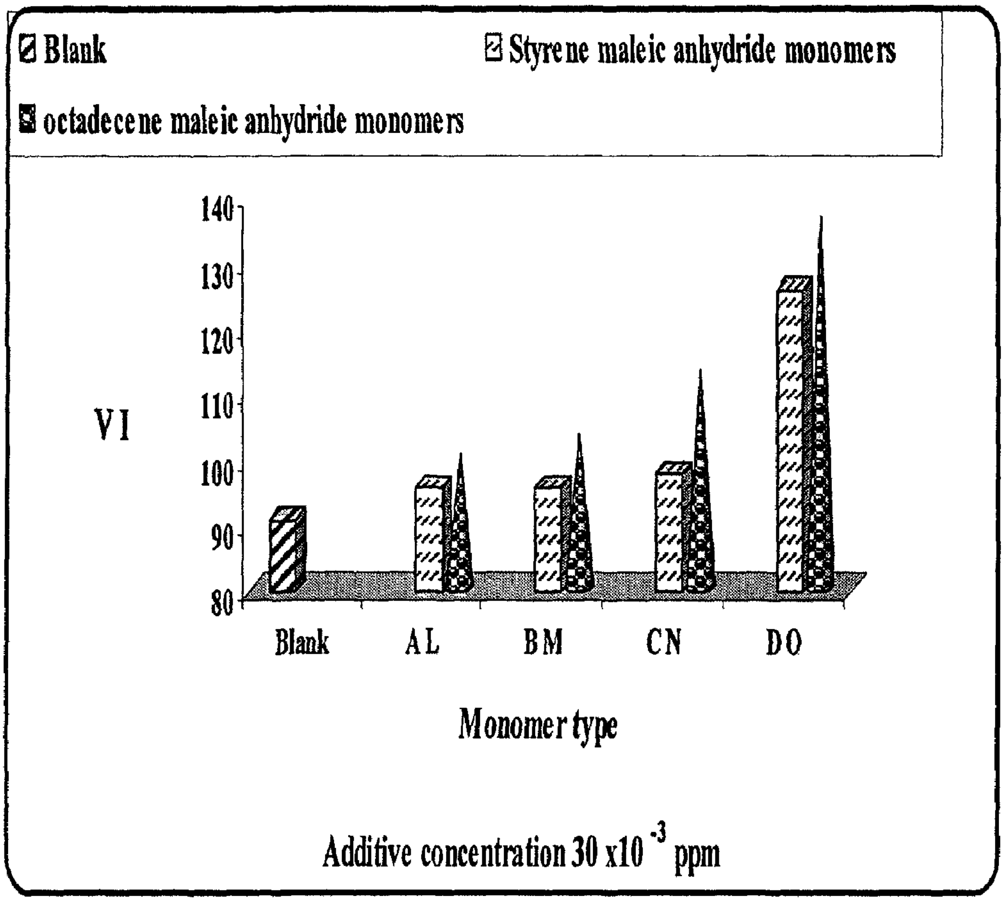


Fig. (3.45): Effect of Monomer type of (AL, BM, CN and DO) additives on VI of lube oil.

