

Chapter-III

*Undecyl methacrylate based polymers
as multifunctional additives for lube oil*

1.3.1 Introduction

The use of poly acrylates and poly methacrylates in lubricating oils as useful additives have been documented for a few years now.¹ The methacrylates are recognized as an efficient pour point depressant (PPD) and the acrylates as an effective viscosity index improver (VII) for the lube oil.^{2,3} PPDs are the additives added for maintaining the flow of oil and its transportation at low temperature. This is because of the fact that the oil's flow ability is completely ceased below a certain temperature called the pour point of that oil.⁴ At this temperature, the oil develops wax crystal network and interferes with the flow of the oil. When added to the oil, the hydrocarbon chain of the PPDs gets inserted into the wax lattice and inhibits or modifies the wax crystal formation. The PPDs are, therefore, also called wax crystal modifiers. The VIIs are the additives added to resist the change in viscosity of the oil with temperature variation. Their performance is denoted by a number called viscosity index that indicates the resistance of a lubricant to viscosity change.⁵ A high viscosity index indicates that the temperature does not influence the viscosity to any large degree and vice versa.

Although the conventional acrylate and methacrylate additives with C₁₀-C₁₄ alkyl groups enhance the viscosity index and C₁₆-C₁₈ alkyl groups contribute mainly towards lowering of pour point of the base oils, but with the new standards regarding the emissions of gases and with the associated changes in the engine designs, it became necessary to bring about a modification in lubricant composition and formulation.⁶ This directed all lubricant technologists toward the development of novel polymeric additives with multifunctional activity and ability to maintain clean engine operations. Lubricant manufacturers are, therefore, trying out copolymerization with different

monomers to induce additional viscometric and rheological benefits into the additives. Again, copolymerization with suitable monomer may also increase the molecular weight and crosslink density of the additives. In addition, with the emerging trend of getting better fuel economy, people have started producing cost effective lubricant additives with multifunctional performances to be added to the lube oil.

Long chain behenyl acrylate (BA, prepared from behenyl alcohol and acrylic acid) was chosen here as a potential candidate for copolymerization with undecyl methacrylate (UDMA) and an extensive analysis of their additive performance along with that of polybehenyl acrylate and polyundecyl methacrylate has been carried out. FT-IR and NMR were used for the structural characterization of the polymers, thermo gravimetric analysis (TGA) was performed to assess their thermal response at high temperature and their molecular weight was determined with gel permeation chromatography (GPC). The results evaluated for the polymers are encouraging and comprises the subject matter of the report.

1.3.2 Experimental section

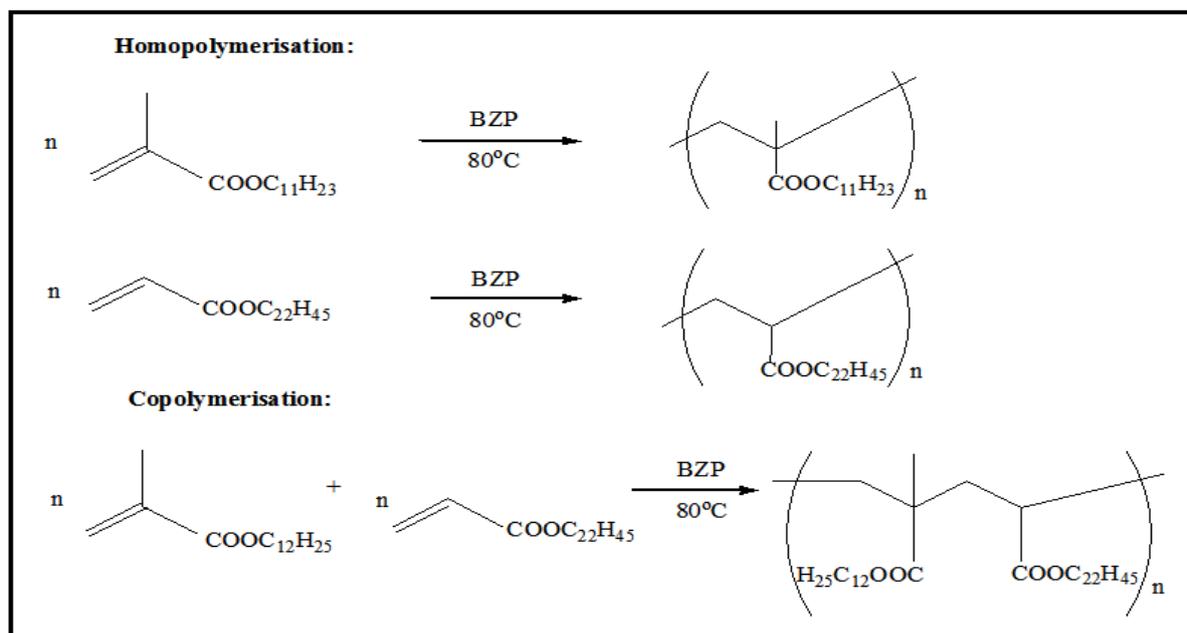
1.3.2.1 Materials

Undecyl alcohol was purchased from Sigma-aldrich. Methacrylic acid, acrylic acid, behenyl alcohol, hydroquinone, H₂SO₄ and BZP were purchased from Merck specialities Pvt., Ltd. Hexane and methanol were obtained from Nice chemicals Pvt., Ltd. The CHCl₃-CH₃OH mixture was used to re-crystallise the initiator BZP and the rest of the chemicals were used as received. Base oil of two different categories (BO1 and BO2) was collected from Indian Oil Corporation Limited, India (Table 1.3.1).

rinsed a number of times with distilled water to eliminate any NaOH (if present in small amount) until it became neutral to pH paper. The esters UDMA and BA were finally left over night on anhydrous CaCl_2 . For further use, CaCl_2 was separated by filtration and toluene was recovered by distillation under reduced pressure and the ester was used in the polymerization reaction.⁷

1.3.2.4 Preparation of homopolymers and copolymers

The copolymers were prepared through free radical polymerization method in four different percentage of BA (10, 20, 30 and 40, w/w) in the compositional mixture of UDMA and BA using BZP as initiator.



Scheme 3: Preparation of homopolymers and copolymers

A three necked round bottom flask connected with a condenser, thermometer and fitted with a magnetic stirrer was used in the polymerization process. The flask was also connected with an inlet for the introduction of nitrogen. In the flask, mixture of exact

percentage of the monomers was heated to 80 °C and maintained at that temperature for half an hour. The initiator BZP (1% w/w, with respect to the total monomers) was then added and heated for 6 hour keeping the temperature constant at 80 °C. The detailed procedure is also mentioned in our other publication.⁸

The two homopolymers, poly-UDMA and poly-BA were also prepared following the same procedure. By FT-IR and NMR analysis 85-90% incorporation of BA was estimated in the polymer backbone (Table 1.3.2).⁹

1.3.3 Measurements

1.3.3.1 Spectroscopic measurements

Infrared spectra (FT-IR spectra) were recorded on a Shimadzu (Japan) FT-IR 8300 spectrometer, within the wavenumber range of 400 to 4000 cm^{-1} using 0.1 mm KBr cells at room temperature. For recording the NMR spectra, Bruker Avance (Germany) 300 MHz FT-NMR instrument was used using a 5 mm BBO probe. CDCl_3 was used here as solvent and tetramethylsilane (TMS) as reference material.

