

CHAPTER II

This chapter is divided into three sections, Section A, Section B and Section C

Section A comprises the Synthesis of Poly(acrylates) and their Copolymer with Styrene and Evaluation of their Performance as Pour Point Depressant for Lubricating Oil

Section B comprises the Evaluation of Poly(acrylates) and their Copolymer as Viscosity Modifiers

Section C comprises the Comparison of Viscometric Parameters of the Homo and Copolymer of Poly(decyl acrylate) in Lubricating Oil

2.1 SECTION A: Synthesis of Poly(acrylates) and their Copolymer with Styrene and Evaluation of their Performance as Pour Point Depressant for Lubricating Oil

2.1.1 Introduction

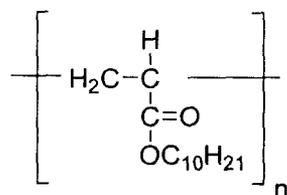
Pour point depressants are used to modify and control wax crystallization phenomena in paraffinic mineral oils. As temperature decreases, waxy components begin to form small, plate-like crystals. The plates eventually row together to form an interlocking network that effectively traps the remaining liquid. Flow ceases unless a force strong enough to break the relatively weak wax gel matrix structure is applied. Control of wax crystallization in lubricants is often described as pour point depressant (PPD). PPDs are used to maintain fluidity of lubricants under various cooling conditions, and their effectiveness depends on the lube oil composition and of course, on their chemistry and concentration [15].

Synthesis of poly(acrylates) (decyl, isodecyl and dodecyl) and their few copolymers with styrene, characterization of these polymers and their evaluation as pour point depressant comprises the subject matter of this chapter. The copolymers were prepared by varying the styrene concentration in the monomer mixture and employing free radical polymerization technique using benzoyl peroxide as initiator in toluene solvent. Characterization of the polymers (both homo and copolymer) was carried out employing IR, NMR and TGA techniques. Viscomertic characterization of these samples was carried out in toluene solvent.

2.1.2 Results and Discussion

Spectroscopic analysis

FT-IR spectrum of the poly(decyl acrylate) (Figure 1) exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1260 and at 1175 cm^{-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. From this discussion and from ^1H NMR spectral data (Figure 2) structure of this polymer may be presented by structure I.

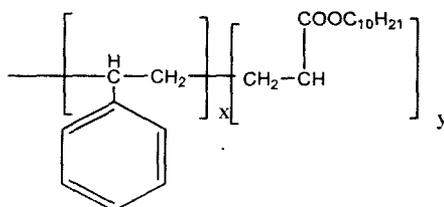


Structure I

The existence of the PDA- styrene copolymer was confirmed by FT-IR and NMR analysis. The copolymer in its IR spectrum (Figure 3) showed broad peak ranging from 1732 to 1720 cm^{-1} . This was attributed to the stretching vibration of the ester carbonyl group whereas the absorption bands at 758, 711, 695 and 662 cm^{-1} were due to C-H bond of the phenyl group of styrene.

In the ^1H NMR spectra (Figure 4) of one of the respective copolymers, a broad multiplet centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet at 4.06 ppm was due to the proton of the $-\text{OCH}_2$ group. The absence of singlet between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer.

The proton decoupled ^{13}C NMR spectrum (Figure 5) of the above sample of copolymer was in complete agreement with the original structure-II



Structure II

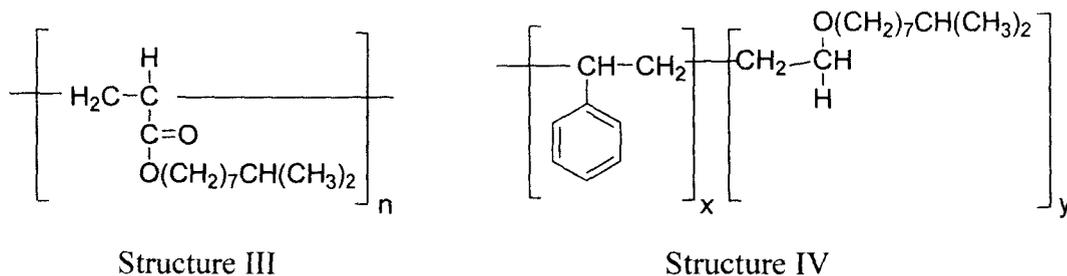
The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of $-\text{OCH}_2$ group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports [16, 17].

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 blends of known quantities of an ethylene-propylene

and poly(decyl acrylate) in which varied quantities of PDA were present. The comparative results obtained on comparisons are presented in Table 1.

FT-IR spectra (Figure 6) of homopolymer of isodecyl acrylate exhibited absorption at 1732 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at 1456.2, 1379, 1260 and 1166.9 cm^{-1} , owing to the CO stretching vibration and absorption bands at 750 and 710 cm^{-1} were due to the bending of C-H bond. In its ^1H NMR spectra (Figure 7) homopolymer of isodecyl acrylate showed a broad singlet centred at 4.02 ppm due to the proton of $-\text{OCH}_2$ group, a broad singlet at 0.86 ppm was due to methyl's of isodecyl chain. The proton decoupled ^{13}C -NMR (Figure 8) of the above sample was in complete agreement with the homopolymer.

The existence of its copolymer with styrene was confirmed by FT-IR, ^1H -NMR and ^{13}C -NMR analysis. In its FT-IR spectra (Figure 9) of the copolymer showed a broad peak ranging from $1722\text{--}1732\text{ cm}^{-1}$ along with other peaks at 753.56, 712.15, 700.75, 667.98 cm^{-1} were due to C-H bond of the phenyl group of styrene. In the ^1H NMR spectra (Figure 10) of the copolymer, a broad multiplet ranging from 7.23 to 7.58 ppm indicated the presence of phenyl group of styrene. Broad singlet at 4.06 ppm was due to the proton of $-\text{OCH}_2$ group. Methyls of the isodecyl chain appeared between 0.81 to 0.86 ppm at the absence of singlets between 5 and 6 ppm indicated the absence of any vinylic proton in the copolymer. The existence of copolymer was further confirmed by the presence of aromatic carbon ranging between 124 to 141 ppm in the ^{13}C -NMR spectrum (Figure 11) of the polymer. The carbonyl carbon appears at 174.47 ppm along with other carbons. From the above discussions probable structure of poly(isodecyl acrylate) and its copolymer with styrene was assigned as structure III and structure IV respectively.

