

## **Chapter II**

### **Synthesis and a Study as a Multifunctional Ecofriendly Lubricating Oil Additives of Castor Oil Based Polymer**

### 2.2.1 Introduction

Lubricating oil is a complex mixture of paraffinic, aromatic, and naphthenic hydrocarbons, and the main function is to lubricate the engine. The functioning and longevity of lubricating are very poor in an automotive engine without any additive. Therefore, the addition of additives to lubricating oil is very essential for the smooth running of the modern engine. Lubricants are generally liquids or semiliquids which are used to lubricate the automotive engine for their longevity and better performances. The main functions of lubricating oil are to reduce friction, to keep moving parts apart, transfer heat, protect against wear, prevent rust and corrosion, as detergents/dispersants as an antioxidant, etc. The petroleum-based lubricants exhibit satisfactory performance but they are not environmentally benign due to their ecotoxicity and non-biodegradability. The research on vegetable oils as base stocks or their derivatives as additives for base stocks is increasing significantly due to their biodegradable property and availability in nature. Moreover, they show excellent anti-wear properties [1]; enhanced extreme pressure (EP) additives performance [2]; high viscosity index [3] and low volatility [4]. There are lots of research papers, where chemically modified vegetable oils have been used as an additive for base oil or base stocks in the formulation of bio-lubricant [5]. Castor oil contains a high percentage of triacylglycerols of ricinoleic acid (85–95%) which is a C–18 fatty acid. It contains a double bond at C–9 and a hydroxyl group at C–12 [6]. Castor oil is widely used in different important fields such as lubricants, pharmaceuticals, paints, adhesives, rubber, cosmetics, etc. [7]. The high flash point and due to the presence of polar hydroxyl group of castor oil make it efficient in the synthesis of additives for lubricating oil as well as bio lubricant [8], [9]. However research articles regarding the application of castor oil–styrene copolymer green multifunctional additive for

lubricant are very scanty. Therefore, in this work we have synthesized homopolymer of castor oil and copolymer with styrene in different percentage ratios to get thermally stable, cost-effective as well as eco-friendly lubricant additives. Styrene was chosen because due to incorporation it enhances the thermal stability of lubricant. Performance evaluation of polymeric additives was carried out as pour point depressant, viscosity index improver, and antiwear according to the respective ASTM method.

## 2.2.2 Experimental section

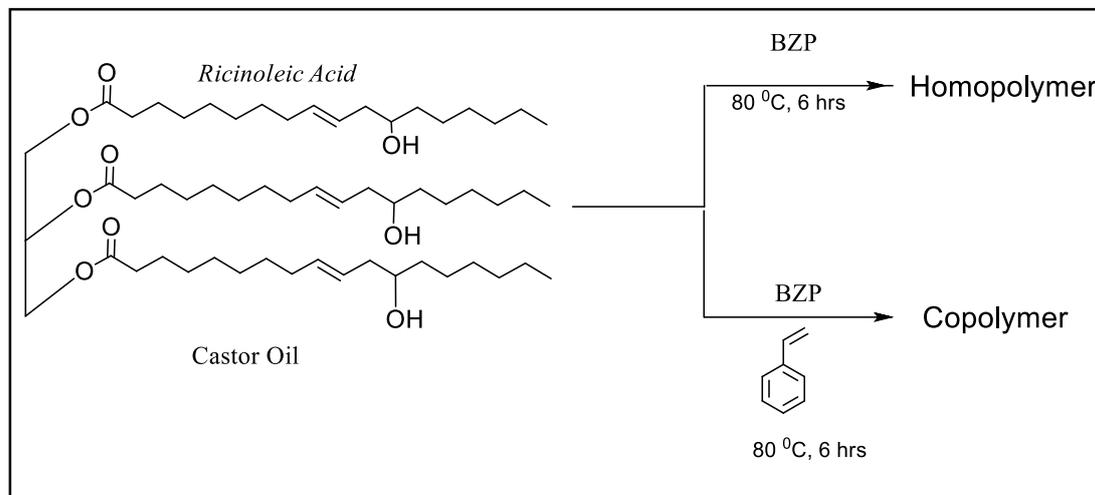
### 2.2.2.1 Materials

Castor oil (~85% unsaturation) was collected from the local grocery store and its fatty acid composition and properties are given in **Table 2.2.1**. Benzoyl peroxide (98%, LOBA Chemie, India) was used after recrystallization from the chloroform-methanol mixture. The mineral base oil SN150 was collected from IOCL, Dhakuria, West Bengal, India.

### 2.2.2.2 Synthesis of the polymers

The copolymers were prepared by taking the monomers of castor oil and styrene at different ratios (**Table 2.2.3**) in presence of BZP as the initiator by free radical polymerization method without any solvent. The polymerization was carried out in a three-necked round bottom flask with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. In the flask, a definite amount of castor oil and styrene was heated to 80<sup>0</sup> C and maintained for 20 minutes. Initiator BZP (0.5% w/w, with respect to the total monomer) was then added and heated for 6 hours keeping the temperature constant at 80<sup>0</sup>C.

**Scheme 2.2.1 Reaction for the preparation of homopolymer of castor oil and its copolymer with styrene**



## 2.2.3 Measurements

### 2.2.3.1 Spectroscopic measurements

NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe.  $\text{CDCl}_3$  and tetramethylsilane (TMS) were used as a solvent and as reference material respectively. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm potassium bromide cells at room temperature within the wavenumber range of 400 to 4000  $\text{cm}^{-1}$ .

### 2.2.3.2 Molecular weight determination

The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) were measured by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at 35 °C at a flow rate of 1 mL/min.

### 2.2.3.3 Thermogravimetric analysis (TGA)

TGA data were measured on Shimadzu TGA-50 system, at a heating rate of 10 °C / min.

#### **2.2.3.4 Performance evaluations of viscosity index**

Viscosity index (VI) is an important parameter that determines the change of viscosity of the lubricant with temperature change. It was calculated according to ASTM D 2270–10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40<sup>0</sup>C and 100<sup>0</sup>C

#### **2.2.3.5 Evaluation of pour point**

The pour point of the additive blended lube oil was determined according to the ASTM D 97–09 method using the cloud and pour point tester model WIL–471 (India).

#### **2.2.3.6 Evaluation of anti-wear performance**

The antiwear performance in terms of wear scar diameter (WSD) of the lubricant compositions was determined by Four–ball wear test apparatus (FBWT) following the ASTM D 4172–94 method. In this experiment, 392 N (40 Kg) load at 75<sup>0</sup>C for 60 min was applied to measure the wear scar diameter. The rotating speed and diameter of the ball were 1200 rpm and 12.7 mm respectively.

#### **2.2.3.7 Biodegradability test (Disc diffusion method)**

The biodegradability test was carried out for the prepared polymers against *Alternaria alternata* fungal. All the experiments were carried out in Petri dishes and were kept *in an* incubator at 37<sup>0</sup>C for 30 days after the addition of about 1g of the polymer sample. The change of yellow to blackish colour confirmed fungal growth. Culture media strain was prepared by mixing a suitable amount of potato extract, dextrose, and agar powder. After 30 days, the polymer samples were collected from the fungal media by CHCl<sub>3</sub> and then purified and dried. The dried samples were weighed.

