Copolymer of Decyl acrylate and Styrene: Synthesis, Characterization and Viscometric Studies in Different Base stocks

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ABSTRACT

In continuation of our studies towards the development of polymeric additives for lubricating oil we report herein the synthesis, characterization and viscometric studies of homo polymer of decyl acrylate and its copolymer with styrene in different base stocks at 40^0C. In order to get more information about the structure and morphology of the polymer when dissolved in base stocks (i.e. in field application), viscometric measurements of the synthesized homo polymer as well as that of the co polymer were performed in the base oils at 40^0C. Different equations were used to calculate intrinsic viscosity and viscometric constants values and molecular weight of the synthesized polymers.

Keywords: Homopolymer, copolymer, viscometric measurements, pour point depressant, lubricating oil.

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INTRODUCTION

Base oil also known as lubricant base oil, is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and napthenic hydrocarbons with molecular weights ranging from medium to high values, very low volatility and with high viscosity index. The proportions of different hydrocarbon components determine the characteristics of the base oils.

The performance of lubricant base oils is often governed by their rheological properties such as low temperature fluidity, viscosity and viscosity temperature relationship. For example, to provide an effective performance at low temperatures as well as at high temperatures, an engine lubricant should have good low temperature fluidity and minimal variations of its viscosity with temperature.

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Properties of such base oils can be improved by the incorporation of suitable performance polymer, generally called additives.

They added to base oils to impart specific property to the oil. Some of them impart new and useful properties to the lubricant, and others enhance properties already present. These additives are more active than the base oils. However, some of their properties are very often controlled by the chemical compositions of the base oils whereas some properties are controlled by the structure of the chemical additives designed for that purpose.

Acrylate based polymers and copolymers used in lubricant compositions for improving the viscometric and rheological properties of the lubricant [1,2]. They also looked upon to provide additional performance characteristics such as improved low temperature fluidity and disparsancy. However, owing to less thermal stability, they readily undergo depolymerization with a constant decrease of the oil viscosity compounded with these polymers. Therefore, the recent research on acryalate based additives has been concerned on copolymerization of it with stabilizing monomers. Since it is well known that inclusion of styrene in the composition of an additive increases the thermal stability of the copolymer, copolymerization of decyl acrylate with two different mass concentration of styrene has been carried out which may be a very useful performance additive such as pour point depressant or viscosity modifier for petroleum and synthetic oil.

Recent research [3] towards the understanding of additives performance in base oils indicated that the performance of additives when used in lubricating oil and applied in field conditions are very much dependent on the structure and morphology of the polymer dissolved in it. Therefore, viscometric studies (that can be carried out in any laboratory owing to the simplicity of equipment required), with these additives in base oils may give valuable information as far as the base stock employed and morphological feature of the polymer in a dilute solution in the base oils is concerned[4]. Therefore, the study may be very useful for predicting the performance of the additive in base oils of different compositions.

The commonly used equations employed to determine the viscometric parameters of the polymer are [4-7]

Mark Houwink – Sukurda: $[\eta] = KM^a$ (1)

Where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, the values of parameter 'K' and 'a' depends on the type of polymer, solvent, and temperature.

Huggins $\eta_{sp} / C = [\eta]_h + k_h[\eta]_h{}^2 C$ (2)
Kreamer $\ln \eta_r/C = [\eta]_k - k_k[\eta]_k{}^2 C$ (3)
Martin $\ln (\eta_{sp}/C) = \ln[\eta]_m + k_m[\eta]_m C$ (4)
Schulz-Blaschke $\eta_{sp}/C=[\eta]_{sb}+k_{sb}[\eta]_{sb}\eta_{sp}$ (5)

Where,
η_r = t/t_0, (t_0 is the time flow of pure solvent and t is time flow of polymer solution) relative viscosity or viscosity ratio ; $\eta_{sp} = \eta_r -1$ specific viscosity

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$[\eta]_h$ =   intrinsic viscosity, respective to Huggins equation.