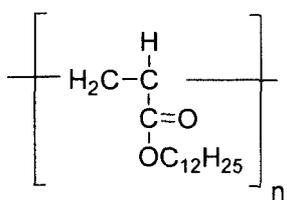


The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of signal of $-\text{OCH}_2$ group at 4.6 ppm and the area of signal of phenyl

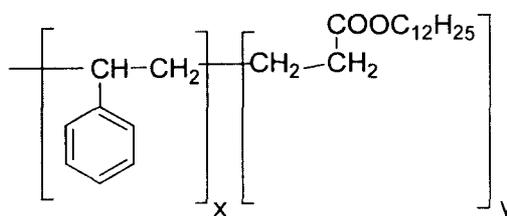
group at 7.41 ppm based on earlier reports [16, 17]. It was further confirmed through FT-IR spectral data. The intensity of carbonyl absorption in FT-IR spectra of the copolymer as compared to the same in a standard by analyzed for quantitative determination of the content of acrylate component in the copolymer (Table I).

FT-IR spectra (Figure 12) of the homopolymer of dodecyl acrylate exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration along with other peaks at 1456, 1260, 1164.9, 1112, 1028 and 711 cm^{-1} due to the bending of C-H bond. ^1H NMR spectra (Figure 13) of the homopolymer indicated the existence of $-\text{OCH}_2$ group at 4.02 ppm (broad singlet) along with the methyl protons ranging between 0.86 to 0.90 ppm together with methylene proton ranging between 1.3 to 1.6 ppm. The proton decoupled ^{13}C -NMR (Figure 14) of the above sample was in complete agreement with the homopolymer.

The existence of copolymer of dodecyl acrylate with styrene was confirmed by the analysis of FT-IR, ^1H NMR and ^{13}C -NMR spectra of the copolymer. FT-IR spectra (Figure 15) of the copolymer showed sharp peak at 1732 cm^{-1} for the ester carbonyl along with other peaks at 1028, 900, 760, 700 due to C-H bond of phenyl group of styrene. ^1H NMR spectra (Figure 16) of the copolymer showed broad singlet at 4.02 ppm due to $-\text{OCH}_2$ protons. A broad multiplet centered at 7.45 ppm was due to aromatic protons. The absence of singlet between 5 to 6 ppm indicated the absence of vinylic protons in the copolymer. ^{13}C -NMR spectrum (Figure 17) of the above sample showed the presence of ester carbonyl at 173 ppm with the aromatic carbon appeared in the range 125 to 134 ppm. The extent of incorporation of styrene in the polymer chain was also determined by the method as applied earlier and tabulated as Table I. The structure of poly(dodecyl acrylate) and its copolymer with styrene presented by structure V and structure VI.



Structure V



Structure VI

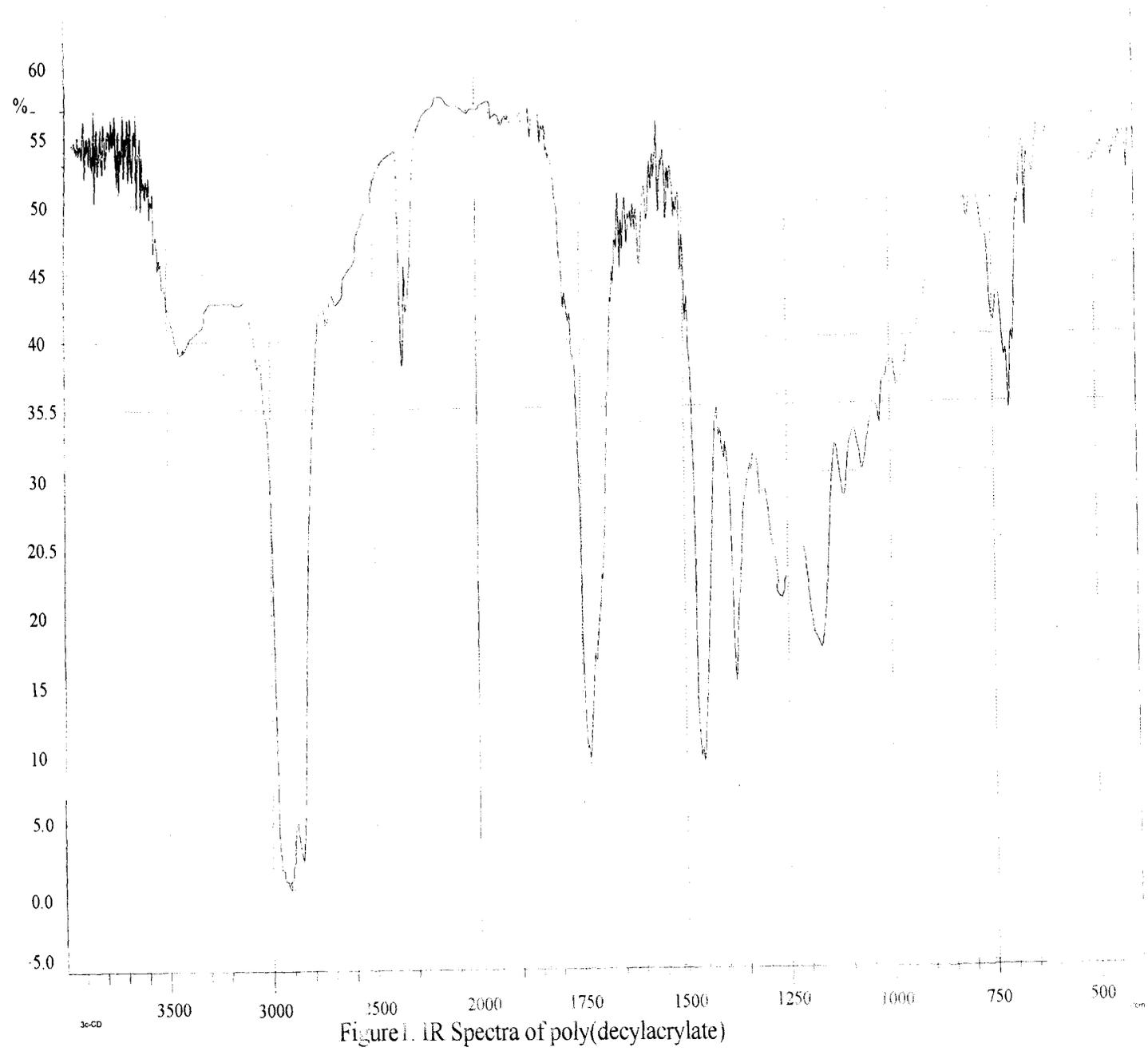
Thermal stability of the prepared compounds

Table 2 presents thermal stability data of all prepared sample. Introduction of styrene increases thermal stability of the acrylate polymer as was observed in our earlier studies [18].

Viscometric analysis

Viscometric data were obtained using the six equations mentioned in Part I, Chapter I. 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–Blascke (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–Blascke (SB) equation is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems. In this work, this value was used.