## 2.2.4 Results and discussion

### 2.2.3.1 Spectroscopic data analysis

The homopolymer of castor oil exhibited an IR absorption band at  $1735.0\text{ cm}^{-1}$  for the ester carbonyl group. The peaks at  $2854.4\text{ cm}^{-1}$  and  $2922.1\text{ cm}^{-1}$  are the stretching vibration of  $-\text{CH}_2-\text{CH}_3$  group. A broad peak at  $3442.9\text{ cm}^{-1}$  is due to the free  $-\text{OH}$  group present in castor oil (**Figure 2.2.1**). The absorptions peak at  $1739.5\text{ cm}^{-1}$  indicates the presence of the ester carbonyl group in the copolymer. Peaks at  $724.5\text{ cm}^{-1}$  and  $699.9\text{ cm}^{-1}$  were showed the presence of C-H bond of the phenyl group of styrene in the copolymer. In the  $^1\text{H}$  NMR spectra of the homopolymer of castor oil, the peaks in the range of 4.118–4.323 ppm indicates the protons of  $-\text{COOCH}_2$  group of castor oil. The peaks in the range of 3.60–3.71 ppm are for the  $-\text{OH}$  group of castor oil. No peaks in the range of 5–6 ppm indicate the polymerization was carried out successfully. The broad peaks that appeared in the range of 7.16 to 7.83 ppm indicate the protons of the benzene ring of styrene moiety in the copolymer. In the  $^{13}\text{C}$  NMR spectra of the homopolymer of castor oil, the ester carbonyl group appears in the range of 172.95–177.41ppm. The carbons of  $-\text{OOCH}_2$  group of castor oil appear at 62.10–68.86 ppm. The peak at 71.50 ppm is the carbon which is joined to  $-\text{OH}$  group of castor oil. No peaks in the range of 120–150 ppm indicate that polymerization was carried out successfully. The carbons of the benzene ring showed peaks in the range of 125.35 to 132.89 ppm in the copolymer. The peaks in the range of 172.86 to 176.77 ppm indicate the presence of the ester carbonyl group in the copolymer.

### 2.2.3.2 Molecular weight data analysis

The experimental values of number average molecular weights ( $M_n$ ), weight average molecular weights ( $M_w$ ) of the prepared polymers (P–1 to P–5) are given in **Table 2.2.2**. From the experimental data, it is seen that among the five polymers, P–5 has the

highest molecular weight. Moreover, it is also observed that with increasing the percentage of styrene in the backbone of castor oil, the molecular weight increases. Therefore, the percentage of styrene has a significant role during polymerization.

### 2.2.3.3 Analysis of TGA data

The TGA values of the five polymers are given in **Table 2.2.3**. From the table, it is clear that the thermal degradation of polymer P-1 is higher than the other polymers which signifies that P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4, and P-5 are almost identical. In the case of polymer P-1, major decomposition starts at 155<sup>0</sup>C with a 30% weight loss. For polymers P-3, P-4, and P-5, major decomposition starts approximately at 265<sup>0</sup>C with 18% weight loss. Due to the copolymerization of castor oil with styrene, the thermal stability increases. Therefore, copolymerization with styrene has significant importance to improve thermal stability.

### 2.2.3.4 Analysis of viscosity index values

VI was calculated at different concentrations ranging from 1% to 5% (w/w) to the base oil. The experimental values of VI are given in **Table 2.2.4**. From the table, it is found that VI values increase with increasing the concentration of polymers in the base oil. The viscosity of lubricating oil decreases with increasing temperature but an expansion of polymer molecules takes place with increasing temperature and due to this, the size of the micelle increases. This increased in micelle size interfere with the reduction of the viscosity of the lubricant [10]. Moreover, with increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer micelle in lube oil and improves the VI property [11]. It has been observed that the VI value increases by the incorporation of styrene in the backbone of the homopolymer of castor oil. This may be due to the higher crosslink density of the copolymers. The copolymer

P-5 has the highest effect on VI increments followed by P-4, P-3, P-2, and P-1. The higher values VI in the case of P-5 are due to the greater volume of the solvated additive molecule i.e. micelle compared to others. This may be due to its higher average molecular weights and lower PDI value.

#### **2.2.3.5 Analysis of Pour point values**

The pour points of the lubricants prepared by blending the polymers at different concentration levels ranging from 1% to 5% (w/w) are shown in **Table 2.2.5**. All the polymers are effective as PPD and the efficiency as pour point increases with increasing the concentration of polymers up to a certain limit (4% concentration). This indicates that at this concentration, the polymer interacts with the paraffinic wax of base oil effectively and decreases the size of crystals of the paraffinic wax [12]. Among the prepared five polymers, P-4 showed better performance as PPD. It may be due to a higher PDI value.

#### **2.2.3.6 Analysis of anti-wear properties**

The tribological properties of the lubricant compositions were determined by measuring WSD through FBWT apparatus applying 392 N load and values are given in **Table 2.2.6**. The anti-wear performance of the lube oil is significantly improved when the polymers are blended with it and is reflected in the lower WSD values of the lubricant compositions. The copolymers showed better results compared to the homopolymer. The polymer P-5 at 5% concentration showed the highest reduction in WSD values compared to the other polymers. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in castor oil [13], [14].

### 2.2.3.7 Analysis of biodegradability test results

The biodegradability test was carried out against *A. alternate* fungal. The percentage loss of mass after biodegradation of the polymers is given in **Table 2.2.7**. After biodegradation, the molecular weight of the recovered samples was determined by the GPC method and the results were compared with the respective samples before biodegradation and given in **Table 2.2.2**. Among the five polymers, polymer P-1 is highly biodegradable and polymer P-5 is the least [14].

### 2.2.5 Conclusions

From the above study, it was found that the homopolymer of castor oil and copolymer with styrene showed better performance as viscosity index improver, pour point depressant, and antiwear additive for base oil. Copolymers are more effective than homopolymers. The average molecular weight and thermal stability of copolymers increase with increasing the percentage of styrene. Due to biodegradability, the additives are eco-friendly also. Therefore, the above study is definitely a potential approach to formulate a green lubricant composition.

### 2.2.6 References

References are given in *BIBLIOGRAPHY* under “Chapter II of Part II” (Page No.146-147).