$[\eta]_k$ =   intrinsic viscosity, respective to Kreamer equation ;

$[\eta]_m$ =   intrinsic viscosity , respective to Martin equation,

$[\eta]_{sb}$ =   intrinsic viscosity or limiting number, respective to Schulz – Blaschke equation;

k_h, k_k, k_m and k_{sb} Huggins , Kraemer , Martin and Schulz- Blaschke coefficients, respectively,
C is the concentration in g/cc.

Apart from the above, some relations have also been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analysed in short period of time, particularly in industrial laboratories. Most useful of them [4-8] are Solomon- Ciute (SC, Eq. 6) and Deb –Chatterjee (DC, Eq. 7) relations

$[\eta] = [2(\eta_{sp}- \ln\eta_r)]^{1/2}/C$ (6)
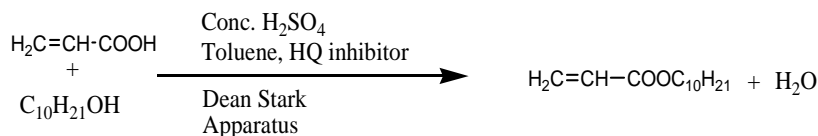
$[\eta]   = (3\ln\eta_r + 3/2\eta_{sp}^2 - 3\eta_{sp})^{1/3}/ C$ (7)

The use of these equations has been derived under the supposition of the validity of the relationship [4]
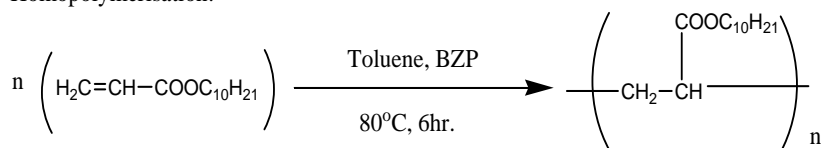
$k_h+ k_k = 0.5$

Scheme I

Esterification:
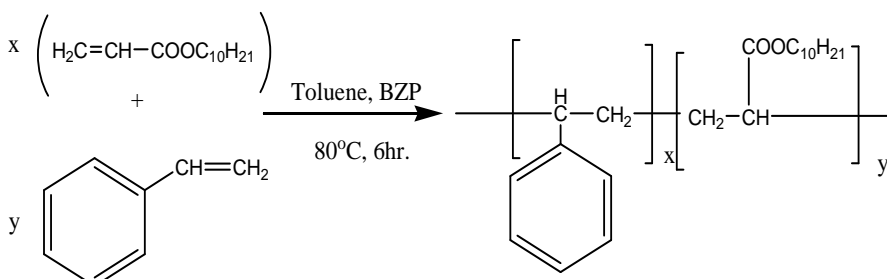

Scheme-II
Homopolymerisation:

Scheme-III
Copolymerisation:

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MATERIALS AND METHODS

Esterification of decylacrylate (DA) from acrylic acid and decyl alcohol.
Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1.1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 130^0C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, decyl acrylate.

Purification of prepared ester
The prepared ester was purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h, and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distil water to remove any traces of sodium hydroxide; the ester was then left over night on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

Preparation of homo polymer of DA and its copolymer with styrene and their purification
The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask was placed desired mass of DA and initiator (BZP) followed by the desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313K. A homo polymer of DA was similarly prepared and purified under the same conditions for use in reference experiments.

Preparation of Polymer –base oil blend
Base oils of two different viscosity grades, BO1 and BO2 (Table 1) were collected from two different refineries, A and B. In all the cases blending of the additives with the oils were carried out by taking required amount of polymer in the calculated amount of oil (w/w) and then heating the mixture at 60^0C for 30 min with constant stirring.

MEASUREMENTS
Spectroscopic measurements
IR spectra were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1mm KBr cells and the spectra were recorded at room temperature within the wave number range (400 to 4000) cm^{-1}. NMR spectra were recorded in Brucker Avance 300MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl$_3$ was used as solvent and TMS as reference material.