1.3.3.2 Evaluation of thermal stability

A Mettler TA – 3000 apparatus was used to record the thermal stability of the polymers having a heating rate of 10 °C min^{-1} .

1.3.3.3 Measurement of average molecular weight

A GPC instrument (Waters Corporation, USA) was used to calculate the average

molecular weights of the polymers having calibrated polystyrene standards in THF. The PDI was also calculated using the instrument. The values are presented in Table 1.3.3. A gradual increase in the molecular weight was observed for the polymers with the increase in the percentage of BA in the feed.

1.3.3.4 Evaluation of viscosity index

The VI of the two different base oils blended with the polymers was calculated to verify the potential of the synthesized polymers as viscosity index improver. The VI was calculated using an Ubbelohde viscometer which was calibrated at 40 °C and 100 °C with purified methanol and triply distilled water prior to the experiment.¹⁰ The time taken by the polymer solutions to pass through the two calibrated marks in the viscometer was recorded with a digital stopwatch. The VI was evaluated using the kinematic viscosity (ν) of the sample solutions from the following equation,¹¹

$$\nu = (Kt - L/t) \rho \quad \text{Eq. (1)}$$

where t and ρ are the flow time and density of the polymer solution respectively.

A DMA 4500M vibrating-tube density meter (Anton paar, Austria) was used to compute the densities of the polymer solutions. The VI was evaluated from the given empirical equation,¹²

$$\text{VI} = 3.63 (60 - 10^n) \quad \text{Eq. (2)}$$

where n is a constant characteristic for each oil and is calculated by the following equation,¹³

$$n = (\ln \nu_1 - \ln k) / \ln \nu_2 \quad \text{Eq. (3)}$$

where ν_1 and ν_2 are the kinematic viscosities of the polymer doped oil at lower and higher temperature respectively and k is a function dependent solely on temperature.

1.3.3.5 Evaluation of pour point

The pour points of the base oils blended with different percentages of the prepared polymers were tested according to the ASTM D97 method on a cloud and pour point tester (Wadegati labequip Pvt., Ltd., India) in the temperature range of 0 to -71 °C.

1.3.3.6 Photo micrograph and wax modification

The photomicrographs showing wax crystallization behaviour of the base oils blended with different percentages of the prepared polymers were recorded in a Banbros polarizing microscope (BPL-400B, India). The temperature was set at 273 K and it was suitably controlled on the microscope slide by an attached cooling thermostat. The magnification used here was 200X.

1.3.4 Results and discussion

1.3.4.1 Spectroscopic data analysis

FT-IR spectra: The recorded spectra (Fig. 1.3.1) of poly undecyl methacrylate showed signal for the stretching vibration of ester carbonyl (C=O) at 1732.6 cm^{-1} while the ester C–O–C stretching vibration peak appeared at 1164.6 cm^{-1} . The band for the C–H bending vibrations of CH_2 and CH_3 groups appeared at 1464.7 and 722.2 cm^{-1} while the band for the stretching vibrations of the paraffinic C–H bonds appeared at 2879.3 and 2951.1 cm^{-1} . The disappearance of the characteristics peaks of olefins in the product indicates the formation of the polymer.

¹H-NMR spectra: The polymer P-1, in its ¹H-NMR spectra (Fig. 1.3.2), displayed the presence of the protons of –COOCH₂ group by appearing as a broad peak centred at 4.01 ppm; other peaks around 0.86 ppm were due to the methyl protons of undecyl and methacrylate chain. The peaks in the range of 1.1–1.6 ppm were for the methylene protons of the acrylate chain.

¹³C-NMR spectra: The ¹³C-NMR spectra (Fig. 1.3.3) of P-1 showed peaks between 14.2 and 41.4 ppm for all the methyl and methylene carbon atoms. The –OCH₂ carbons of the polymer appeared between 58.3 and 65.1 ppm while the peak around 177.6 ppm is attributed to the carbonyl carbons of the ester groups. Similar absorption bands (both in NMR and FT-IR, Figs. 1.3.4, 1.3.5 and 1.3.6) were also obtained for the BA homopolymer (P-6).

The structural characterization of the copolymers (P-2 to P-5) was also accomplished by their ¹H-NMR, ¹³C-NMR and FT-IR study. Due to similarity in composition, all the copolymers exhibited resembling spectral outline. Selecting the polymer P-5 as a standard copolymer, its FT-IR spectra displayed a strong signal for the stretching vibration of ester carbonyl (C=O) at 1735.4 cm⁻¹ in addition to the signal at 1166.6 cm⁻¹ for the ester C–O–C stretching vibration. The band for the C–H bending vibrations of CH₂ and CH₃ groups appeared near 1456.8 and 712.3 cm⁻¹ while the band at 2872.3 and 2927.2 cm⁻¹ were for the stretching vibrations of the paraffinic C–H bonds (Fig. 1.3.7). In its ¹H-NMR spectra (Fig. 1.3.8), the protons of –COOCH₂ group of UDMA and BA appeared as a broad signal centered at 4.08 ppm while the other peaks between 0.73 and 0.87 ppm were due to the methyl protons of undecyl, behenyl and methacrylate chain. The peaks in the range of 1.2–1.6 ppm were for the methylene protons of the acrylate chains. The ¹³C-NMR spectra (Fig. 1.3.9) of the copolymer showed signals for the methyl and methylene carbon atoms between 14.2 and 45.5

ppm. The $-OCH_2$ carbons of the polymer appeared around 65 ppm while the peak for the carbonyl carbons of the ester groups of UDMA and BA appeared around 176.6 ppm. Moreover, no peaks for unsaturation were present in any of the copolymers.

1.3.4.2 Thermo gravimetric analysis

The thermo gravimetric results of all the polymers (homo and copolymers) are depicted in Table 1.3.4. The results demonstrate that the thermal stability of most of the copolymers is greater than the homopolymers. Moreover, with the increasing percentage of BA in the copolymers, an increase in their thermo oxidative stability is also observed. The proportionate increase in the molecular mass of the copolymers along with their narrower molecular weight distribution must be the reason for their increased stability.

1.3.4.3 Performance as viscosity index improver

The effectiveness of the synthesized polymers as VII was ascertained by evaluating the VI of the polymer doped base solutions. Different percentages of the prepared polymer solutions ranging between 1 and 5 wt% were used to study their performance and the computed VI data are showed in Figs. 1.3.10 and 1.3.11.

From the outcome it is obvious that for all the instances the VI values improved with increasing polymer percentage in the base oils. This is in agreement with our earlier findings.¹⁴ This outcome is because of the increased solubility of polymer with increasing temperature of the base oil. With increased solubility and effective interaction between the polymer chains and the solvent molecules, the polymer

molecules change from a tight coiled micelle to an expanded one.¹⁵ This increased magnitude of polymer micelle volume compensates the reduction of viscosity of the base fluid and, hence, decreases the changes of viscosity of the mixture with temperature alteration. Besides, the overall size and volume of the micelles also gets enlarged with the rise of polymer mass in the base fluid. This increase in micelle volume imparts a higher VI for the polymer solution in contrast to that of the small percentage of the same polymer.¹⁶

Interestingly, the homopolymer of BA (P-6) acted as a better viscosity modifier than the rest of the polymers. The result indicated that the efficiency to act as VII increases with increasing the alkyl chain length of the alcohol moiety. Also, the BA homopolymer is associated with the highest molecular weight among all the polymers. Thus, the outcome is because of the combined effect of the molecular weight and the chain length of the polymer.¹⁷