Table 3 presents intrinsic viscosity $[\eta]$ values related to all equations (eq 2 to 7) for the samples analyzed. Taking into account the data for all the homo and copolymer samples, it can be noticed that, the variation of $[\eta]$ values among each set of homo and copolymers (i.e., P-1 to P-4, P-5 to P-8 and P-9 to P-12) are consistent. There is a gradual decrease in the $[\eta]$ values with the increase in styrene concentration in the feed of the copolymer of PDA-styrene (P1-P4). Again it is observed that there is a sudden drop of the $[\eta]$ value as it proceeds from homopolymer to copolymer followed by a gradual increase in the same value with the increase in the styrene concentration for PIDA – styrene system (P-5 to P-8) and PDDA-styrene system (P-9 to P-12).



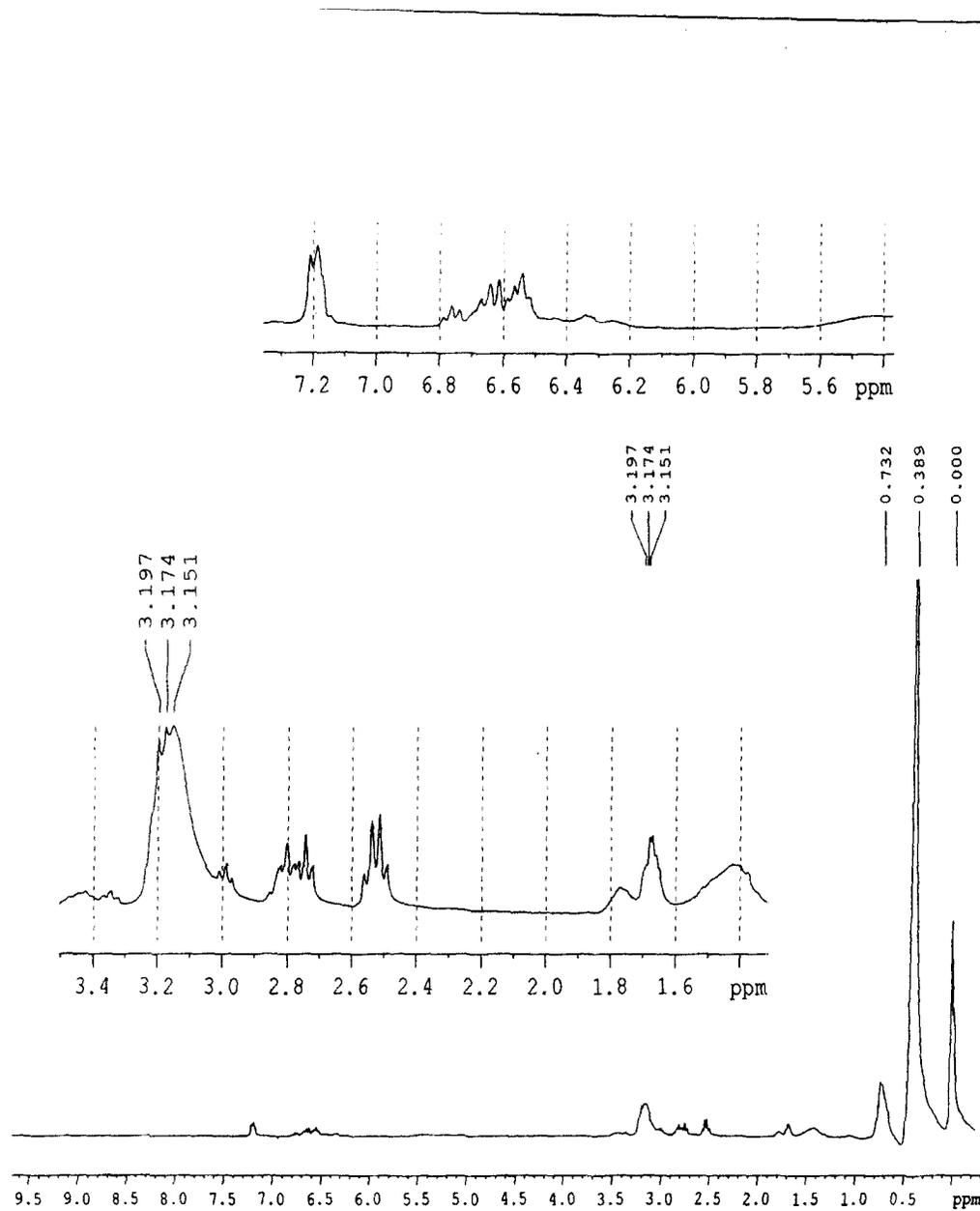


Figure 2. ¹H NMR of poly(decylacrylate)