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Viscometric measurements

Viscometric properties were determined at 313 K in different base stocks, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least five different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and uncertainty was found to be nearly 0.17 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants K = 0.00387 dl/ g and a = 0.725 [3,9] were employed in Mark Houwink – Sukurda relation

Thermo gravimetric analysis (TGA)

The thermograms in air were obtained on a mettler TA – 3000 system, at a heating rate of 10 K·min^{-1}.

RESULTS AND DISCUSSION

Spectroscopic analysis

FT-IR spectrum of the homo polymer (Figure 1) exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1260 and at 1175cm^{-1} can be explained owing to the C-O (ester bond) stretching vibration and the absorption bands at 975,750 and 711 cm^{-1} were due to the bending of C-H bond. The broad peak ranging from 2900-3100 cm^{-1} was due to the presence of stretching vibration.

The existence of the copolymer was confirmed by FT-IR and NMR analysis. The copolymer in its IR spectrum (Figure 2) showed broad peak ranging from 1732 to 1720 cm^{-1}. This was attributed to the stretching vibration of the ester carbonyl group and to C-H bond of the phenyl group of styrene.

In the ^{1}H NMR (Figure 3) spectra of one of the respective copolymers, a broad multiplate centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet centered at 4.06 ppm was due to the proton of the –OCH$_2$ group. The absence of singlets between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer.

The proton decoupled ^{13}C NMR spectrum (Figure 4) of the above sample of copolymer was in complete agreement with the original structure-I

Structure-I

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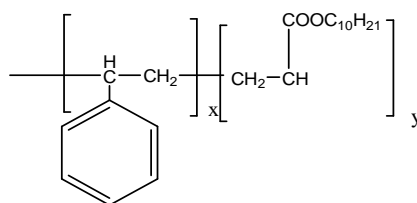
The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of –OCH$_2$ group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports [10] as well as on the basis of our earlier paper [11].

It was further verified through an analysis of FT-IR spectral data [6]. The intensity of C=O absorption in FT-IR spectra of present copolymers, as compared to the carbonyl absorption in a standard, were analyzed for quantitative determination of the content of acrylate component in the copolymer. The comparative results obtained on comparisons are presented in Table-2.
Physical properties of base oils are tabulated in Table 1. Viscometric data were obtained using the six equation mentioned. A linear relation for the plot of logη$_{sp}$ vs log c[η] obtained for all samples [Figure 5a & 5b] indicated that measurements were performed in Newtonian flow[12,13]. Huggins (H), Kraemer (K), Martin (M) and Schulz–Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz–Blaschke (SB) equation is commonly applied in single point determinations because it was found that k$_{sb}$ = 0.28 for many polymer-solvent systems [4-7,14]. In this work, this value was used.

Thermogravimetric analysis (TGA) in Table 3 showed that introduction of styrene raises the thermal stability of the copolymer in comparison to the homopolymer.

Table 4-5 presents intrinsic viscosity [η] values of polymer solution in base oils BO1 and BO2 related to all equations for the samples analysed. Considering the oils (BO1 and BO2) and comparing the values of [η] for homo and copolymers, it is noticed that the higher values were obtained in BO2 oil compared to BO1 oil. Thus considering all the polymers (homo and copolymers), oil BO2 appeared to be more compatible to the polymer and thus pointing towards providing more extended conformations of the polymers. This fact is further supported by the respective k$_h$+k$_k$ values, which is well within 0.5 (Table 7). Lower values in BO1 oil in comparison to the BO2 oil, indicating contracted structures with star like conformation for the additive in this oil. Variation of [η] obtained by graphic extrapolation method (equation 2-5) was found to be less compared to those obtained by single point determination method (equation 6-7) without any restriction to lubricating oil .

It is also observed that [η] values decrease with the incorporation of styrene, but increases with increases in styrene concentration in case of oil BO2 and decreases in oil BO1. [η] values obtained by using DC equation are always higher irrespective of the nature of the base stock.