1.3.4.4 Performance as pour point depressant and wax modification analysis

The synthesized additive compositions were evaluated for their pour points and the data are plotted in Figs. 1.3.12 and 1.3.13. The results showed that all the polymers are excellent as PPD but the efficiency increased with increasing their concentration only up to a certain limit. This can be explained by considering the solvation power of the oil. With decreasing temperature, any solvent gradually becomes less effective in solvation and when the concentration of the solute and its molecular weight increases, the solvation capability becomes even lesser.¹⁸ Again, the interaction between the alkyl chain moieties of the polymer and the paraffin wax constituent in the lube oil is essential in controlling the wax crystal size. Higher the interaction, higher will be the

pour point depression. Long alkyl chain length of the polymer are usually efficient in controlling wax growth but sometimes too long polymer chain becomes ineffective and wax crystal formation is not successfully inhibited. The interaction depends upon various factors like the similarity in structure and chain length of the polymer with that of the waxes, matching crystalline packing of the polymers and the waxes, similarity in the melting point of waxes with the polymers and the molecular weight of the polymers.¹⁹ Here, the polymer P-5 has greater efficiency as PPD among all the polymers. The proper ratio of two different types of polymer chain length must have provided the polymer with the right kind of structure, appropriate melting point and effective molecular weight for the most effective interaction with waxes among all the additives.

The photomicrograph was also used to study the action mechanism of pour point depressant in the lube oil and the results are displayed in Fig. 1.3.14 (a-g). Fig. 1.3.14a is the photomicrograph of pure lube oil where there is large number of rod shaped wax crystals. The photomicrographs of lube oil blended with different polymers (P-1 to P-6) at 3% (w/w) concentration are shown in the Fig. 1.3.14b-g respectively and the images suggests a decrease in the size of wax crystals. The images are thus in good agreement with the pour point values reported earlier (Figs. 1.3.12 and 1.3.13). Thus, an important modification in the wax crystals is observed because of the addition of all the polymers but, polymer P-5 showed the greatest improvement.

1.3.5 Conclusions

All the polymers of undecylmethacrylate and behenylacrylate showed better performances both as viscosity index improver and pour point depressant additive for lube oil. Polymer P-6 acted as a superior viscosity modifier compared to others while

the pour point depressant property of P-5 was much better among all the polymers. BA has a significant role in enhancing the performances of the additives. The long hydrocarbon chain of BA molecule is the key reasons for exhibiting better PPD performance of the copolymeric additives. On the other hand, higher molecular weights of the polymers are responsible for showing superior viscosity index values. In addition, the polymers exhibited remarkable thermal stability and the copolymer with highest BA content showed the maximum thermal stability amongst the other five polymers. Comparative study thus suggests that the polymer P-5 with 40% BA was the most effective multifunctional additive among all the polymers. Therefore, the above study is definitely a constructive approach to formulate a multifunctional and hence cost effective lubricant composition.

1.3.6 References

References are given in BIBLIOGRAPHY section under Chapter-III of Part-I (Page No. 199-201).

1.3.7 Tables and figures

Table 1.3.1: Physical properties of base oils

Properties	Base oils	
	B01	B02
Density (g cm ⁻³) at 313 K	0.83498	0.89653
Viscosity (cSt) at 313 K	6.921	23.837
Viscosity (cSt) at 373 K	1.656	3.993
Viscosity index	80	85
Pour point (°C)	-3	-6

B01: base oil type 1, B02: base oil type 2.

Table 1.3.2: Percentage composition of the copolymers as obtained by spectroscopic method

Polymers	Mass fraction of the polymers		NMR estimation of the mass fraction of BA	FT-IR estimation of the mass fraction of BA
	UDMA	BA		
P-1	1.00	0.0	-	-
P-2	0.90	0.10	0.09	0.08
P-3	0.80	0.20	0.16	0.17
P-4	0.70	0.30	0.25	0.26
P-5	0.60	0.40	0.37	0.36
P-6	0.0	1.00	-	-

P-1: homopolymer of undecyl methacrylate, P-2: 10% BA + UDMA, P-3: 20% BA + UDMA, P-4: 30% BA + UDMA, P-5: 40% BA + UDMA, P-6: homopolymer of behenylacrylate.

Table 1.3.3: GPC results of the polymers

Polymers	GPC values of the polymers		
	M_n	M_w	PDI
P-1	19174	35854	1.87
P-2	23577	39138	1.66
P-3	23703	40532	1.71
P-4	24055	42816	1.78
P-5	25989	43661	1.68
P-6	21365	44864	2.09

Table 1.3.4: TGA results of the polymers

Polymers	TGA values	
	Decomposition temperature (°C)	PWL
P-1	325/458	46/92
P-2	327/468	43/90
P-3	351/487	45/92
P-4	358/495	44/93
P-5	370/524	45/92
P-6	311/462	44/90

PWL: percent weight loss.

Figure 1.3.1: FT-IR spectra of poly undecyl methacrylate (P-1)

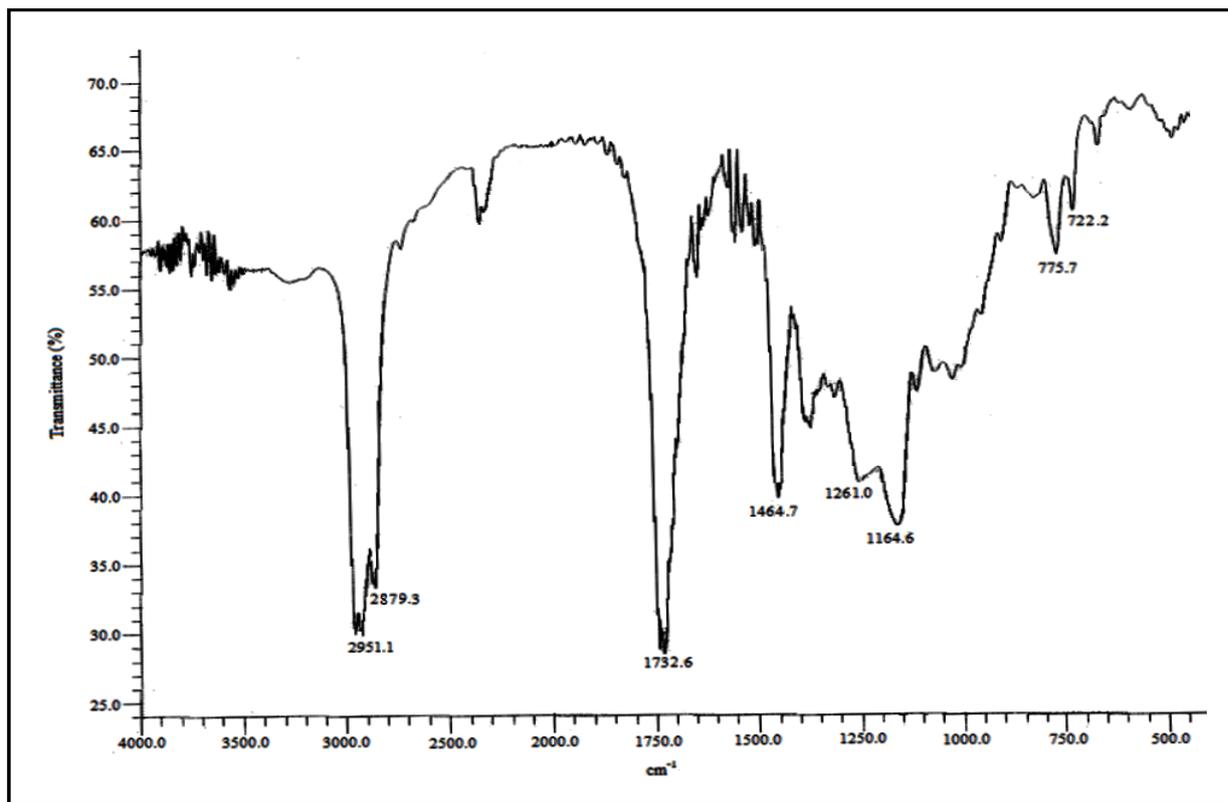


Figure 1.3.2: NMR spectra (¹H) of poly undecyl methacrylate (P-1)