## 2.2.7 Tables and Figures

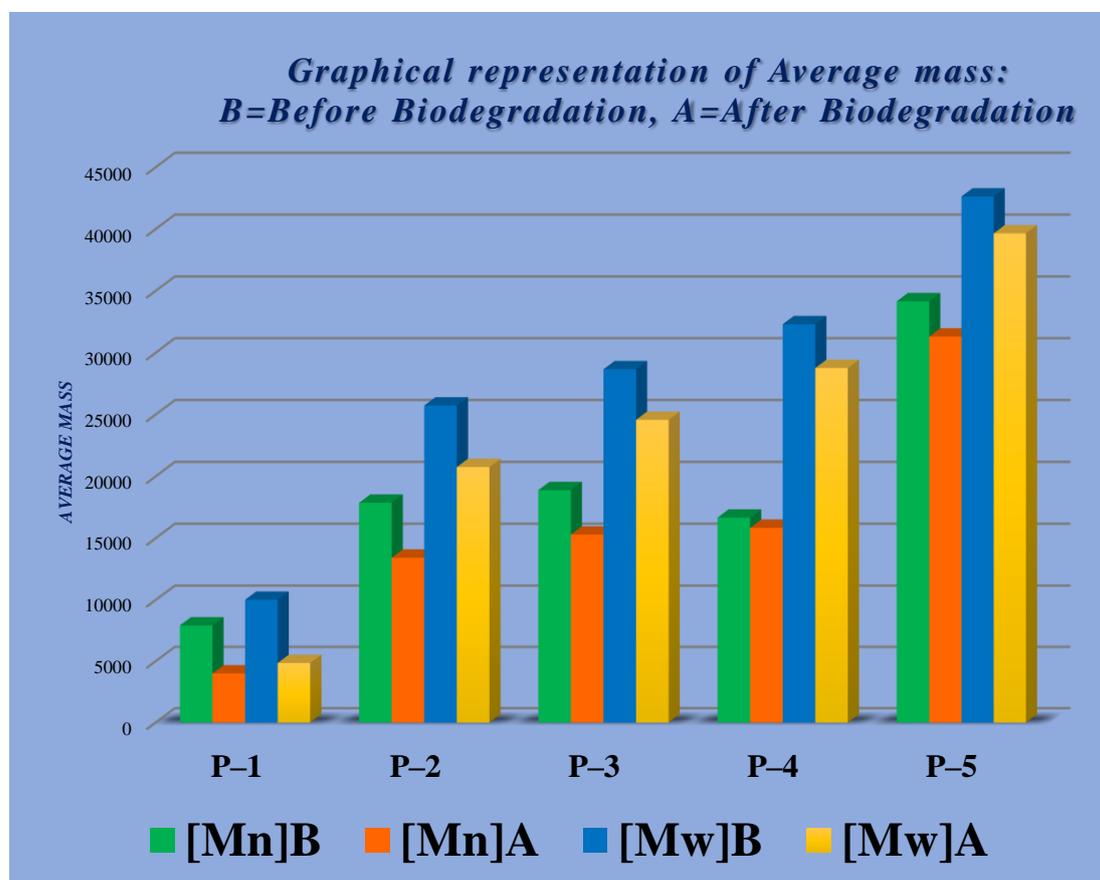
Table 2.2.1: Properties of castor oil

<i>Physical properties</i>	
Density (g.cm <sup>-3</sup> ) at 40 °C	0.95
Kinematic Viscosity (c St) at 40 °C	225.7
Kinematic Viscosity (c St) at 100 °C	18.5
Viscosity index	91
Flash point	210 °C
Pour point	-6 °C
Cloud point	-4 °C
<i>Chemical composition</i>	
<i>Fatty acids</i>	<i>Average percentage range</i>
Ricinoleic acid	83–85
Oleic acid	4–5
Linoleic acid	2–3
$\alpha$ – Linoleic acid	0.5–1
Stearic acid	0.5–1
Palmitic acid	0.5–1
Dihydroxystearic acid	0.3 – 0.5

**Table 2.2.2: Molecular weight of the prepared polymers and its graphical representation**

Polymer Code	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI
P-1	7928	10022	1.26	4014	4865	1.2
P-2	17879	25736	1.44	13432	20766	1.55
P-3	18897	28669	1.52	15302	24585	1.6
P-4	16671	32312	1.94	15846	28772	1.8
P-5	34170	42644	1.25	31320	39664	1.3

*P-1=100% CO; P-2=97.5% CO + 2.5% sty; P-3=95% CO+5% sty; P- 4=92.5% CO + 7.5% sty; P-5=90% CO +10% sty; CO=castor oil; Sty=styrene; Mn=number average molecular weight; Mw=weight average molecular weight; PDI= polydispersity index.*



**Table 2.2.3: Percentage composition and TGA values of the prepared polymers**

<i>Polymer Code</i>	<i>% of monomers</i>		<i>TGA values</i>	
	CO	Sty	Decom. Temp.	PWL
P-1	100	0	155/310	30/82
P-2	97.5	2.5	210/350	24/84
P-3	95	5	262/376	18/80
P-4	92.5	7.5	265/378	18/82
P-5	90	10	265/382	17/78

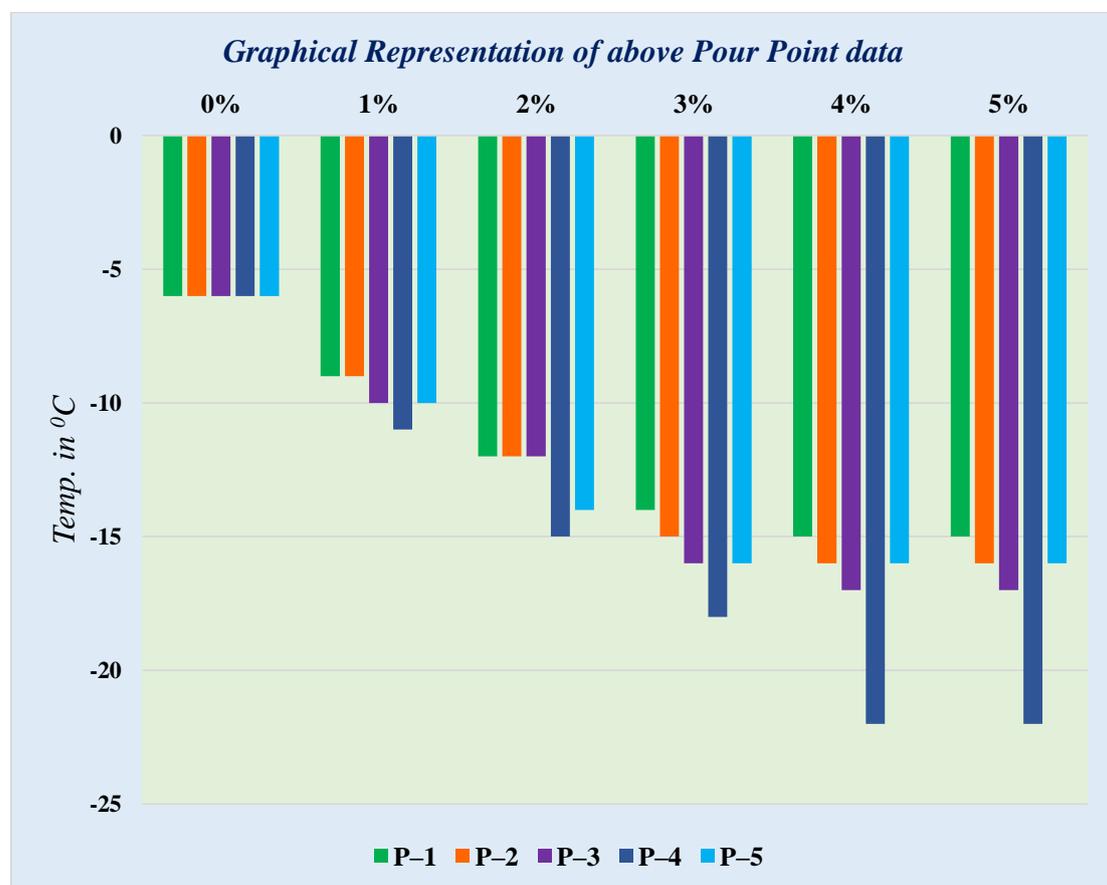
CO = Castor oil; Sty = Styrene; Decom. Temp.=Decomposition temperature;  
PWL= Percentage weight loss.