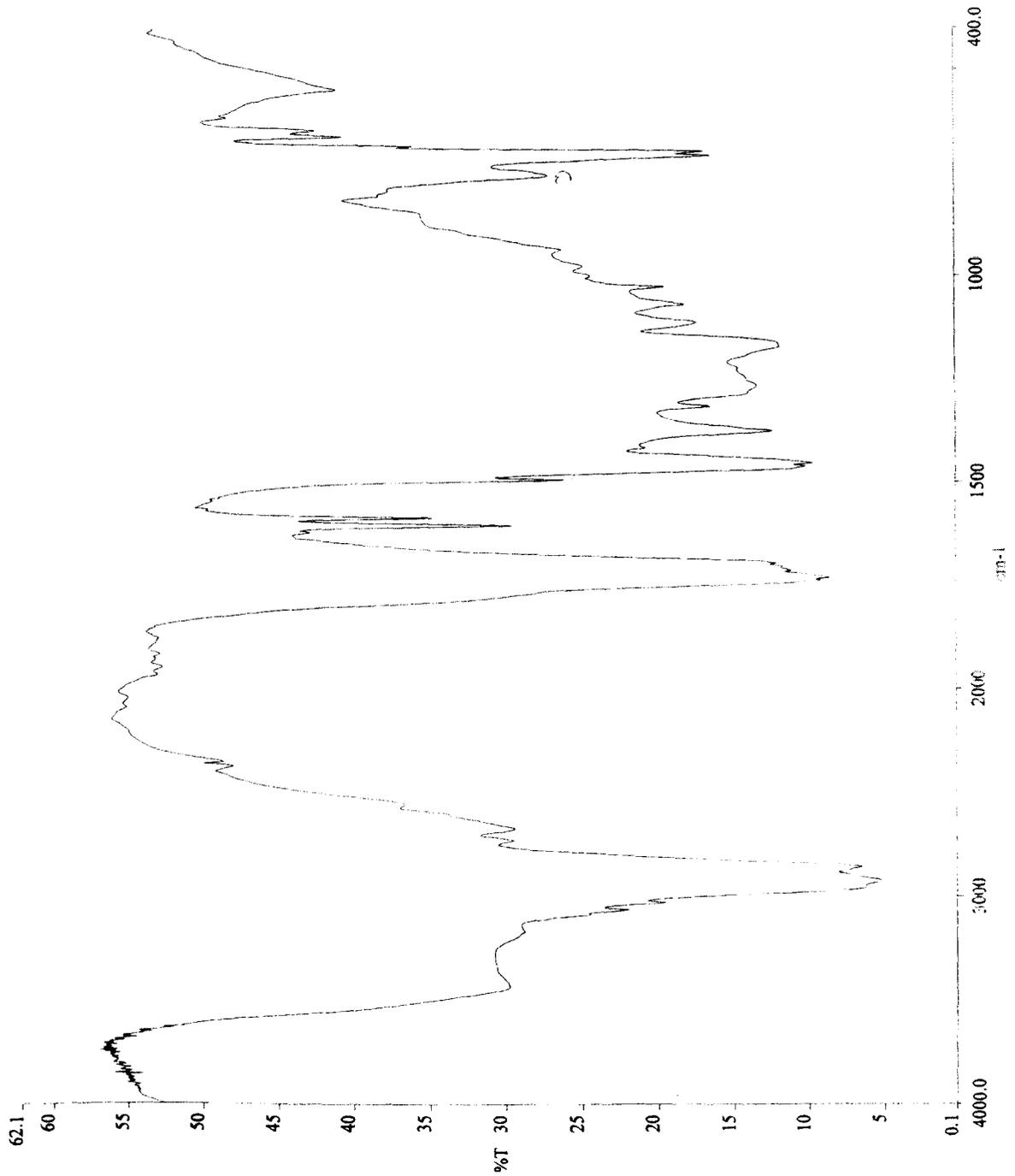
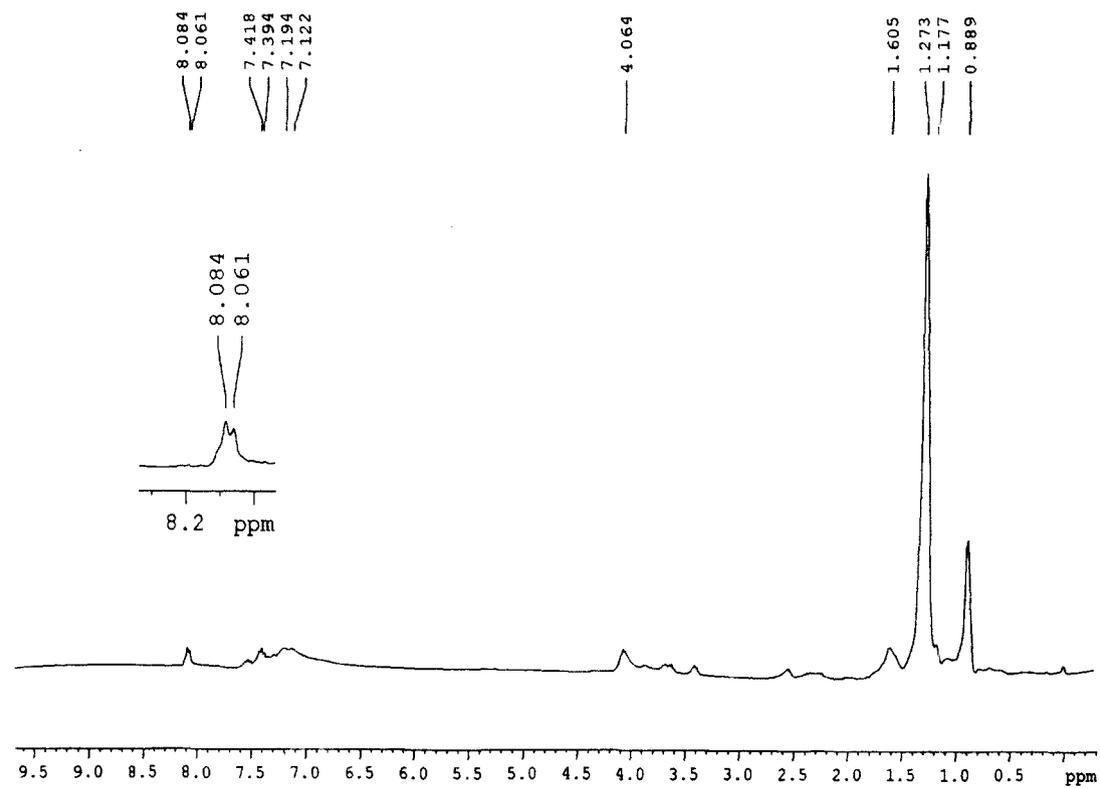