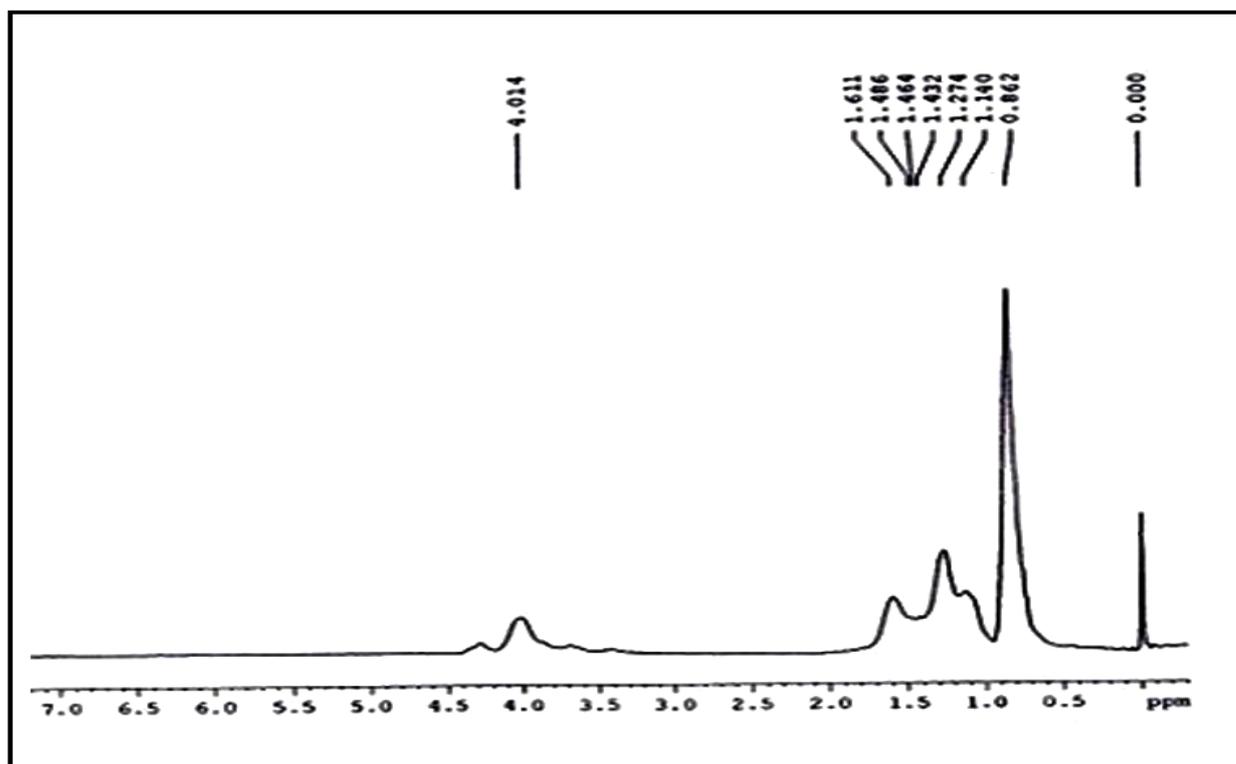


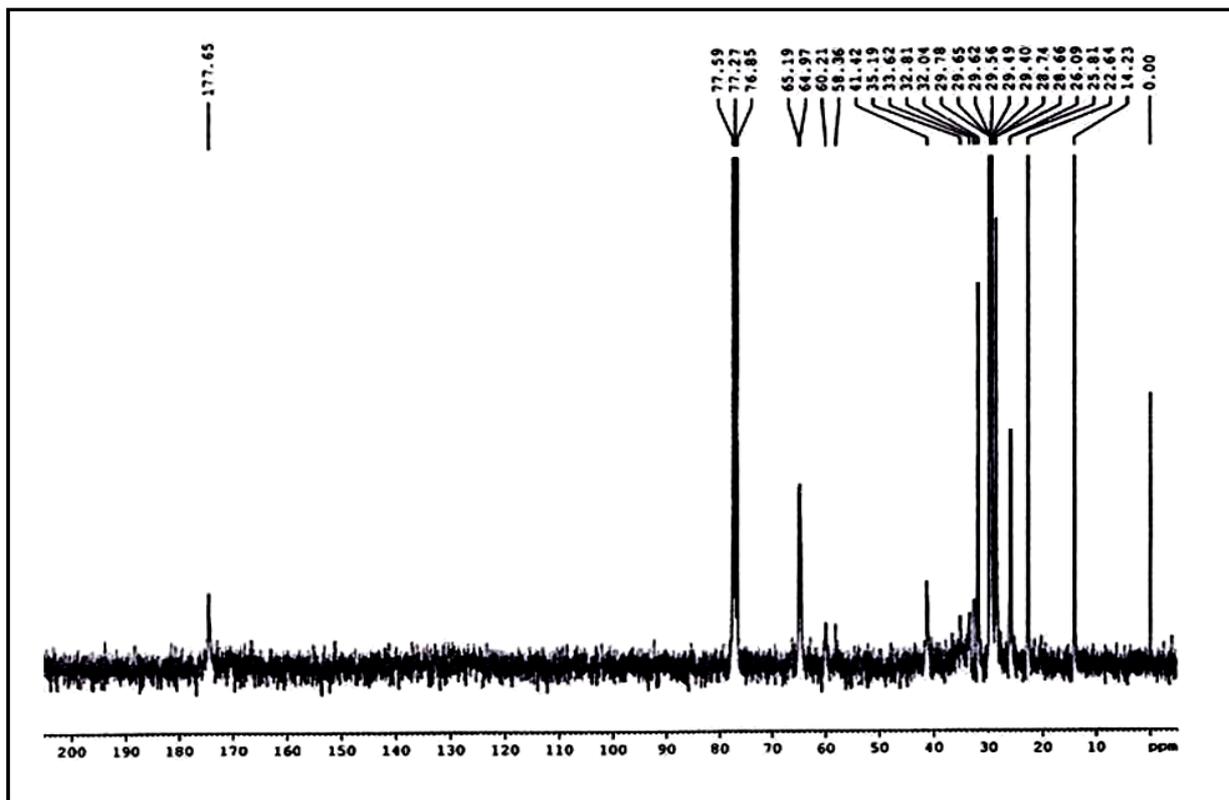
Figure 1.3.3: NMR spectra (^{13}C) of poly undecyl methacrylate (P-1)

Figure 1.3.4: FT-IR spectra of poly behenyl acrylate (P-6)