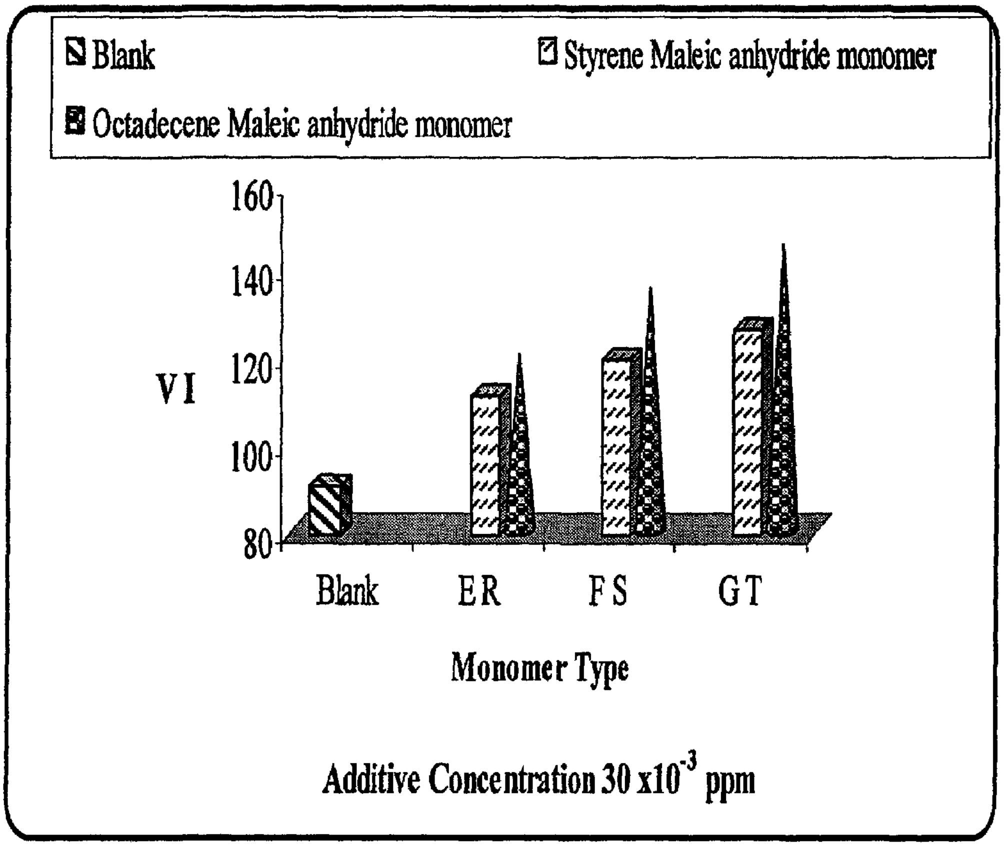


Fig. (3.46): Effect of Monomer type of (ER, FS and GT) additives on VI of lube oil.

3.4.4. Effect of Blending of the Prepared Copolymers on VI

Different concentrations of the blending of the prepared copolymers ranging between 0.00 and 3.0 wt% were used to study the effect of blending of the prepared copolymers on the viscosity index. The data tabulated in Tables (3.17) – (3.18) indicate that viscosity index of esters prepared from styrene–maleic anhydride copolymer were improved by addition of prepared amines from octadecene maleic anhydride.

Table (3.17): Dependence of VI on the concentration of the blending copolymers additives [(D-S), (D-T), (C-S) and (C-T)].

Conc. $x10^{-3}$ ppm	**Viscosity index in presence of**			
	D-S	**D-T**	**C-S**	**C-T**
30.00	131	135	140	142
20.00	127	131	136	140
10.00	120	124	131	135
5.00	113	118	127	128
2.50	101	110	118	120
0.00	91	91	91	91

Table (3.18): Dependence of VI on the concentration of the blending copolymers additives [(O-F), (O-G), (N-F) and (N-G)].

Conc. $x10^{-3}$ ppm	**Viscosity index in presence of**			
	O-F	**O-G**	**N-F**	**N-G**
30.00	131	129	128	129
20.00	127	120	118	120
10.00	120	118	113	113
5.00	101	103	103	101
2.50	98	97	96	98
0.00	91	91	91	91

3.5. EVALUATION OF THE PREPARED COPOLYMERS AS POUR POINT DEPRESSANTS

Pour point depressants have no effect on the crystallization temperature or the number of crystals formed. These depressants obstruct the lateral crystal growth as a result of their adsorption on the precipitating wax [Galin et. al., 1953; Loresen and Hewitt, 1962]. The different concentration of the prepared compounds were tested as pour point depressants ranging from 3.0wt% to 0.0625wt% and the experimental data are grouped in Tables (3.19) and (3.20) which indicates that the prepared compounds are efficient as pour point depressant and the efficiency increases by decreasing concentration of additive. This is explained by the solvation power of the oil .It is well understand that the solvation power of any solvent decreases with decreasing the temperature and vice versa. This reduction in solvation power becomes more obvious when the molecular weight of the solute and its concentration increases. It was found that the prepared compounds D&O are more efficient as pour point depressant than the other compounds (A, B and C) & (L, M and N) and compounds G&T are more efficient as pour point depressant than (E and F) & (R and S), it was found that the prepared copolymers (E, F and G) & (R, S and T) are more effective as viscosity index and pour point depressant than A, B, C and D &L, M, N and O polymers.