**Table 2.2.4: Viscosity index (VI) values of polymer blended base oil**

<i>Polymer Code</i>	<i>VI of polymer blended base oil at different concentrations( w/w)</i>					
	0%	1%	2%	3%	4%	5%
P-1	85.2	90	94.5	102	112	116
P-2	85.2	96	100	110	116	128
P-3	85.2	96	102	114	122	130
P-4	85.2	100	106	114	124	131
P-5	85.2	100.5	110	122.5	132	142

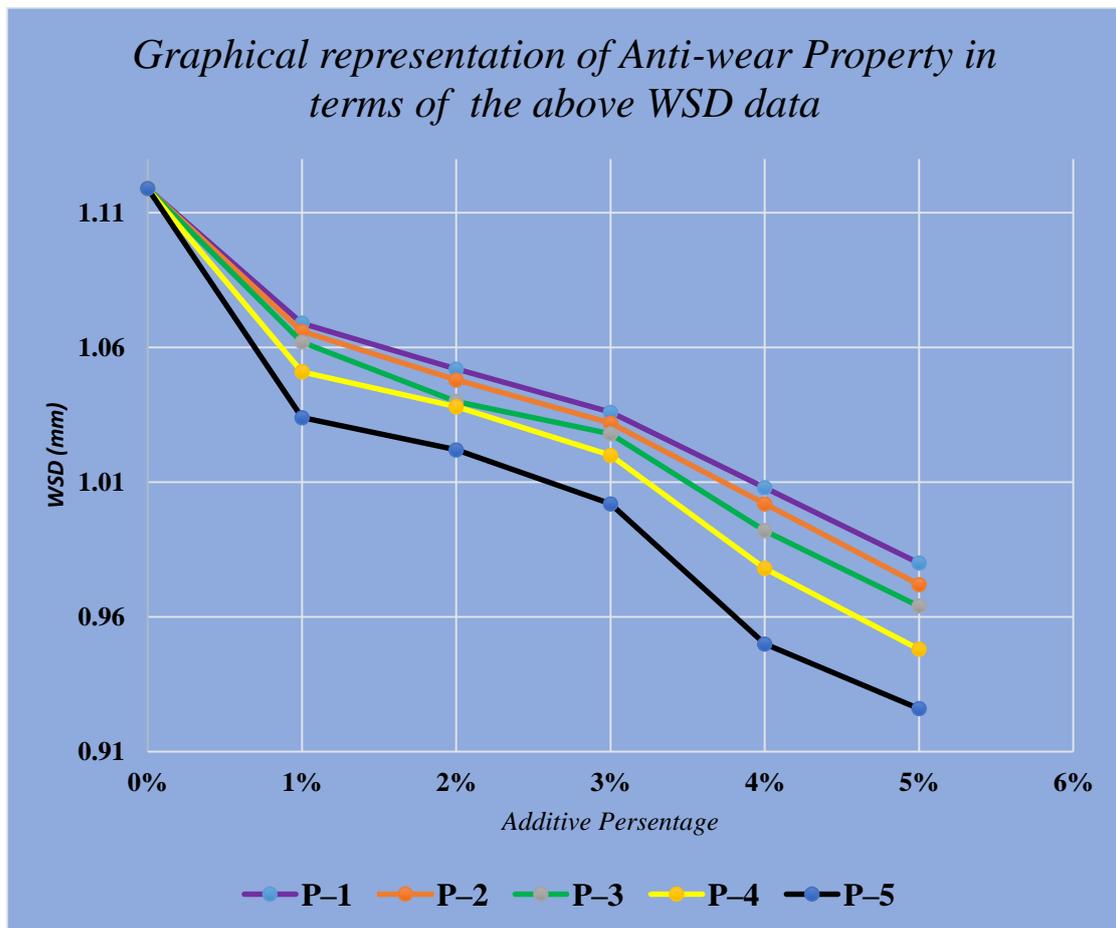
**Table 2.2.5: Pour point values of polymer blended base oil and its graphical representation**

Polymer Code	Pour point ( $0^{\circ}\text{C}$ ) of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-14	-15	-15
P-2	-6	-9	-12	-15	-16	-16
P-3	-6	-10	-12	-16	-17	-17
P-4	-6	-11	-15	-18	-22	-22
P-5	-6	-10	-14	-16	-16	-16



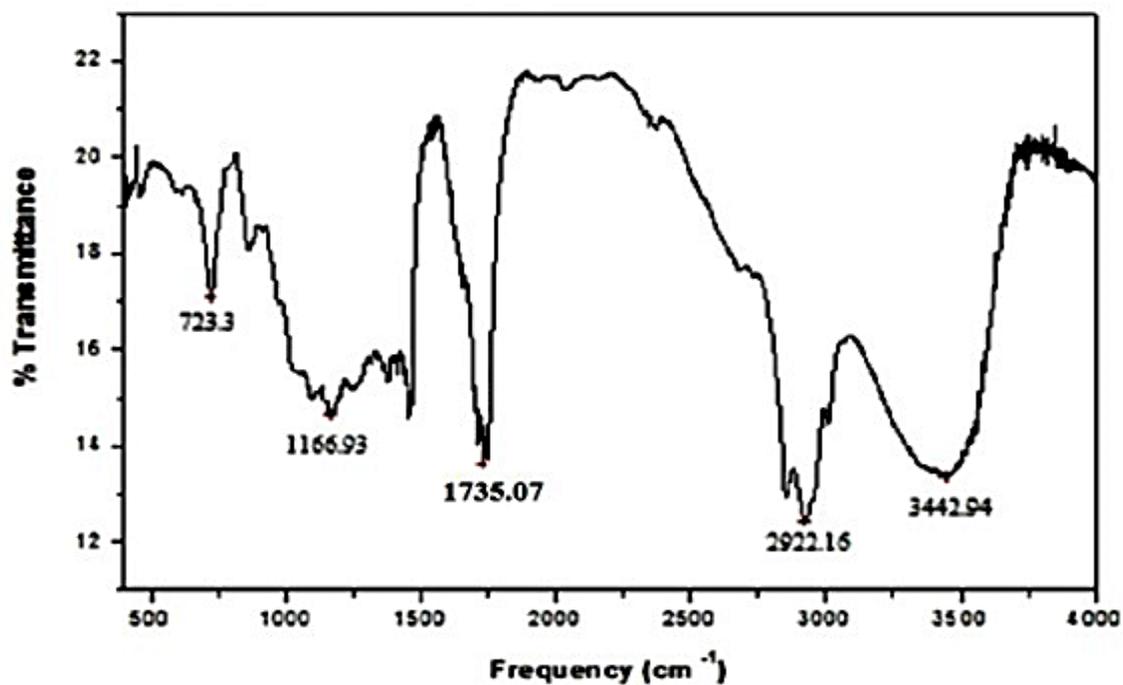
**Table 2.2.6: Ant-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition and its graphical representation**

Polymer Code	WSD of lubricant (in mm) at different polymer concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	1.119	1.069	1.052	1.036	1.008	0.98
P-2	1.119	1.066	1.048	1.032	1.002	0.972
P-3	1.119	1.062	1.04	1.028	0.992	0.964
P-4	1.119	1.051	1.038	1.02	0.978	0.948
P-5	1.119	1.034	1.022	1.002	0.95	0.926



**Table 2.2.7: Results of biodegradability test**

<i>Fungal pathogens</i>	<i>Polymer code</i>	<i>Incubation periods(days)</i>	<i>Initial weight (gm)</i>	<i>Final weight (gm)</i>	<i>Weight loss %</i>
<i>Alternata</i>	P-1	30	1.02	0.55	46.0
	P-2	30	1.04	0.68	34.6
	P-3	30	1.05	0.71	32.4
	P-4	30	1.00	0.78	22.0
	P-5	30	1.08	0.91	15.7