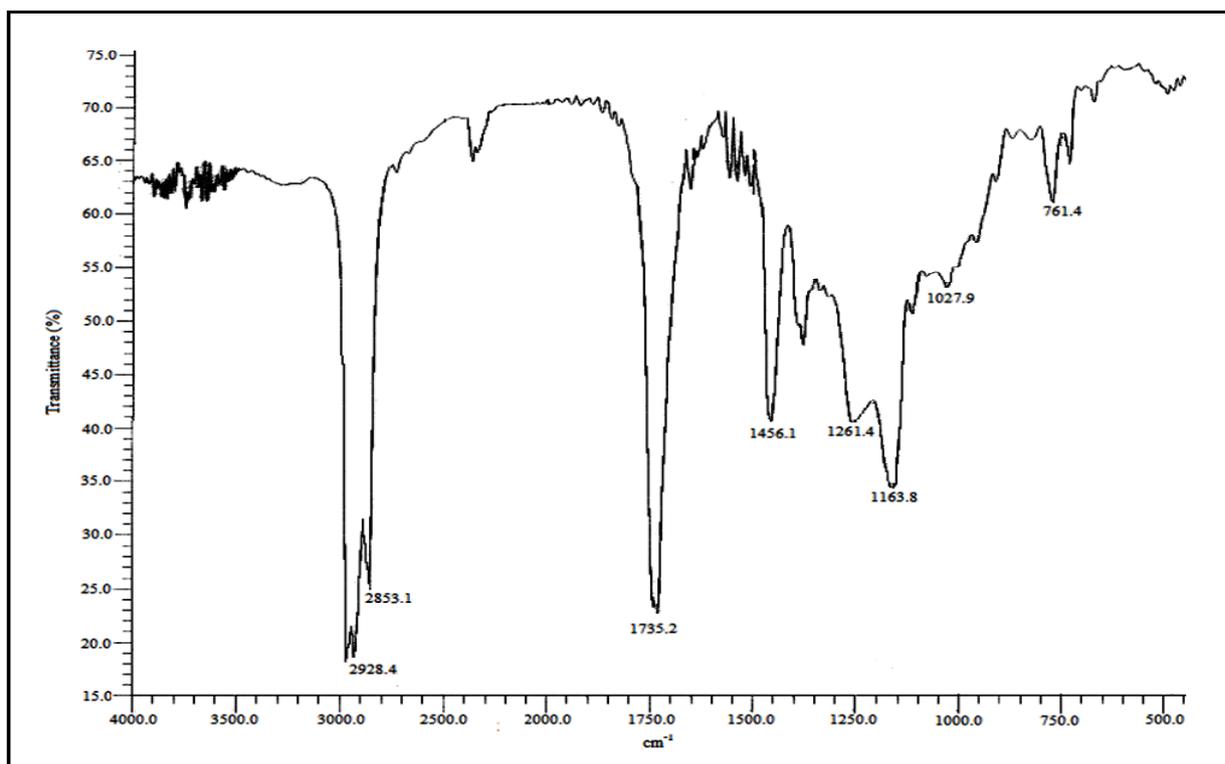


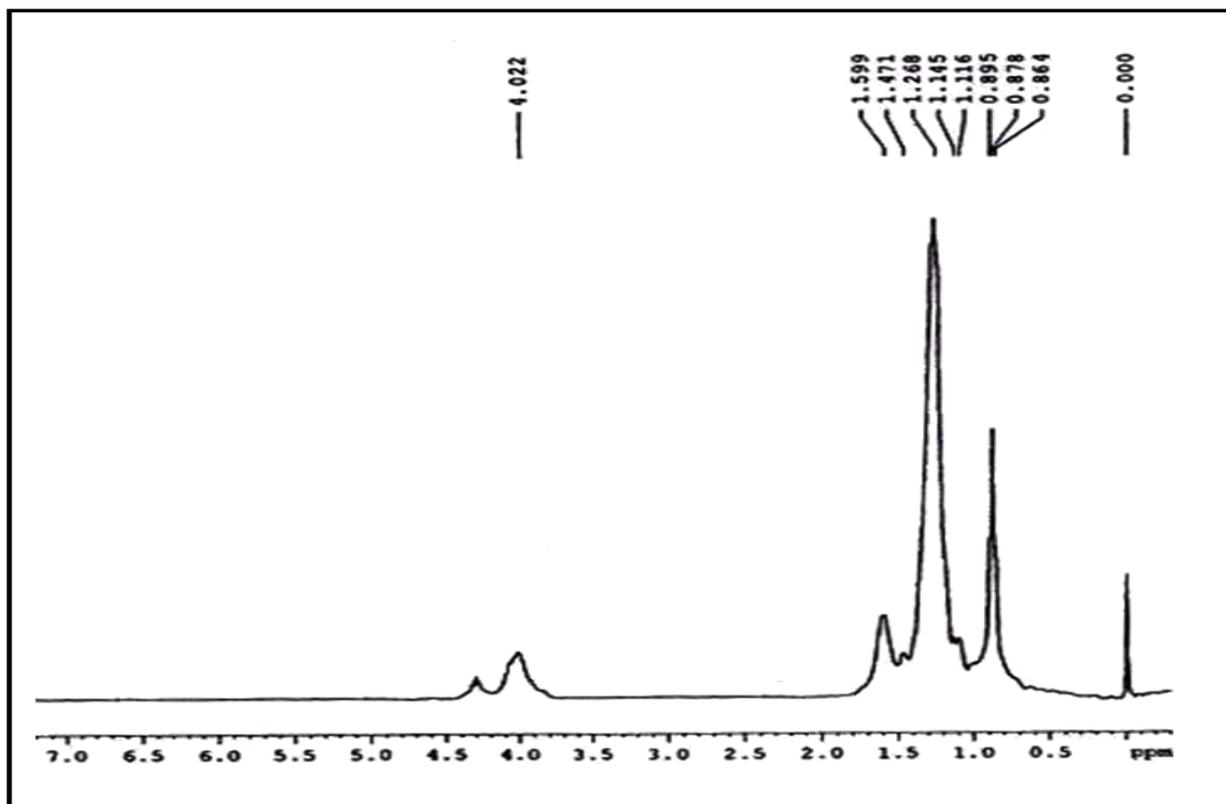
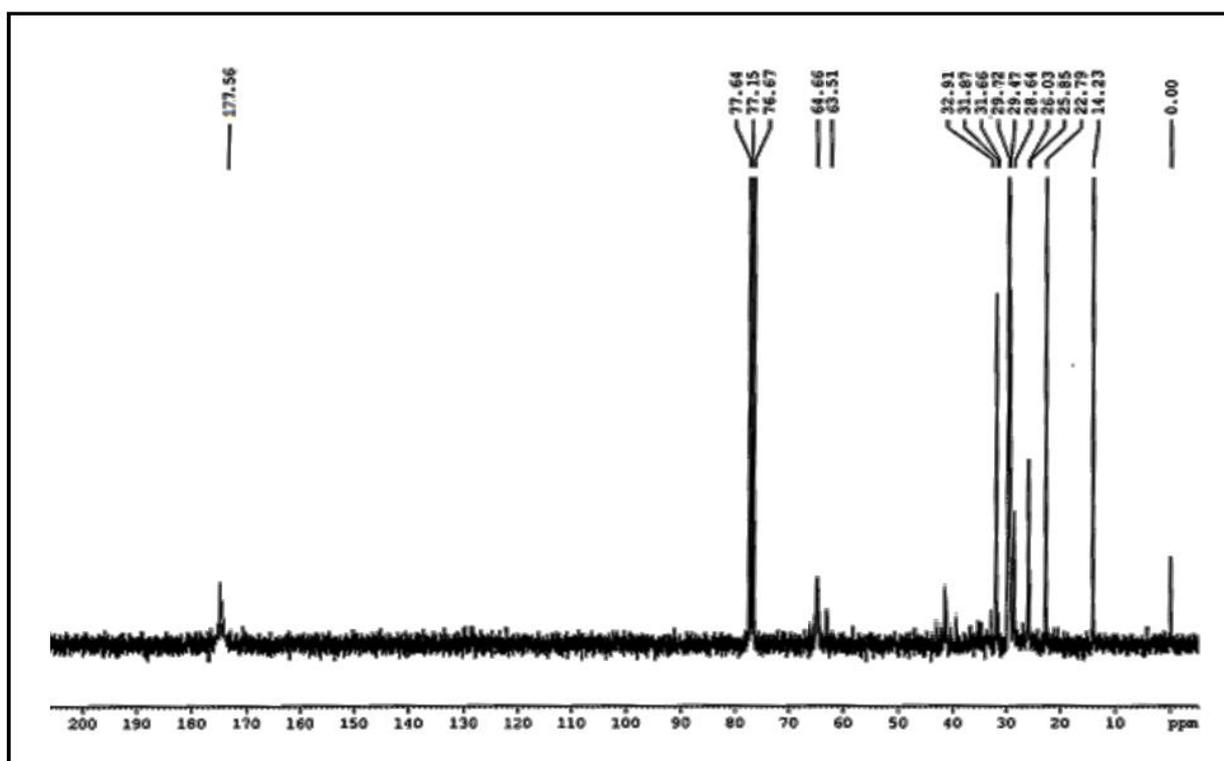
Figure 1.3.5: NMR spectra (^1H) of poly behenyl acrylate (P-6)Figure 1.3.6: NMR spectra (^{13}C) of poly behenyl acrylate (P-6)