It is also observed that there is a drop in intrinsic viscosity values in case of copolymer when added to base oils, particularly in BO1 oil, in comparison to the homopolymer. However, it does not change much with increase in styrene concentration in BO2 oil. Although the change is similar in BO1 oil, but the drop in intrinsic viscosity values of the copolymer is more than what was observed in oil BO2 and the reduction in intrinsic viscosity values gradually increases with the increase in styrene concentration.

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Table 6 & 7 presents values of viscometric constants calculated for homo and co polymers in BO1 and BO2 oil respectively, k_h and k_k fitted in the range of good solvents, whereas sample P-3 in BO1 oil indicating more incompatibility. Although k_{sb} values found different from 0.28 in case of BO1 oil, but it has a close tendency to acquire this value (except P-3) in case of oil BO2. It is also important to observe that the relation $k_h+k_k=0.5$ was not found for the great majority of samples analyzed. However, intrinsic viscosities obtained by using single point determination methods were similar to values obtained by using graphic extrapolation method with small percentage differences. So values different from 0.5 did not put any restriction for the application of SC and DC equation.

Table 1. Base oil properties

Base oil	Density (g.cm^{-1})at 40^{0}C	Viscosity at 40^{0}C	Viscosity at 100^{0}C	Cloud point	Pour point
BO1	0.848	7.47	3.5	-8	-3
BO2	0.904	20.25	5.5	-10	-6

Table 2. Composition of the monomers in the co polymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. P-1 is homopolymer of decyl acrylate (DA); P-2 to P-3 is the copolymer of DA+ different mass fractions of styrene

Sample No	% of weight in the feed		% of weight in copolymer	
	DA	Styrene	By PMR method	By FT-IR
P-1	100	00		
P-2	95	5	1	1.5
P-3	90	10	2	2.1

Table 3. Thermal Gravimetric Analysis Data of all prepared samples

Sample	Decomp.Tempr	PWL
P-1	250/340	23/86
P-2	300/400	45/84
P-3	320/430	60/85

Table 4. Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^b_{SC}$	$[\eta]^b_{DC}$
P-1	2.691	3.075	2.974	2.931	3.515	3.544	3.649
P-2	1.967	2.036	2.054	1.938	2.162	2.18	2.213
P-3	1.294	1.020	1.118	1.343	1.974	1.99	2.005

Table 5. Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^b_{SC}$	$[\eta]^b_{DC}$
P-1	4.642	4.303	4.609	4.571	4.718	4.687	4.746
P-2	3.317	3.538	3.602	3.684	3.836	3.832	3.821
P-3	3.501	3.187	3.430	3.555	3.925	3.921	3.917

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Table 6. Viscometric constant values in BO1 oil

Sample	k_h	k_k	k_m	k_{sb}	$k_h+k_k= 0.5$
P-1	1.08	3.64×10^{-3}	0.692	0.74	1.083
P-2	0.80	-0.186	3.374	1.72	0.614
P-3	0.70	-5.103	0.513	0.524	-4.40

Table 7. Viscometric constant values in BO2 oil

Sample	k_h	k_k	k_m	k_{sb}	$k_h+k_k= 0.5$
P-1	0.063	0.245	1.474	0.107	0.308
P-2	0.66	-0.376	-8.89×10^{-3}	0.77	0.284
P-3	0.535	-0.432	1.44	0.705	0.103

Table 8 - 9 presents the percentual differences of intrinsic viscosity values where Huggins value taken as references. In both the oils it is observed that that differences is smaller in graphic extrapolation method compared to single point determination method. It is also observed that the differences is smaller in oil BO2 compared to oil.BO1

Table 10 – 11 presents viscometric molecular weight of all the polymers (homo and copolymer). Homopolymer showed higher molecular weight than the copolymer. As expected the molecular weights are greater in oil BO2 compared to oil BO1. Again in oil BO1, a gradual decrease in viscometric molecular weight of the copolymer was observed with increase in styrene concentration although such a variation was not observed in oil BO2.