**Figure 2.2.1: FT-IR spectra of homopolymer of castor oil (P-1)**

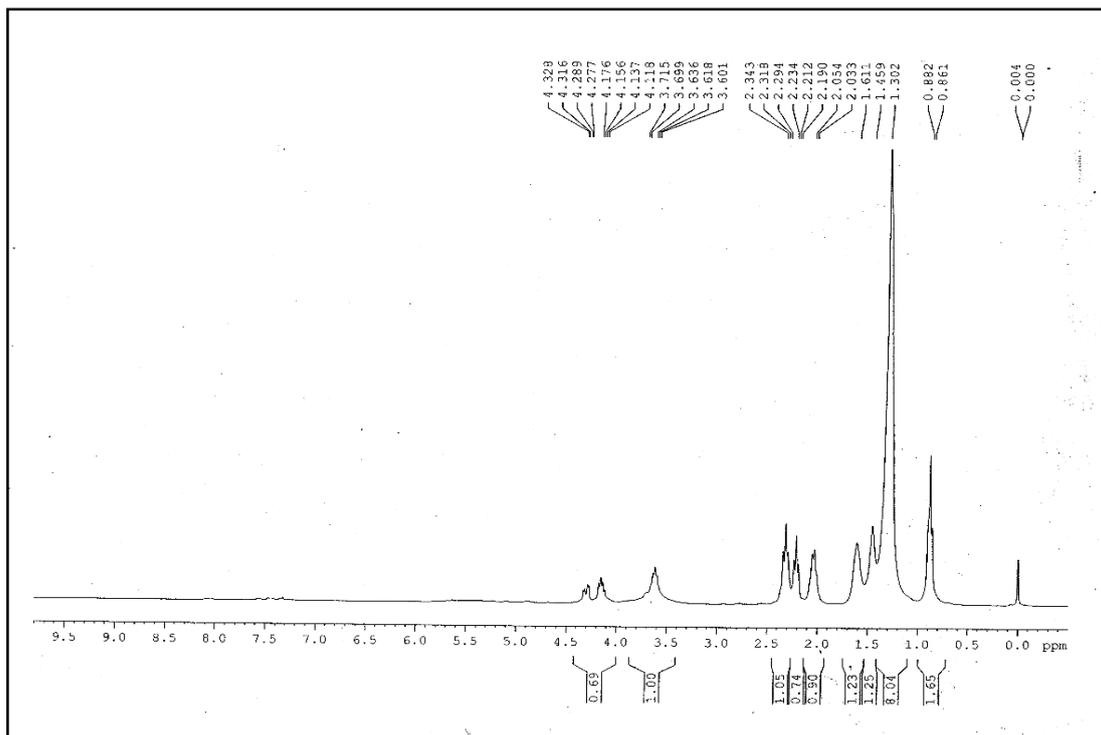


Figure 2.2.2:  $^1\text{H}$  NMR of homopolymer of castor oil (P-1)

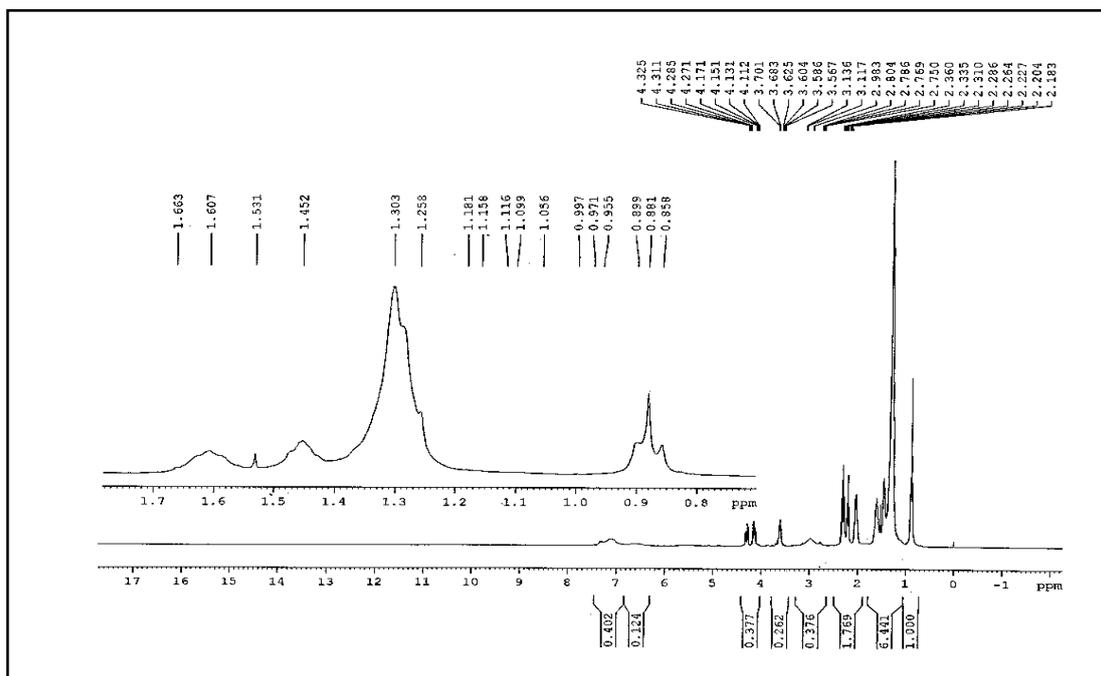
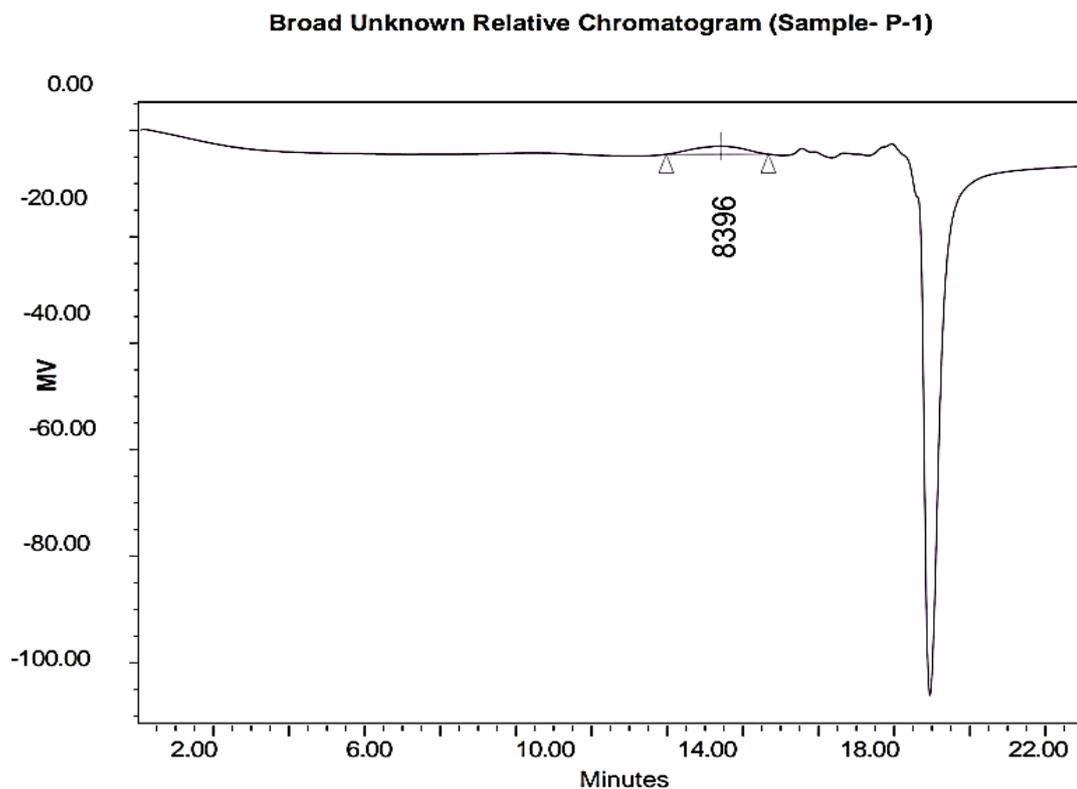
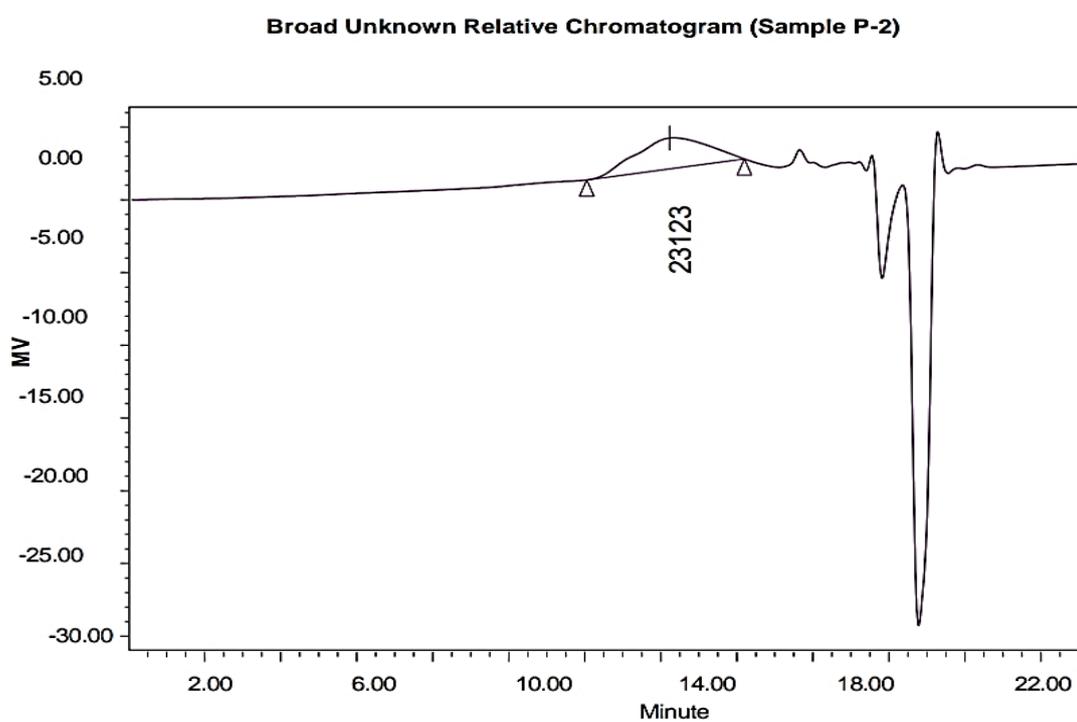