Figure 3. IR Spectrum of copolymer of butyl acrylate with styrene

Figure 4. ^1H NMR of copolymer of decylacrylate with styrene

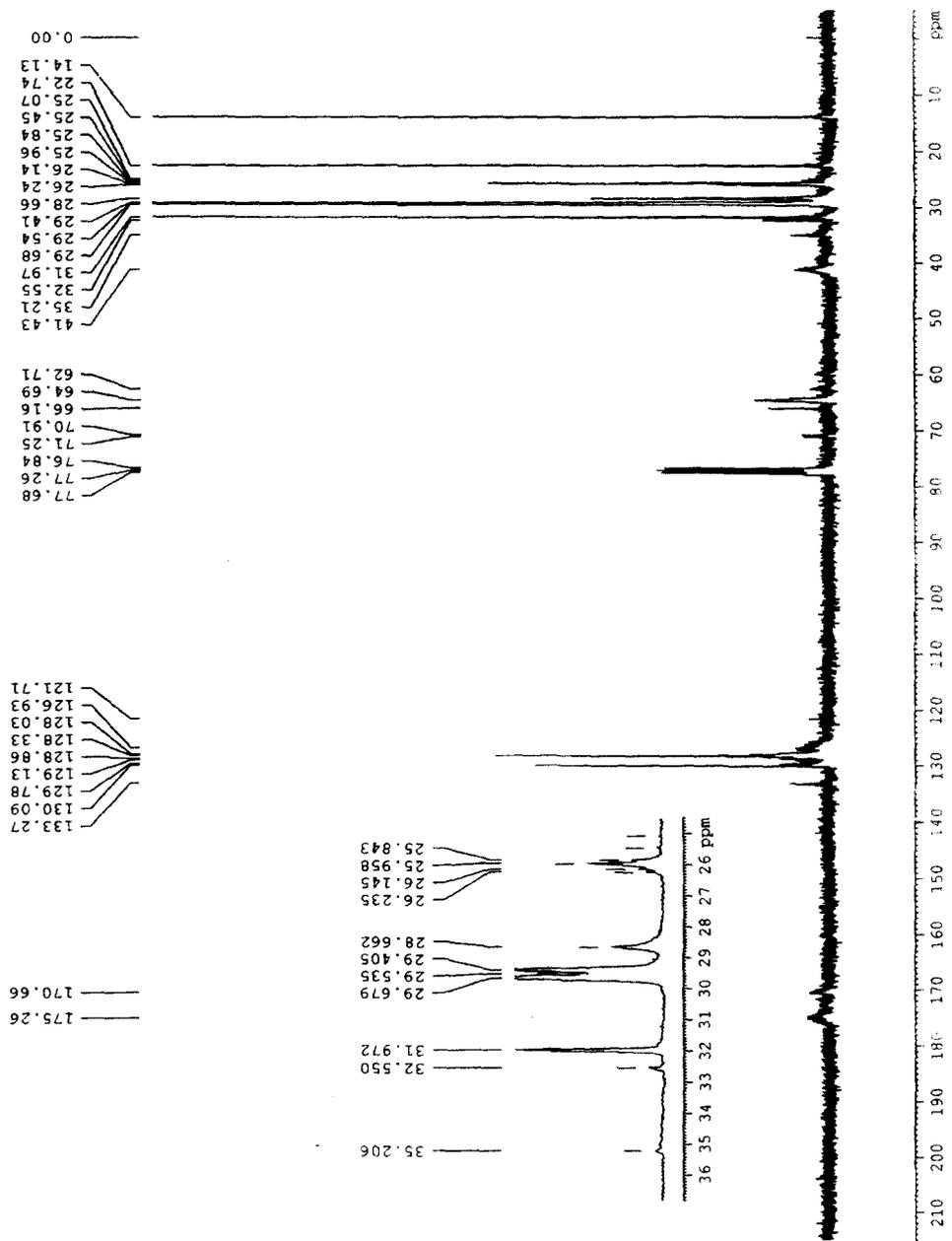


Figure 5. 13C NMR of copolymer of decylacrylate with styrene

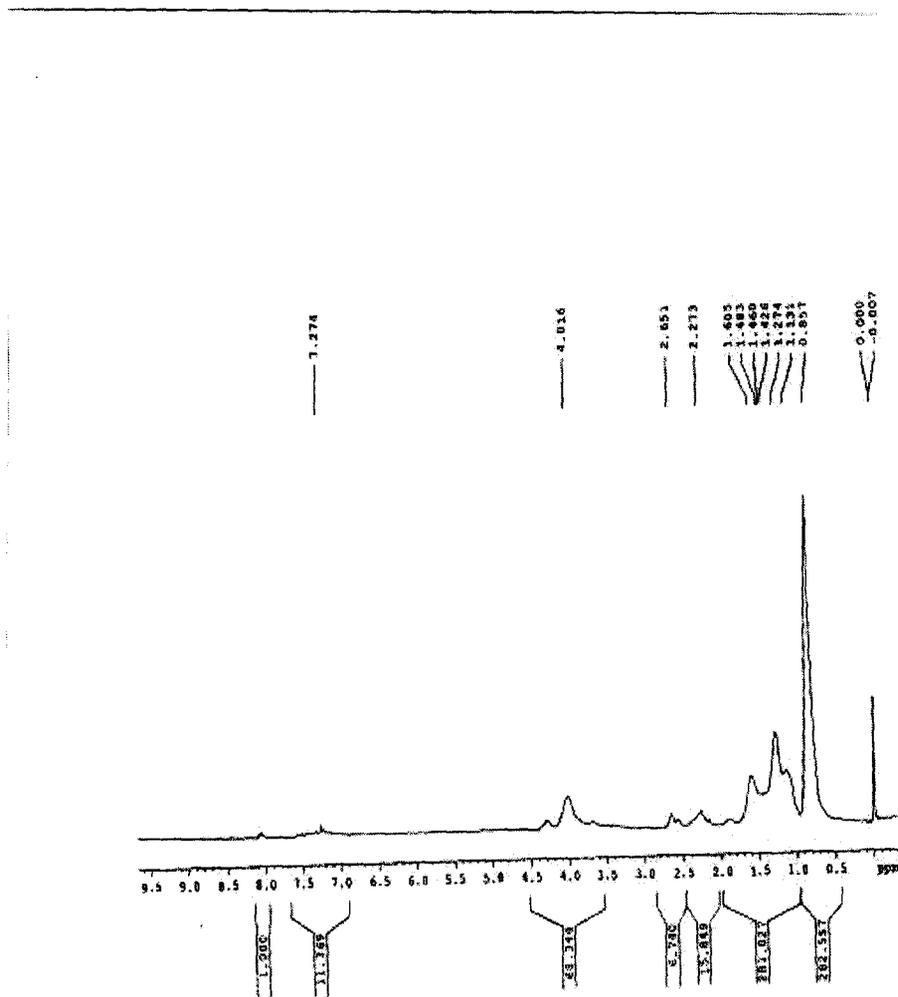


Figure 7. ^1H NMR Spectra of poly(isodecyl acrylate)