Table 8. Percentual differences ($\Delta \% = 100 \times [\eta]/[\eta]_h - 100$) of intrinsic viscosity values (In BO1 oil), Where Huggins value taken as a reference

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	14.27	10.52	8.92	30.62	31.70	35.6
P-2	3.51	4.42	-1.47	9.91	10.83	12.51
P-3	-21.17	-13.6	3.79	52.55	53.79	54.95

Table 9. Percentual differences ($\Delta \% = 100 \times [\eta]/[\eta]_h - 100$) of intrinsic viscosity values (In BO2 oil) ,Where Huggins value taken as a reference

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	-7.30	-0.71	-1.53	1.64	0.97	2.24
P-2	6.66	8.59	11.06	16.46	15.53	15.19
P-3	-8.97	-2.03	1.54	12.11	11.99	11.88

Table 10. Viscometric molecular weight of all prepared sample in BO1 oil by using Mark –Houwink equation $[\eta] = KM^a$,Where K= 0.00387 and a = 0.725.

Sample	$M_h{}^a$	$M_k{}^a$	$M_m{}^a$	$M_{sb}{}^a$	$M_{sb}{}^b$	$M_{SC}{}^b$	$M_{DC}{}^b$
P-1	8315	9995	9545	9355	12019	12156	12656
P-2	5396	5659	5729	5287	6148	6219	6349
P-3	3029	2181	2475	3188	5423	5484	5541

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Table 11. Viscometric molecular weight of all prepared sample in BO2 oil by using Mark –Houwink equation
[η] = KM^a ,Where K= 0.00387 and a = 0.725.