Figure 2.2.3:  $^1\text{H}$  NMR of copolymer of castor oil and styrene (P-2)



**Figure 2.2.4: GPC chromatogram of the copolymer P-1**



**Figure 2.2.5: GPC chromatogram of the copolymer P-2**

Broad Unknown Relative Chromatogram (Sample P-3)

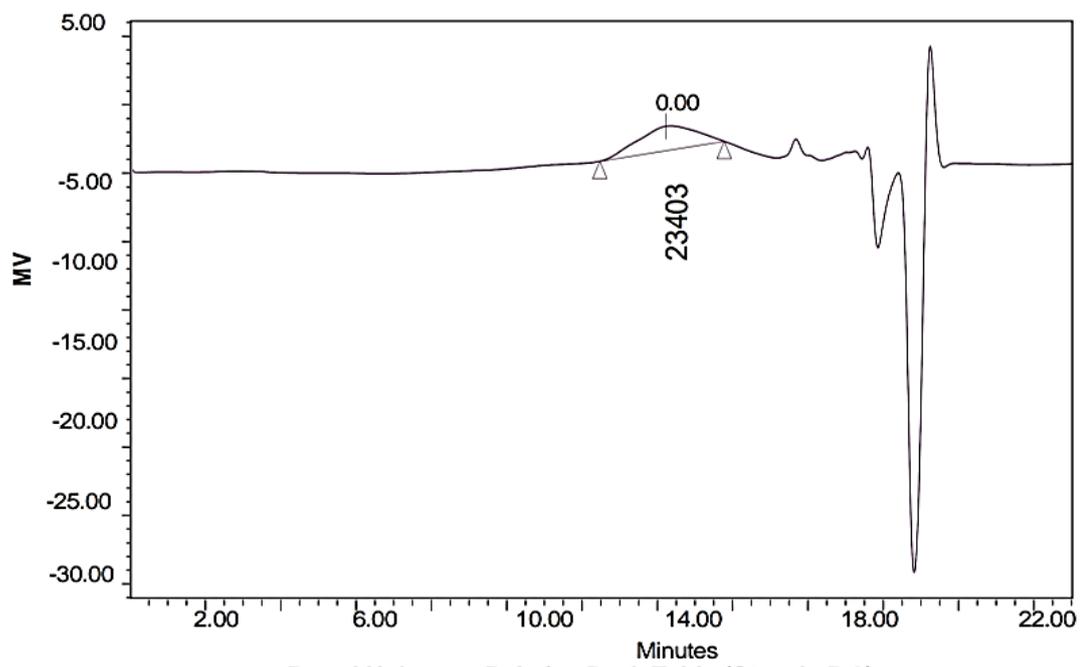


Figure 2.2.6: GPC chromatogram of the copolymer P-3

Broad Unknown Relative Chromatogram (Sample P- 4)