Figure 1.3.7: FT-IR spectra of the copolymer P-5 (selecting as a standard copolymer)

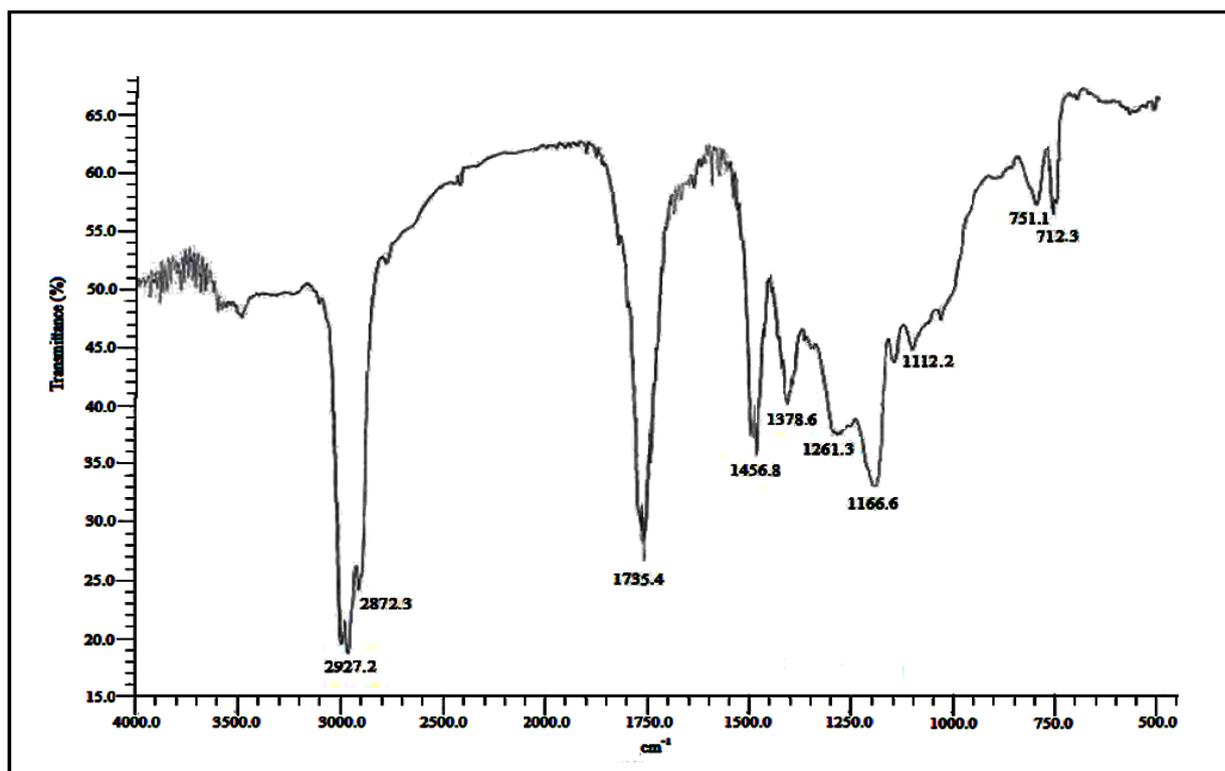
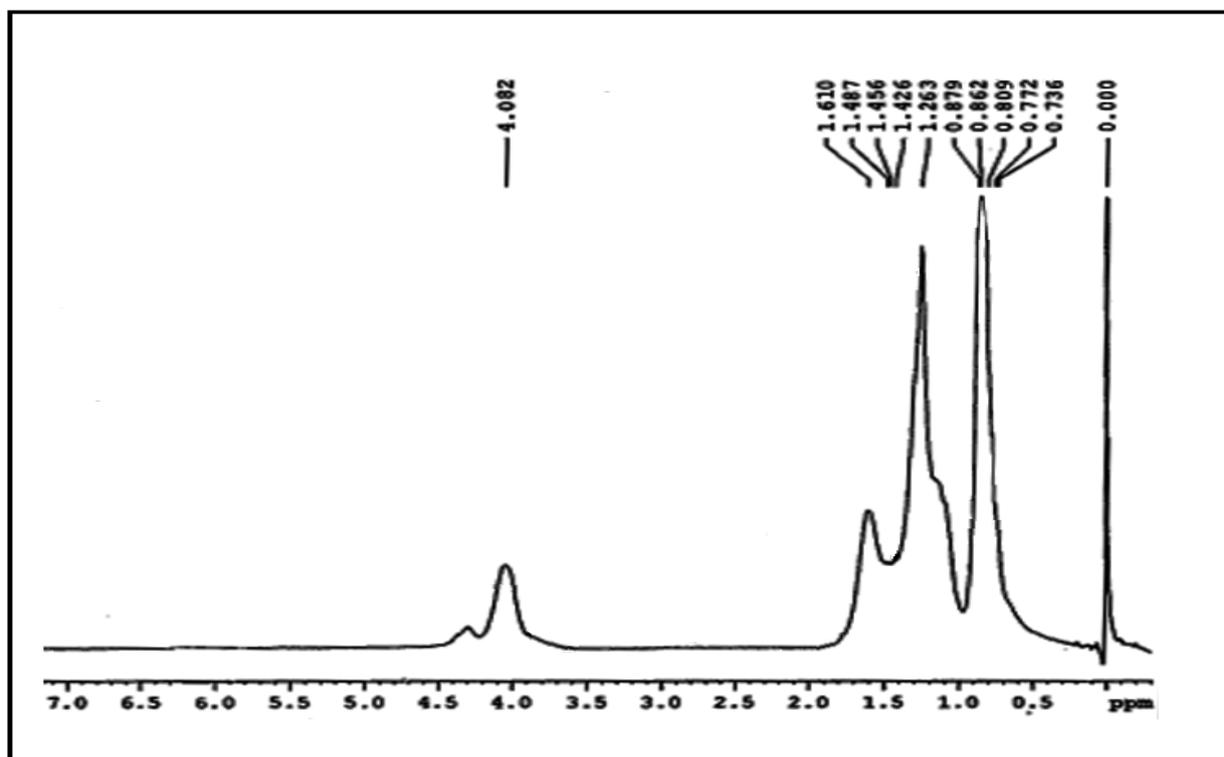
Figure 1.3.8: NMR spectra (¹H) of the copolymer P-5 (selecting as a standard copolymer)