Sample	$M_h{}^a$	$M_k{}^a$	$M_m{}^a$	$M_{sb}{}^a$	$M_{sb}{}^b$	$M_{SC}{}^b$	$M_{DC}{}^b$
P-1	17639	15887	17467	16951	18039	17876	18187
P-2	11095	12128	12432	12824	13559	13540	13486
P-3	11954	10500	11620	12208	13995	13975	13956
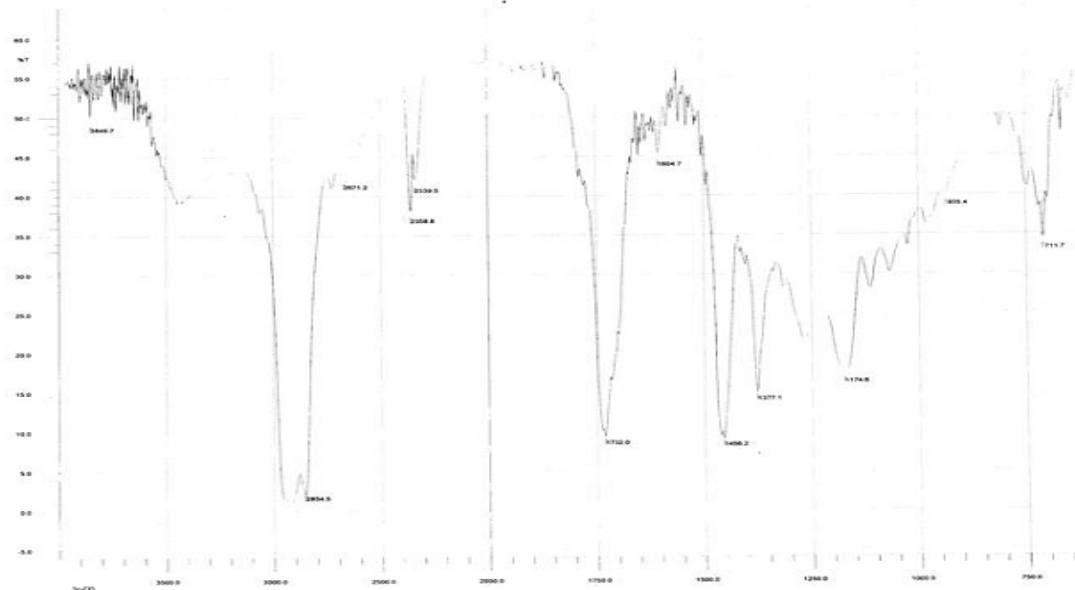
Figure 1. FT-IR spectrum of poly decylacrylate
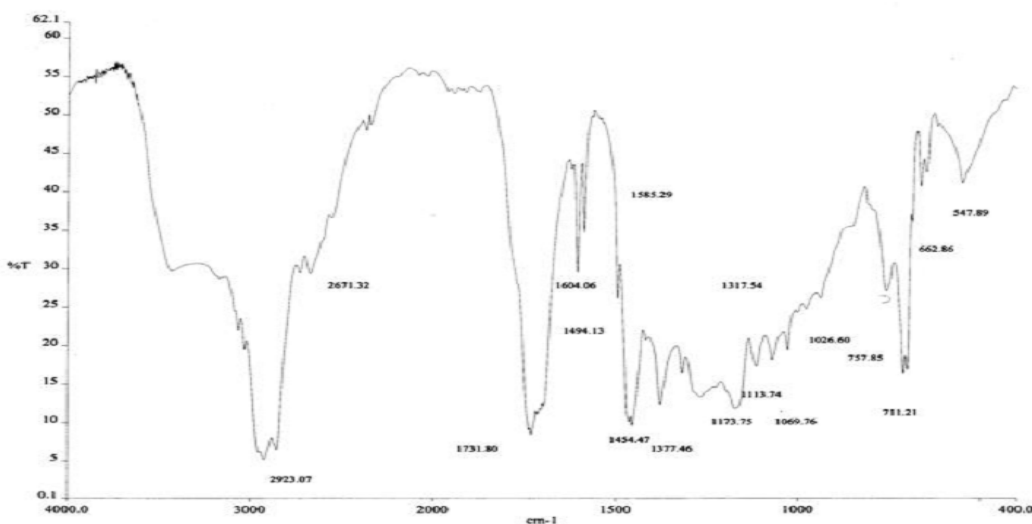
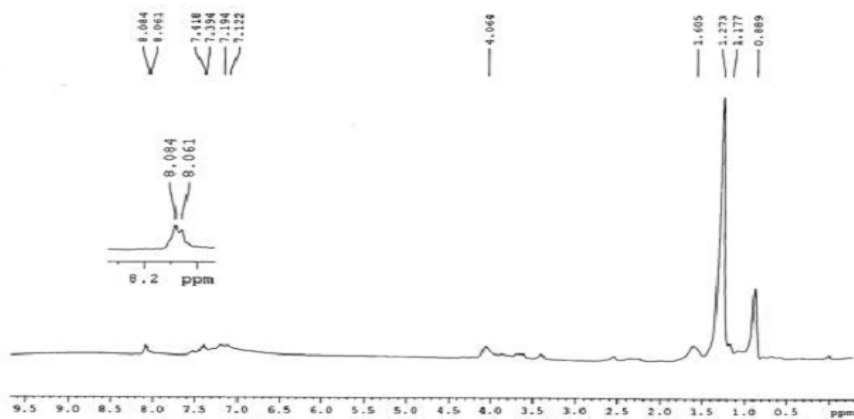**Figure 2. FT-IR spectrum of copolymer of decyl acrylate with styrene**

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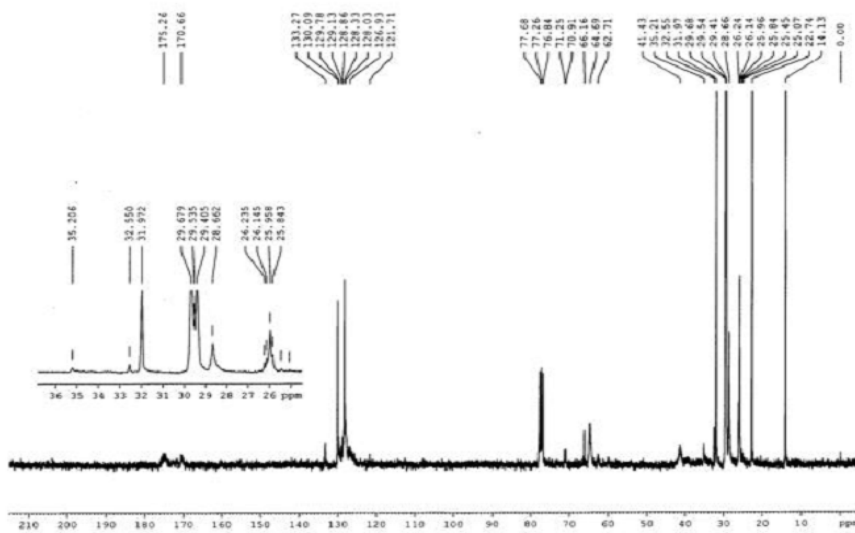**Figure 3. ^{1}H NMR spectrum of copolymer of decyl acrylate with styrene**