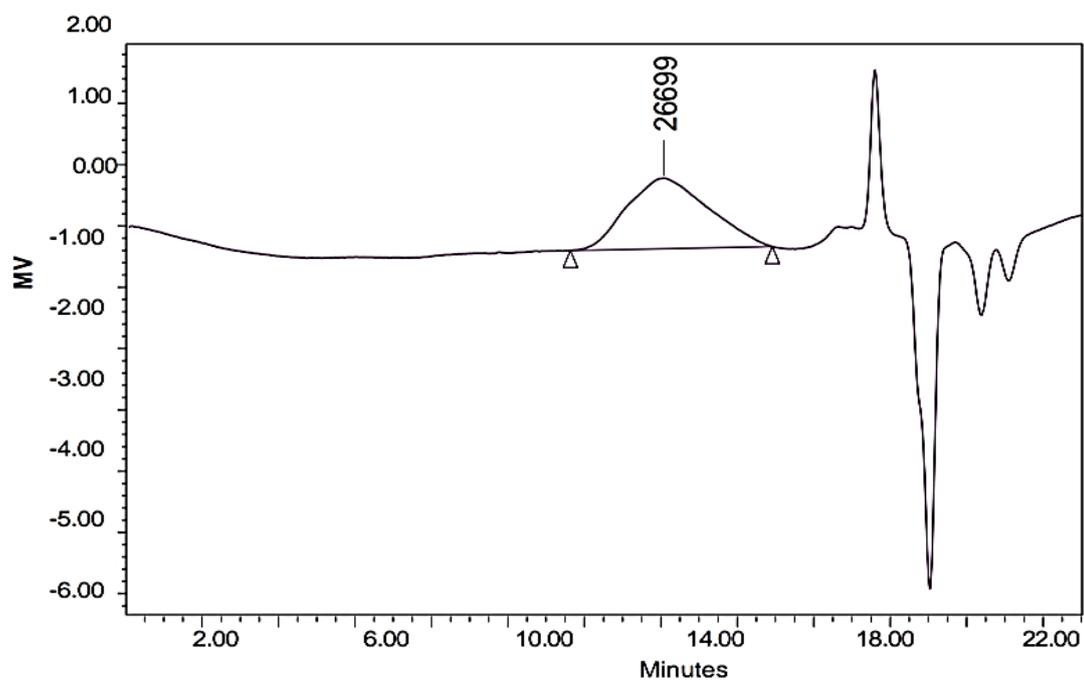
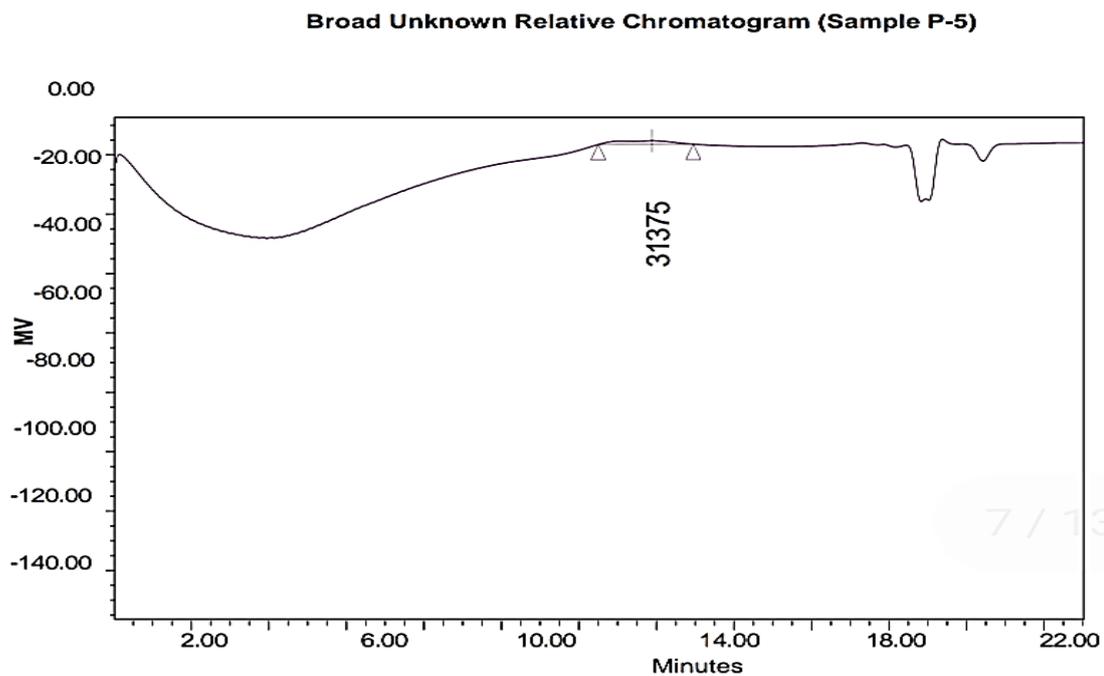
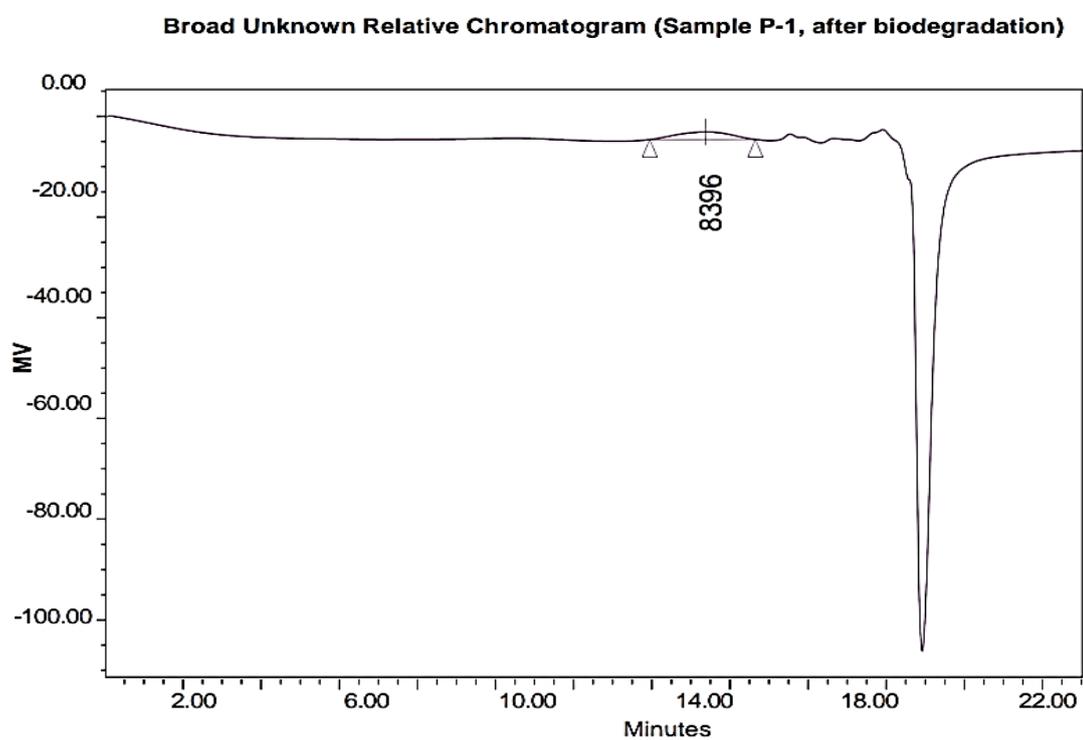


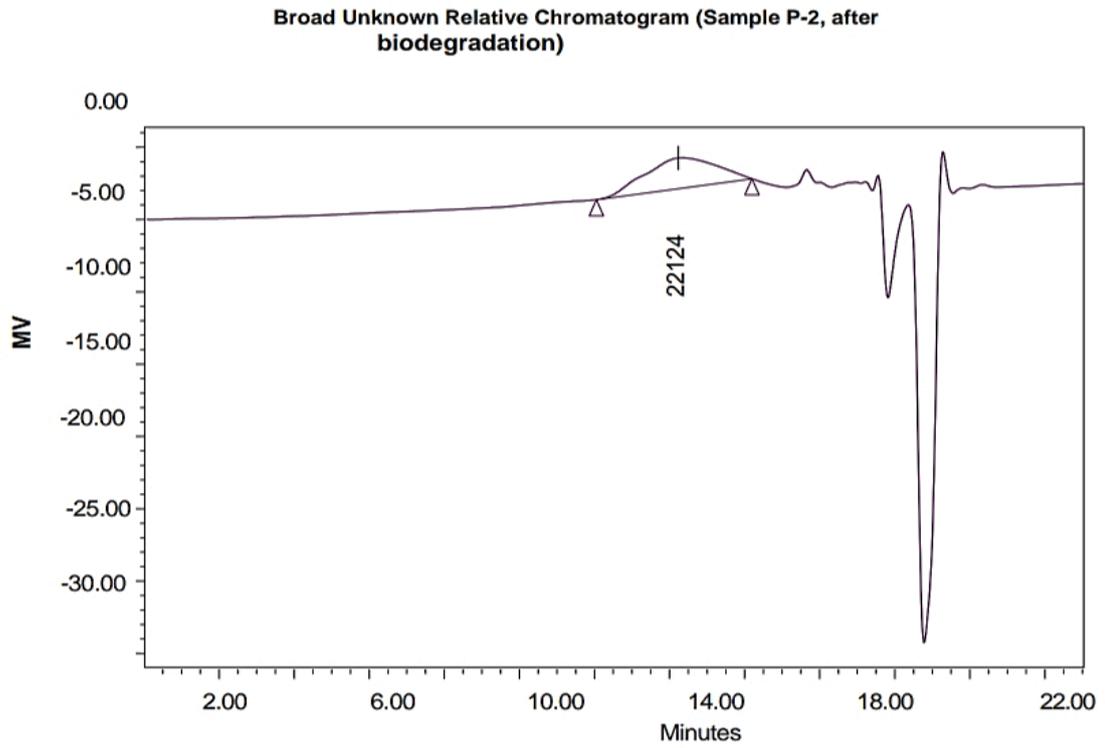
Figure 2.2.7: GPC chromatogram of the copolymer P-4