Figure 1.3.9: NMR spectra (^{13}C) of the copolymer P-5 (selecting as a standard copolymer)

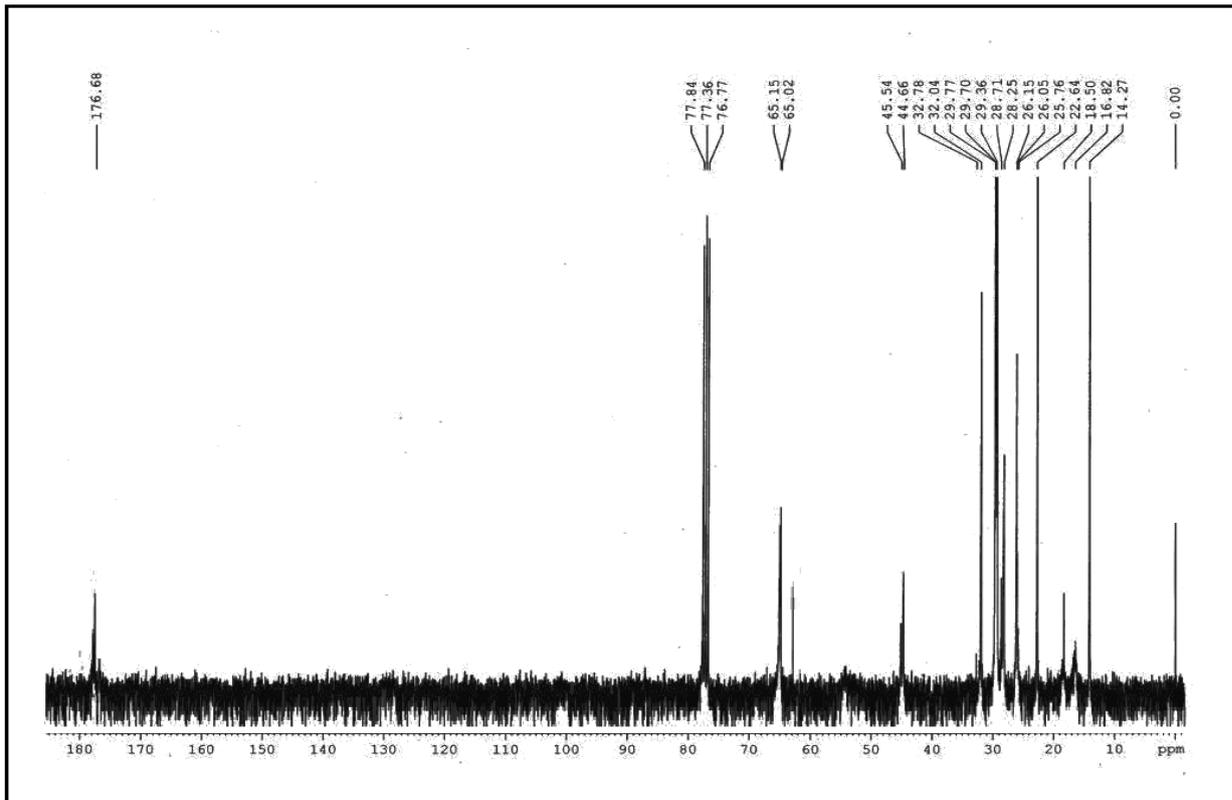


Figure 1.3.10: Viscosity index (VI) values of polymers P-1 to P-6 doped in base oil B01

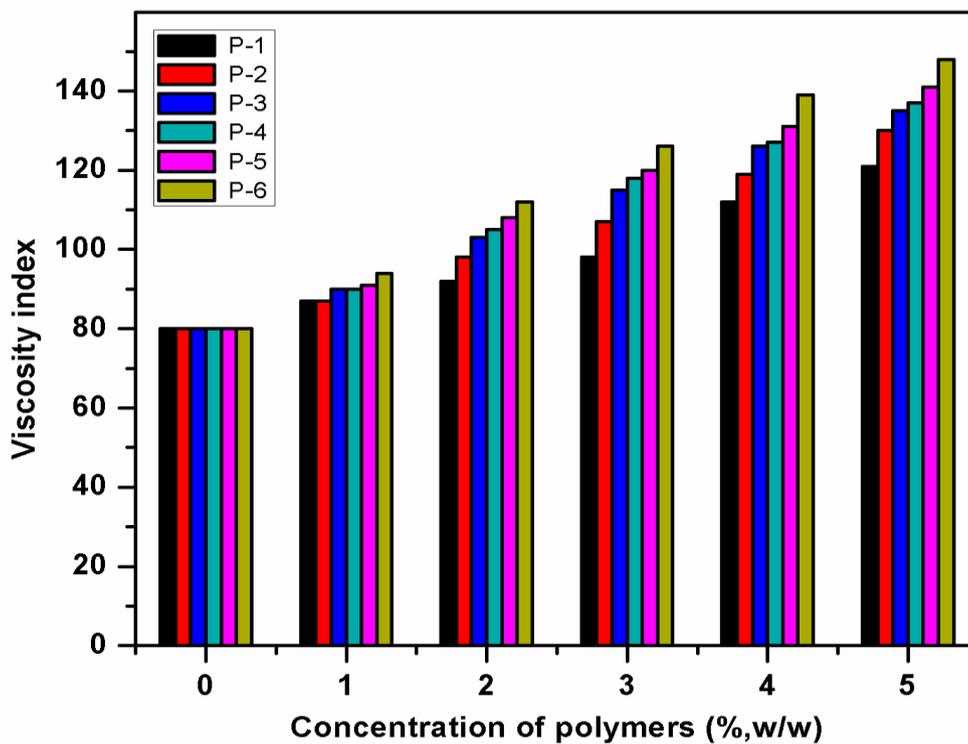


Figure 1.3.11: Viscosity index (VI) values of polymers P-1 to P-6 doped in base oil B02