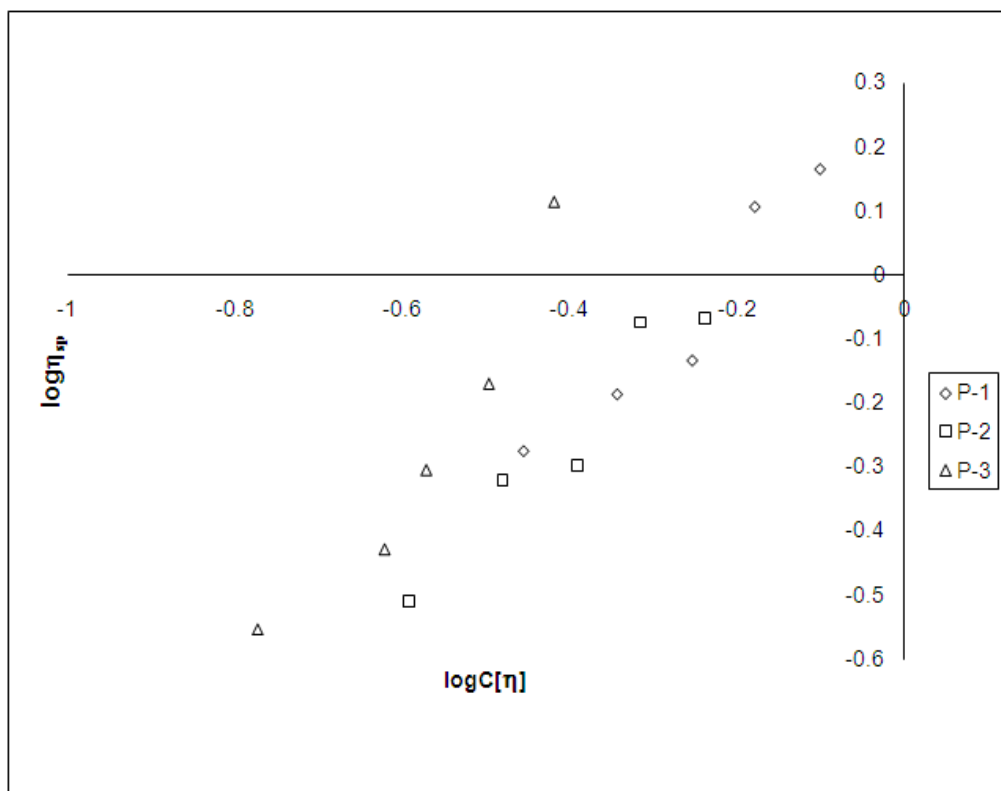**Figure 4. 13C NMR spectrum of copolymer of decyl acrylate with styrene**

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Figure 5a. Plot of logη$_{sp}$ vs logC[η] for BO1.

CONCLUSION

Viscometric analysis of the polymer may be carried out in lubricating oil to get more information about their morphological structure when added to the oil as a performance additive. Oil compatibility of the additive can be predicted easily through Viscometric analysis. Study also indicated that styrene incorporation enhances the thermal stability of this acrylate copolymer used as performance additive in lubricant formulation. This work is probably the first report of viscometric studies of polymeric additives in base oils.

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