By evaluation the blending of the prepared compounds as pour point depressants, it was found that there is an antogisum effect. So we can not use these blending as pour point depressants for lube oil.

Table (3.19): Dependence of PP on the concentration of additives (A, B, C and D).

Conc. x10^{-3} ppm	**Pour Point (°C) in presence of**			
	A	**B**	**C**	**D**
30.00	-7	-7	-10	-10
20.00	-7	-10	-13	-13
10.00	-10	-13	-16	-16
5.00	-10	-13	-16	-19
2.50	-13	-13	-19	-19
1.25	-13	-16	-19	-22
0.625	-16	-19	-22	-25
0.00	-1	-1	-1	-1

Table (3.20): Dependence of PP on the concentration of additives (E, F and G).

Conc. x10^{-3} ppm	**Pour Point (°C) in presence of**		
	E	**F**	**G**
30.00	-7	-13	-16
20.00	-7	-16	-19
10.00	-10	-16	-19
5.00	-13	-16	-22
2.50	-13	-19	-22
1.25	-16	-19	-25
0.625	-16	-22	-25
0.00	-1	-1	-1

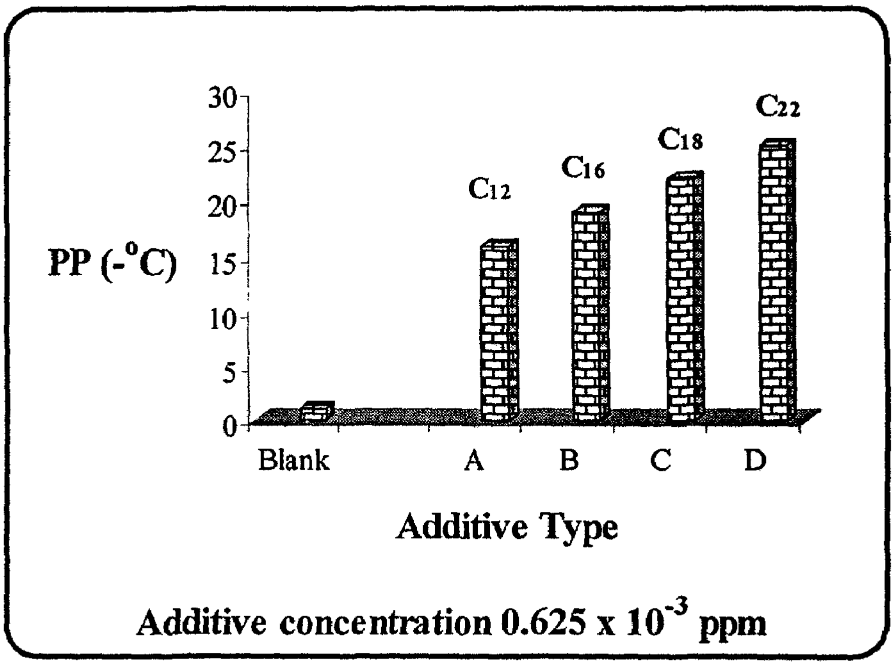
Table (3.21): Dependence of PP on the concentration of additives (L, M, N and O).

Conc. x10^{-3} ppm	**Pour Point (°C) in presence of**			
	L	**M**	**N**	**O**
30.00	-7	-10	-10	-13
20.00	-10	-13	-13	-16
10.00	-10	-13	-16	-16
5.00	-13	-16	-16	-19
2.50	-16	-19	-19	-22
1.25	-16	-19	-22	-22
0.625	-19	-22	-25	-25
0.00	-1	-1	-1	-1

Table (3.22): Dependence of PP on the concentration of additives (R, S and T).