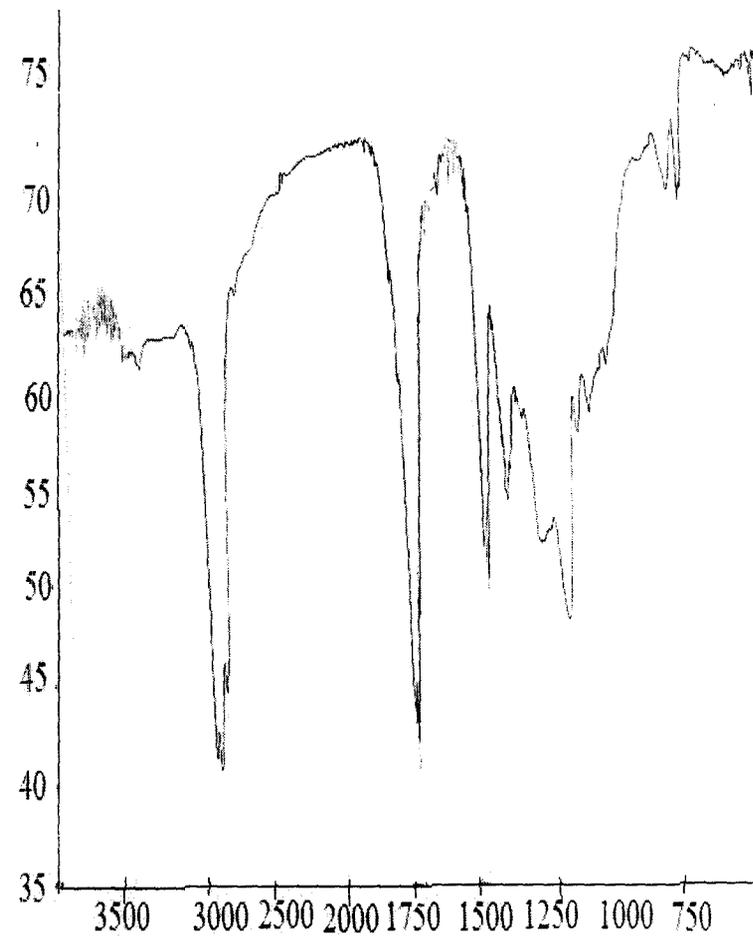
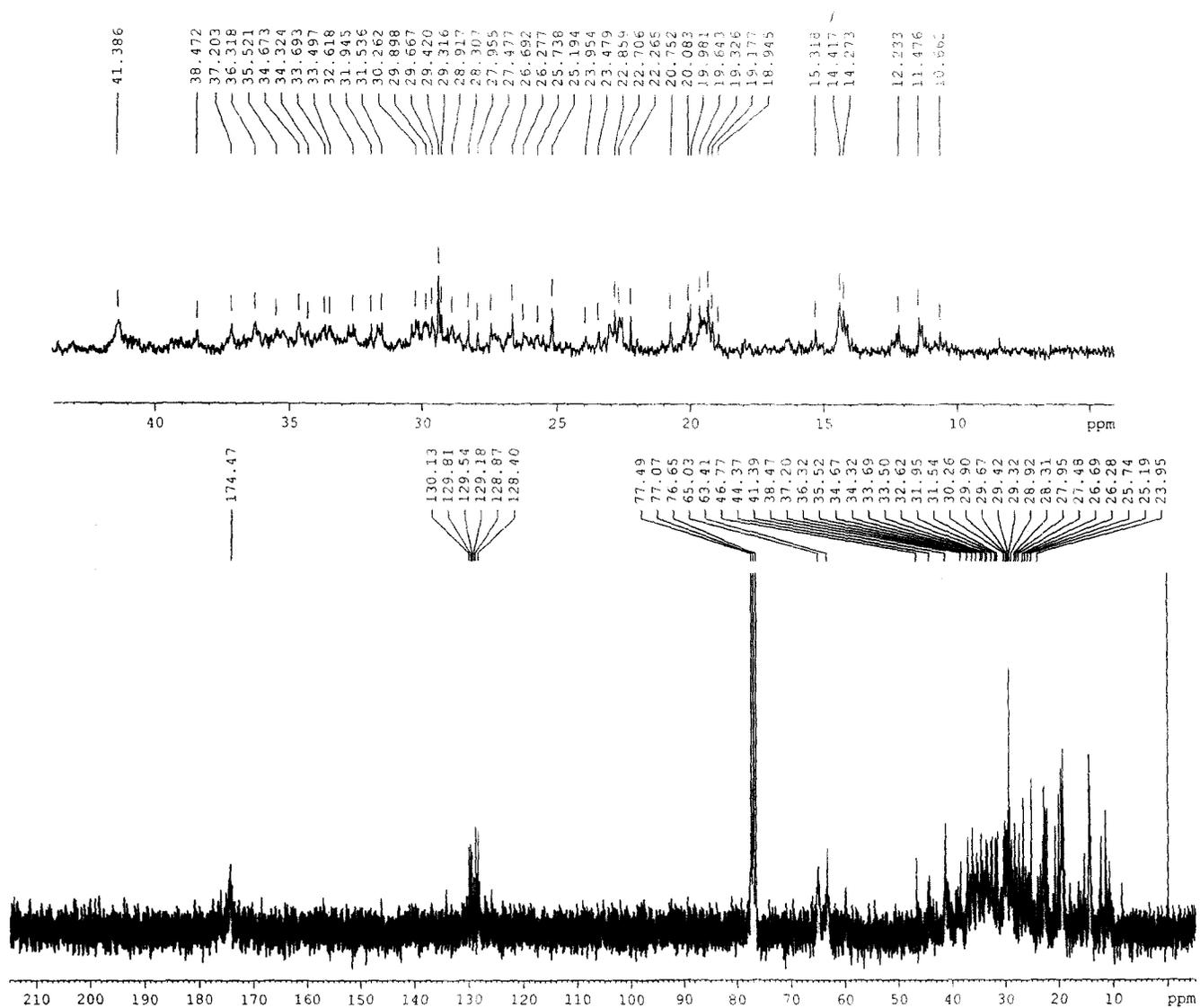


Figure 6. IR Spectra of poly(isodecyl acrylate) $1/\text{cm}$



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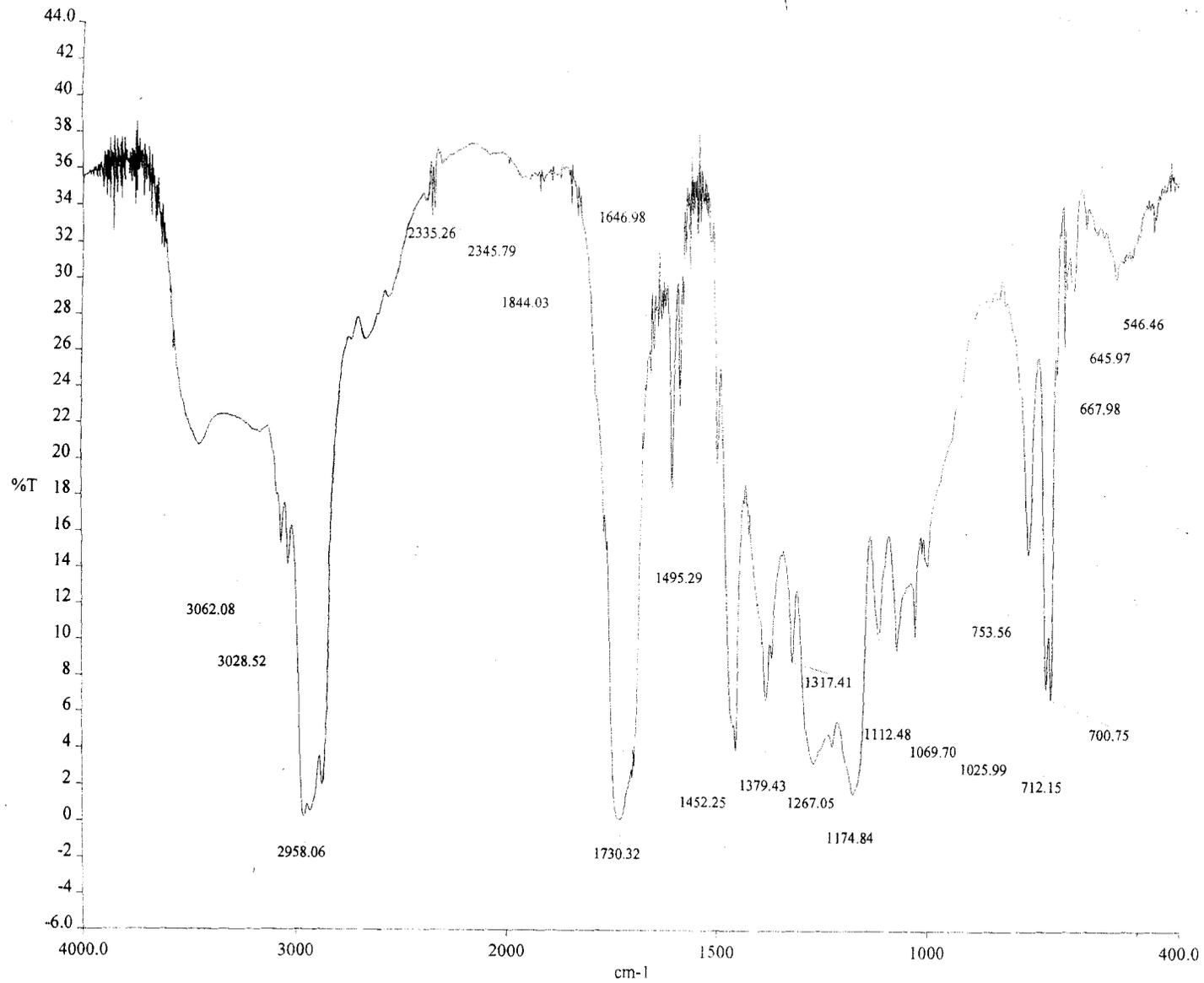
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Figure 8. ^{13}C NMR spectra of poly(isodecylacrylate)