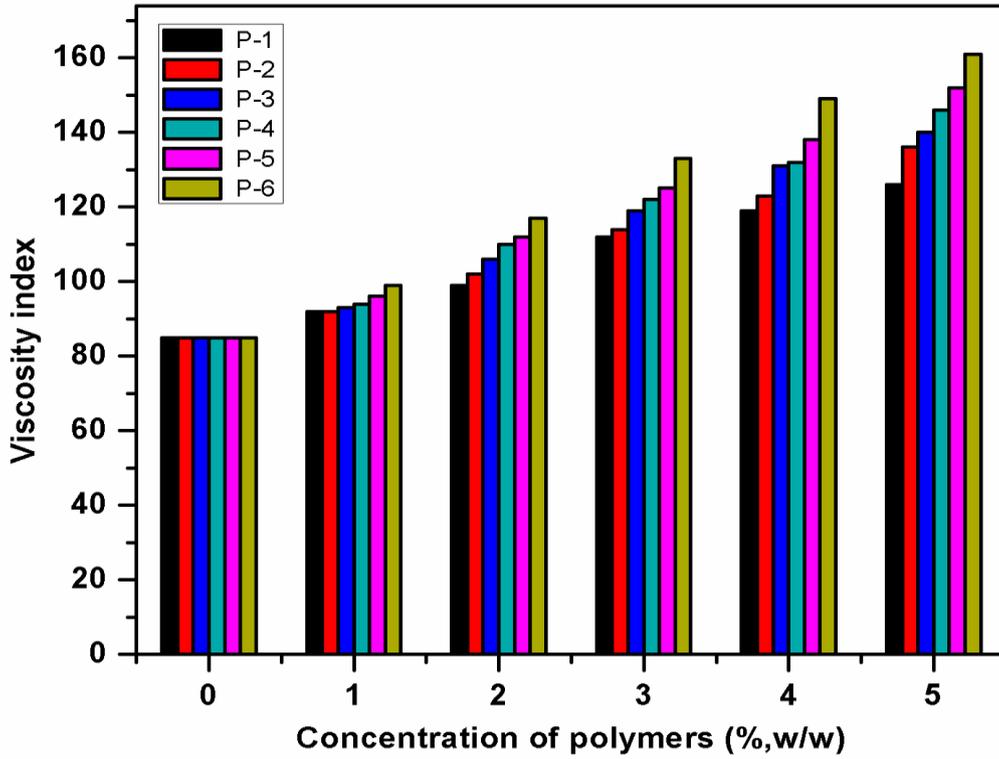


Figure 1.3.12: Pour point (PP) of the polymers P-1 to P-6 doped in base oil B01

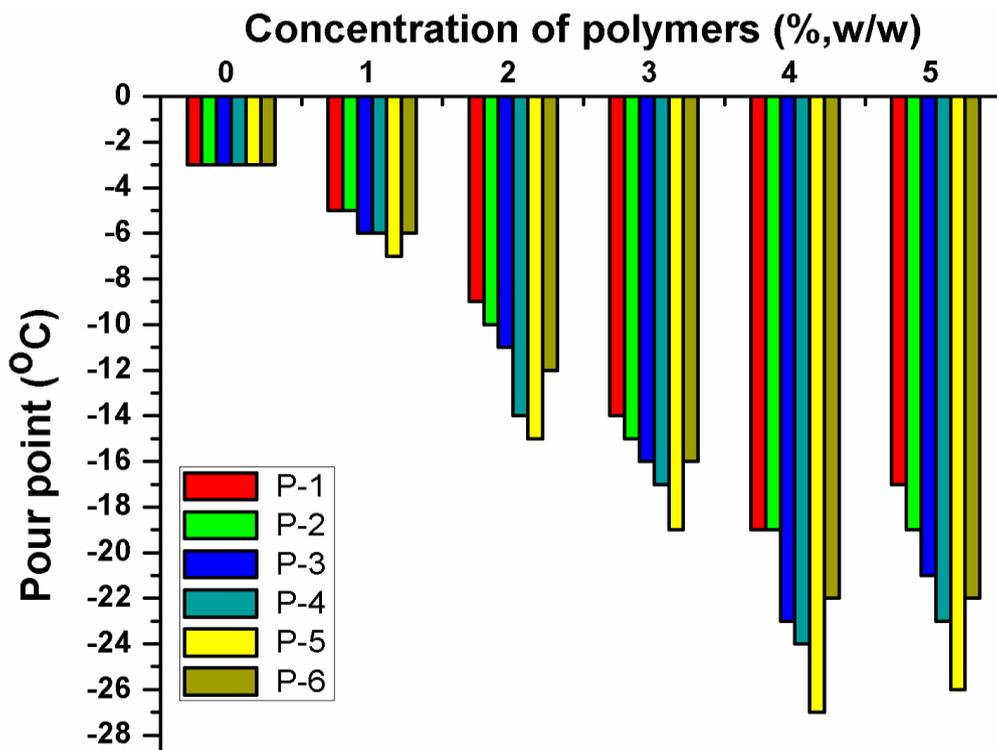


Figure 1.3.13: Pour point (PP) of the polymers P-1 to P-6 doped in base oil B02

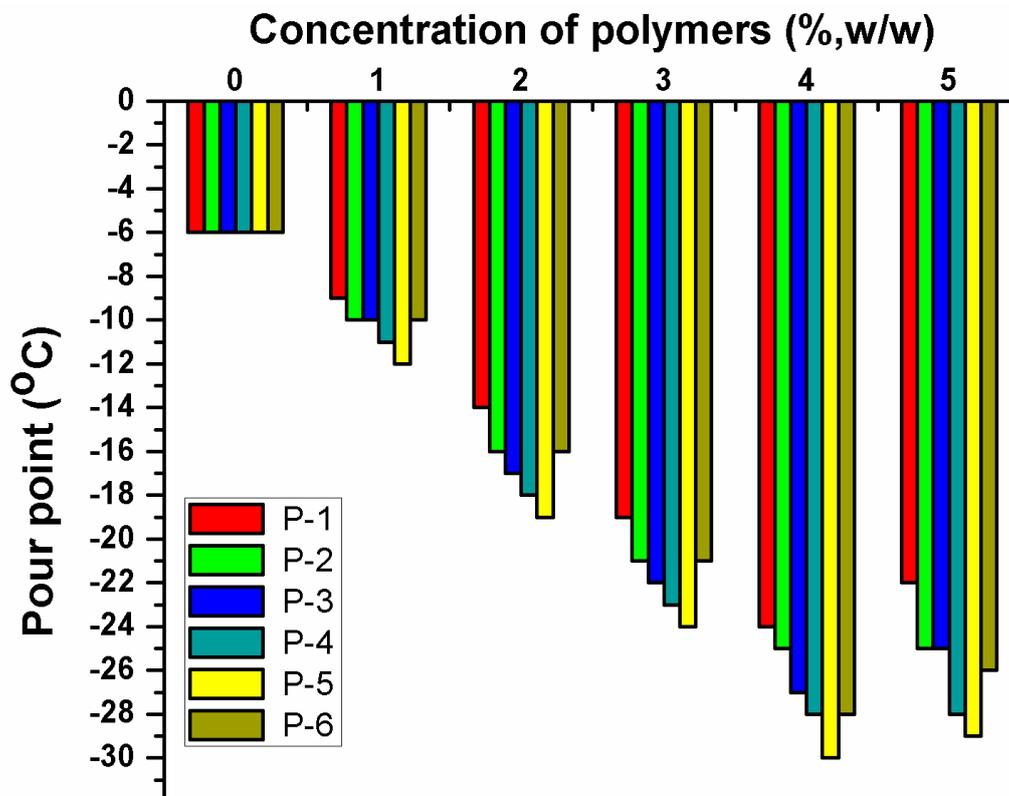


Figure 1.3.14: Photomicrograph of: (a). pure base oil B01 (b). B01 blended with polymer P-1 (3%, w/w) (c). B01 blended with polymer P-2 (3%, w/w) (d). B01 blended with polymer P-3 (3%, w/w) (e). B01 blended with polymer P-4 (3%, w/w) (f). B01 blended with polymer P-5 (3%, w/w) (g). B01 blended with polymer P-6 (3%, w/w)