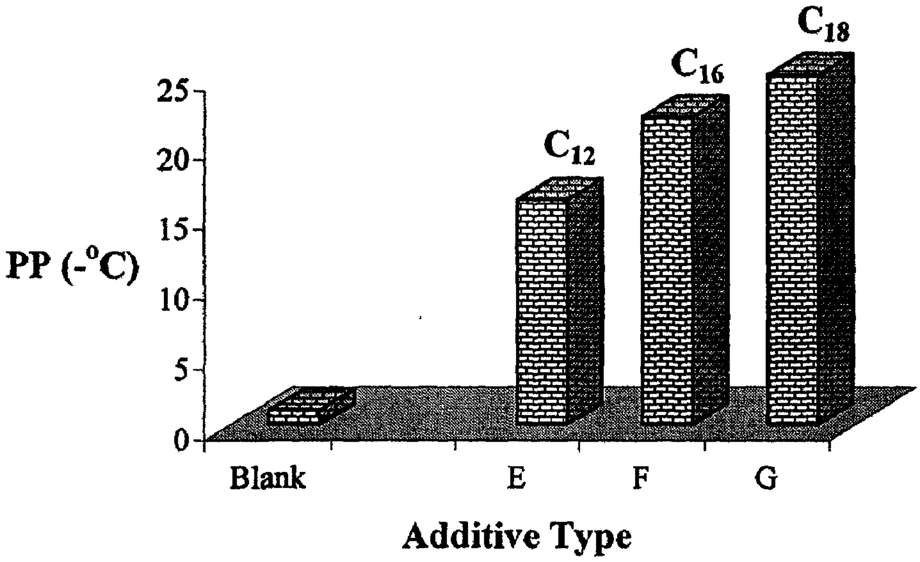
Conc. x10^{-3} ppm	**Pour Point (°C) in presence of**		
	R	**S**	**T**
30.00	-10	-10	-13
20.00	-10	-13	-16
10.00	-13	-16	-19
5.00	-13	-16	-19
2.50	-16	-16	-22
1.25	-16	-19	-25
0.625	-19	-22	-25
0.00	-1	-1	-1

The effect of alkyl chain length on the efficiency of the prepared additives as pour point depressants are given in Figs. (3.47)- (3.50), which indicate that PP increases by increasing alkyl chain length of the prepared copolymers.



Additive concentration 0.625 x 10^{-3} ppm

Fig. (3.47): Effect of alkyl chain length of additives (A, B, C and D) on PP for lube oil.



Additive concentration 0.625 x 10^{-3} ppm

Fig. (3.48): Effect of alkyl chain length of additives (E, F and G) on PP for lube oil.

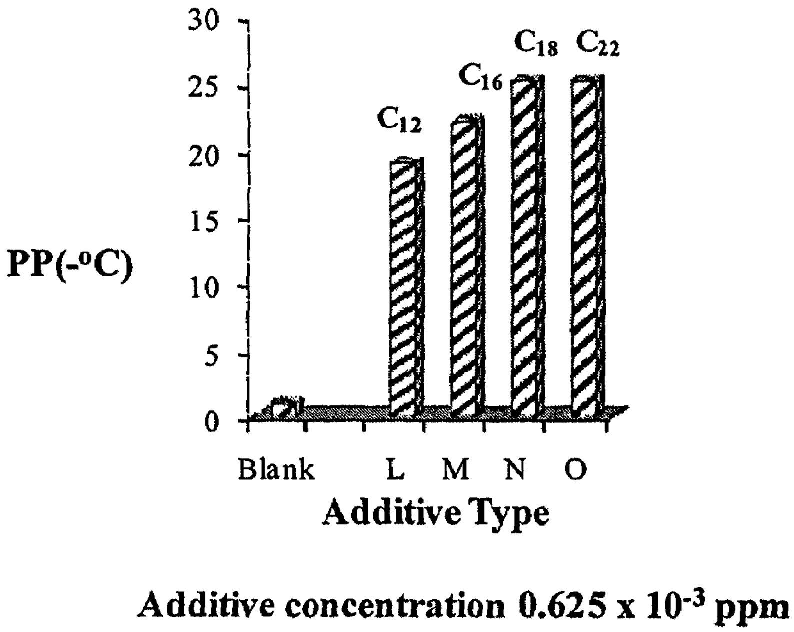


Fig. (3.49): Effect of alkyl chain length of additives (L, M, N and O) on PP for lube oil.