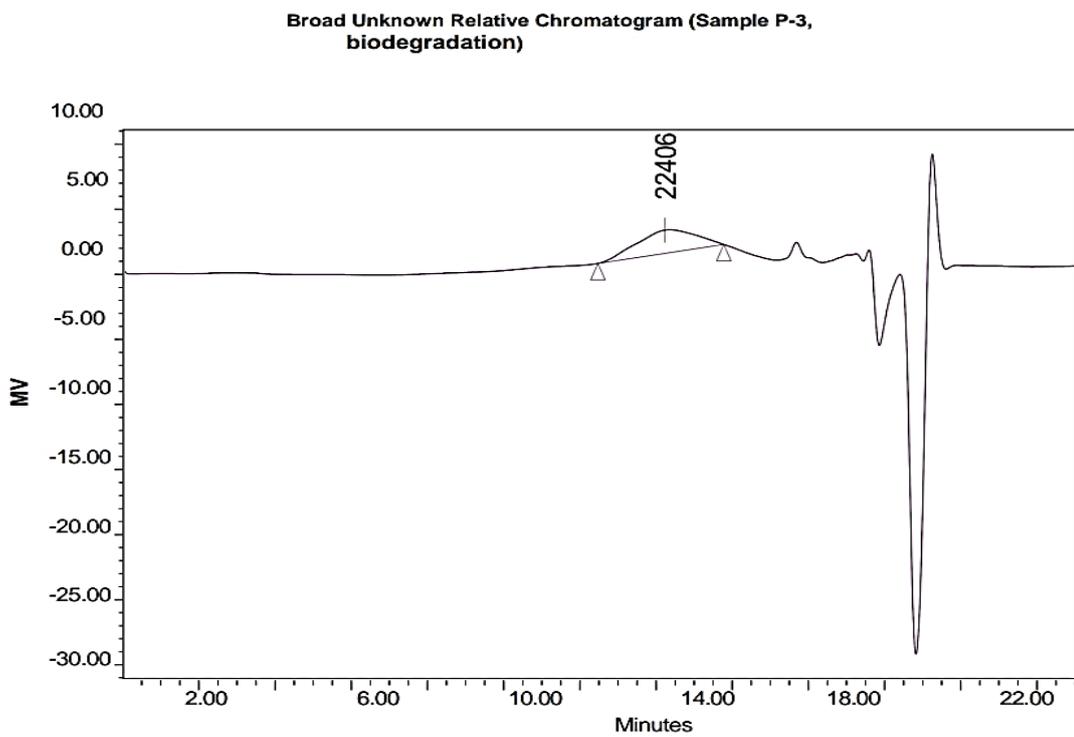
**Figure 2.2.8: GPC chromatogram of the copolymer P-5**



**Figure 2.2.9: GPC chromatogram of the copolymer P-1, after biodegradation**

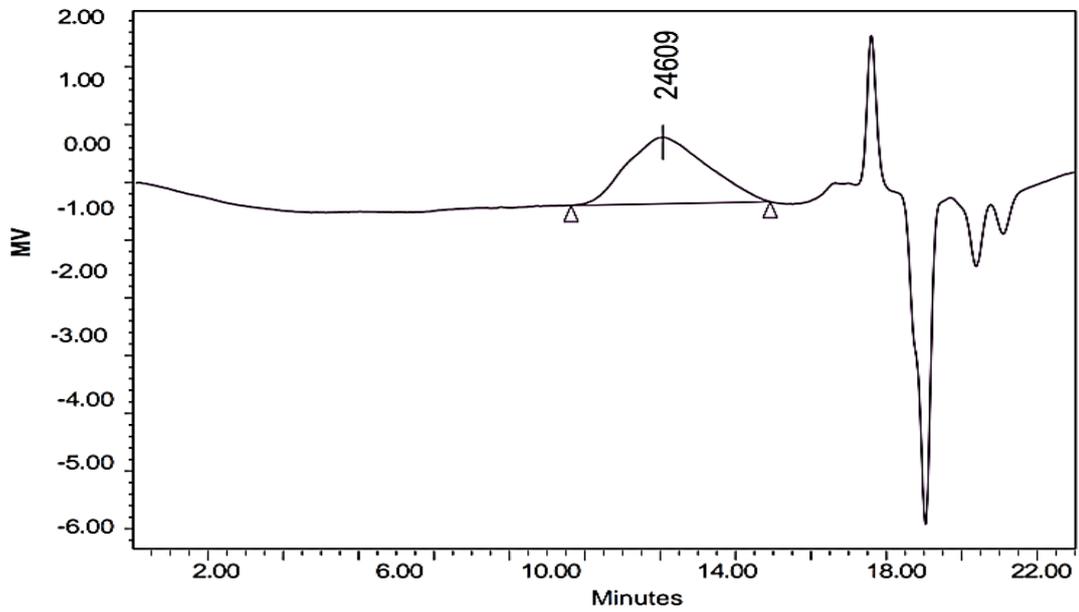


**Figure 2.2.10: GPC chromatogram of the copolymer P-2, after biodegradation**



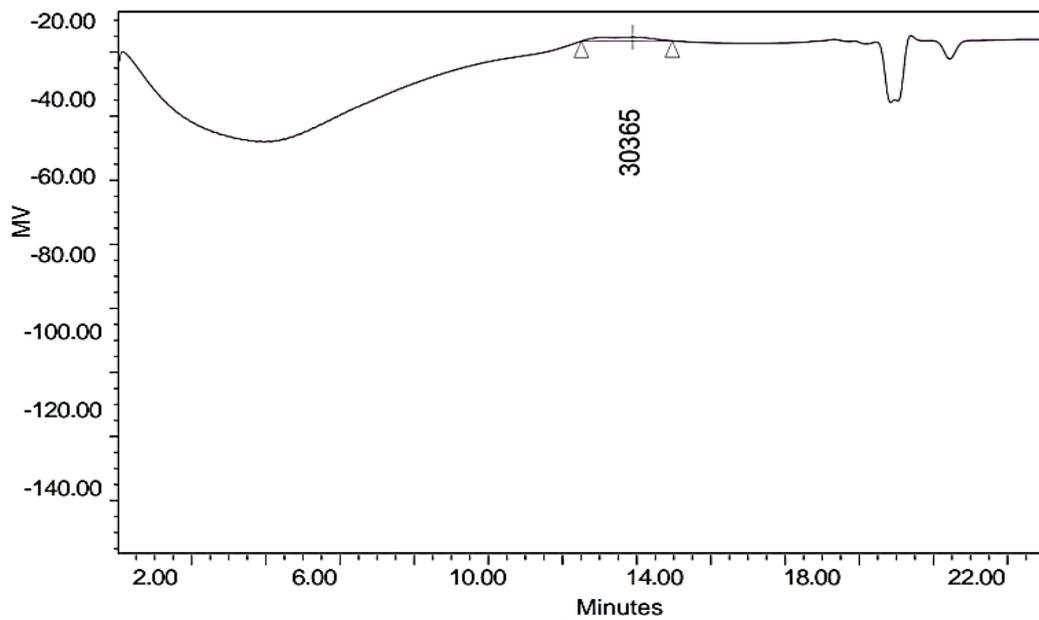
**Figure 2.2.11: GPC chromatogram of the copolymer P-3, after biodegradation**

**Broad Unknown Relative Chromatogram (Sample P-4, after biodegradation)**



**Figure 2.2.12: GPC chromatogram of the copolymer P-4, after biodegradation**

**Broad Unknown Relative Chromatogram(Sample P-5, after biodegradation)**



**Figure 2.2.13: GPC chromatogram of the copolymer P-5, after biodegradation**