63

Figure 9. IR spectra of copolymer of isodecylacrylate + styrene

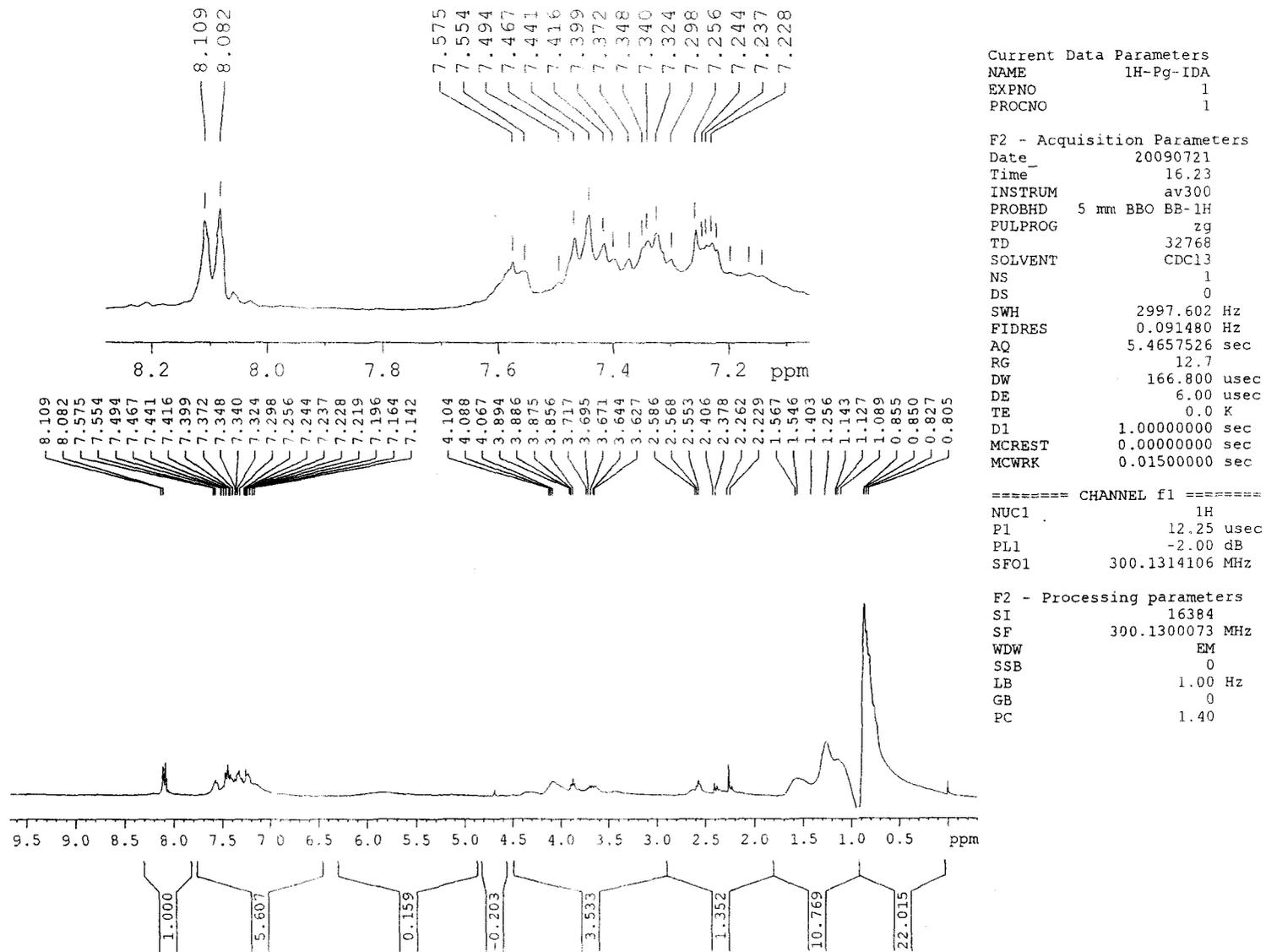
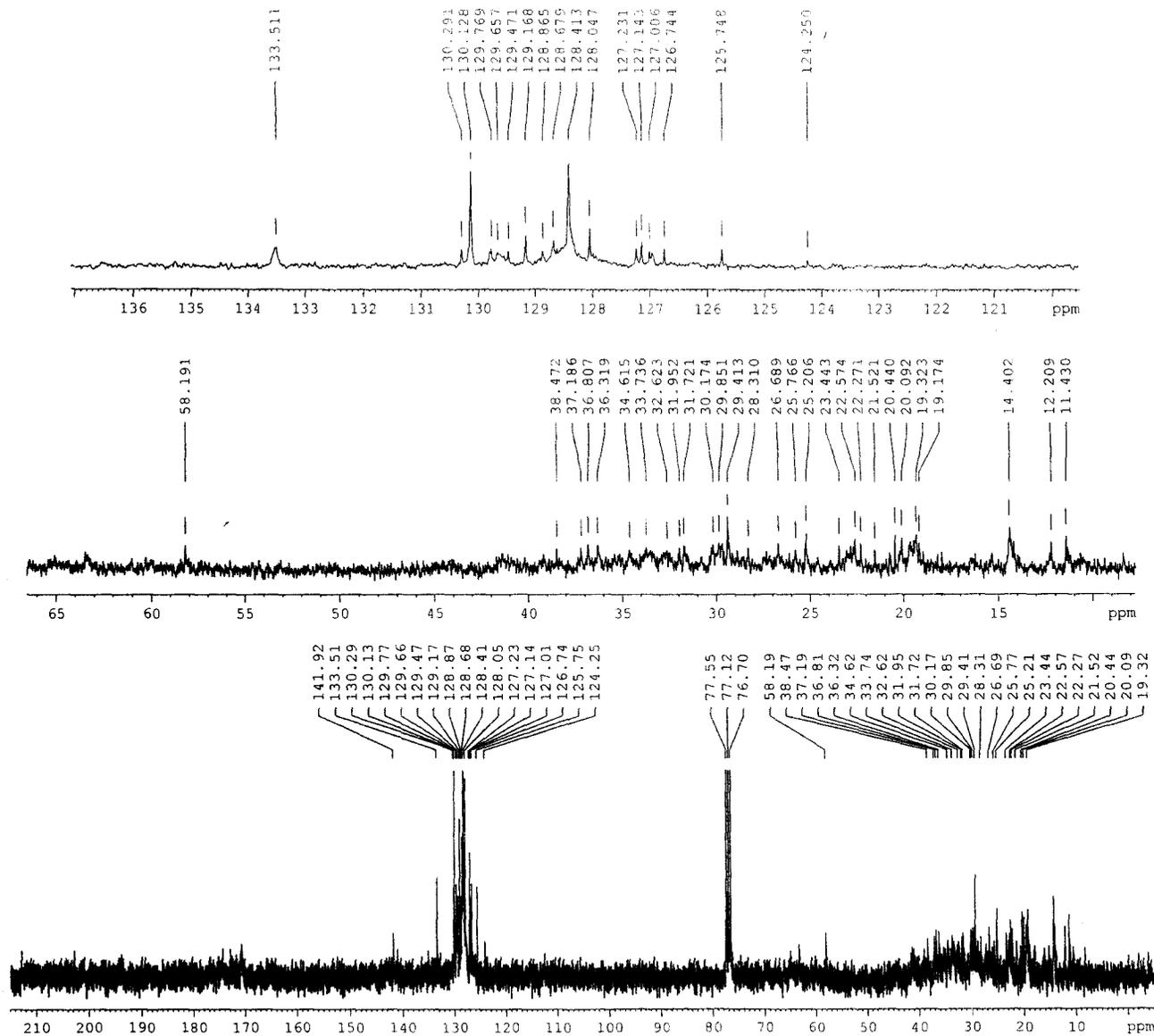