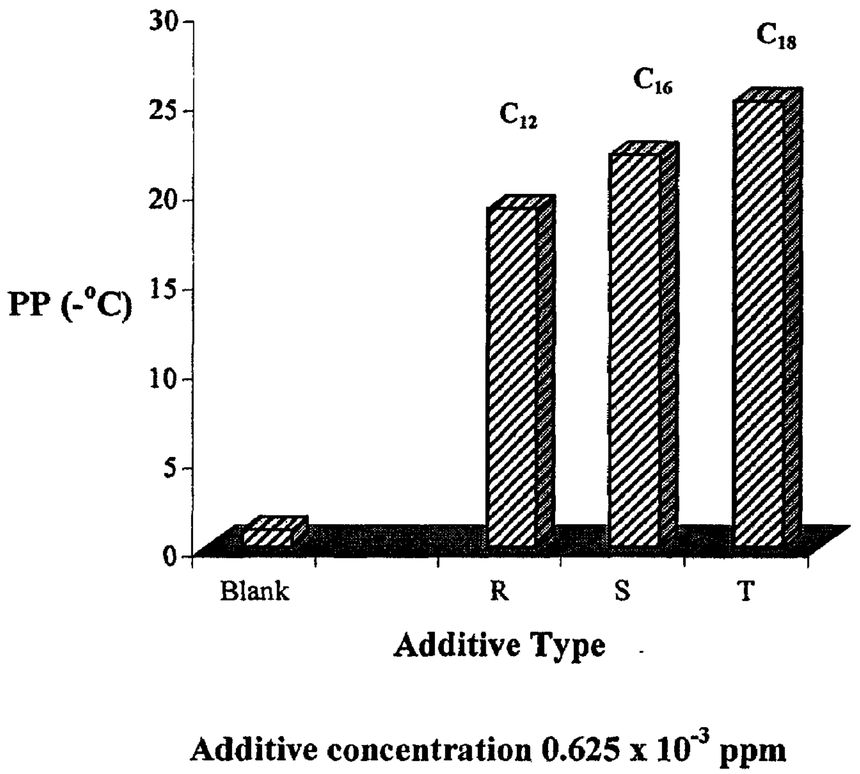


Fig. (3.50): Effect of alkyl chain length of additives (R, S and T) on PP for lube oil.

3.6. EVALUATION OF THE PREPARED COPOLYMERS AS DISPERSANTS

The oil sample containing 2%wt of the prepared compounds (F-G) and (R-T) were subject to sever oxidation condition using Indiana test method at 165.5°C with continuous stirring at constant rate. Samples were taken at intervals of 24 hr and up to 72 hr of oxidation and tested for dispersancy. Results given in Tables (3.21)-(3.22) show that the prepared compounds have very good to excellent dispersancy for sludge and the solid particles formed during lube oil oxidation compared with the lube oil only. This may be explained by the fact that –NH group form hydrogen bonds with polar groups of oxidation products such as alcohols, aldehyde, ketones and acids [Nehal, 2001].

Table (3.21): Dispersancy of lube oil sample and its blends containing additives (E, F and G) after different oxidation periods.

Sample	Dispersancy Time, hours		
	24	**48**	**72**
Lube oil only	35	33	32
Lube oil+2% additive **E**	70	75	82
Lube oil + 2% additive **F**	75	80	86
Lube oil + 2% additive **G**	80	82	90

Table (3.22): Dispersancy of lube oil sample and its blends containing additives (R, S and T) after different oxidation periods.

Sample	Dispersancy Time, hours		
	24	**48**	**72**
Lube oil only	35	33	32
Lube oil + 2% additive **R**	80	87	91
Lube oil + 2% additive S	86	90	94
Lube oil + 2% additive T	91	95	96