Figure 10. ^1H NMR spectra of copolymer of isodecylacrylate + styrene



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F2 - Processing parameters
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Figure 11. ^{13}C NMR spectra of copolymer of isodecylacrylate + styrene

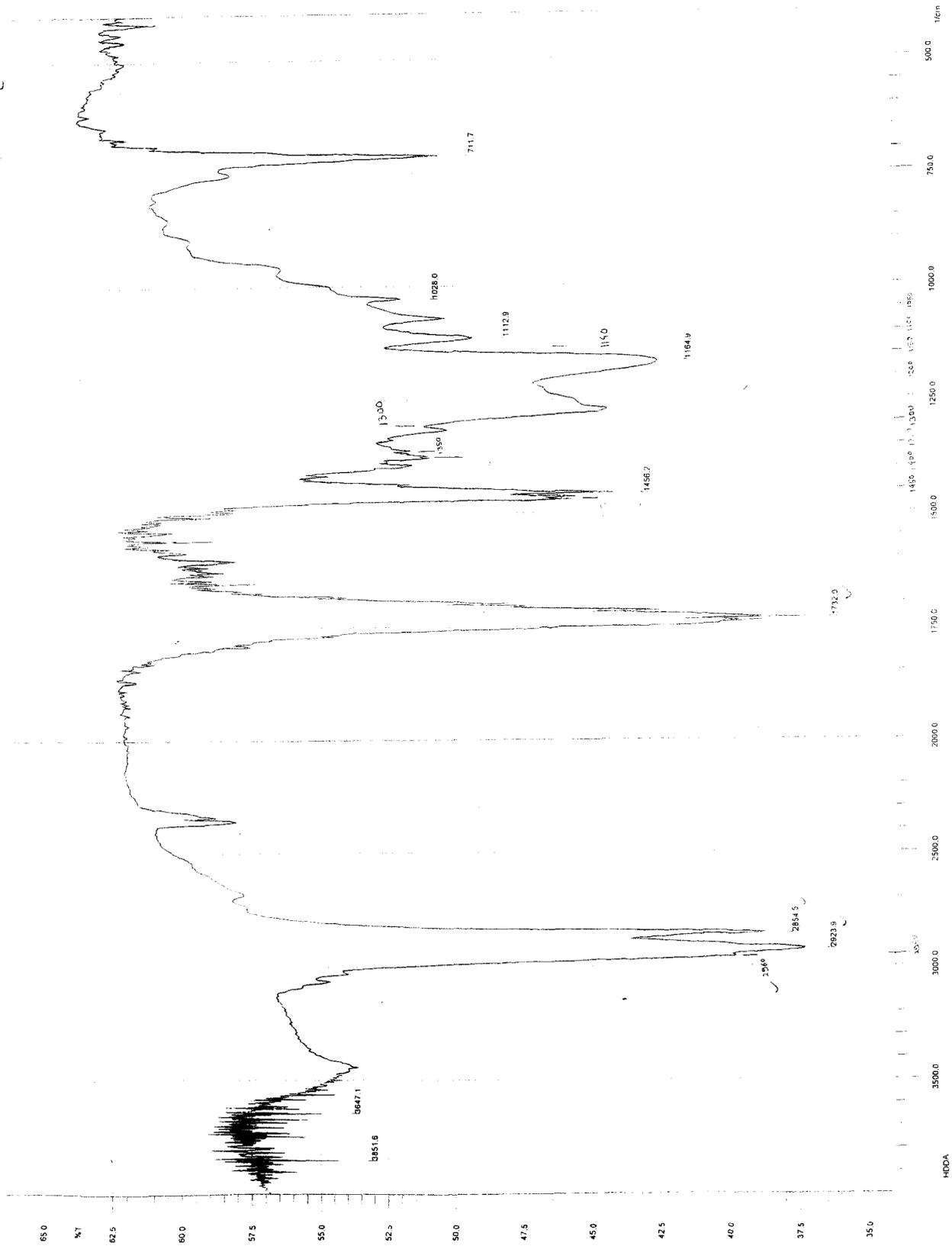


Figure 12. IR spectra of poly(dodecylacrylate)

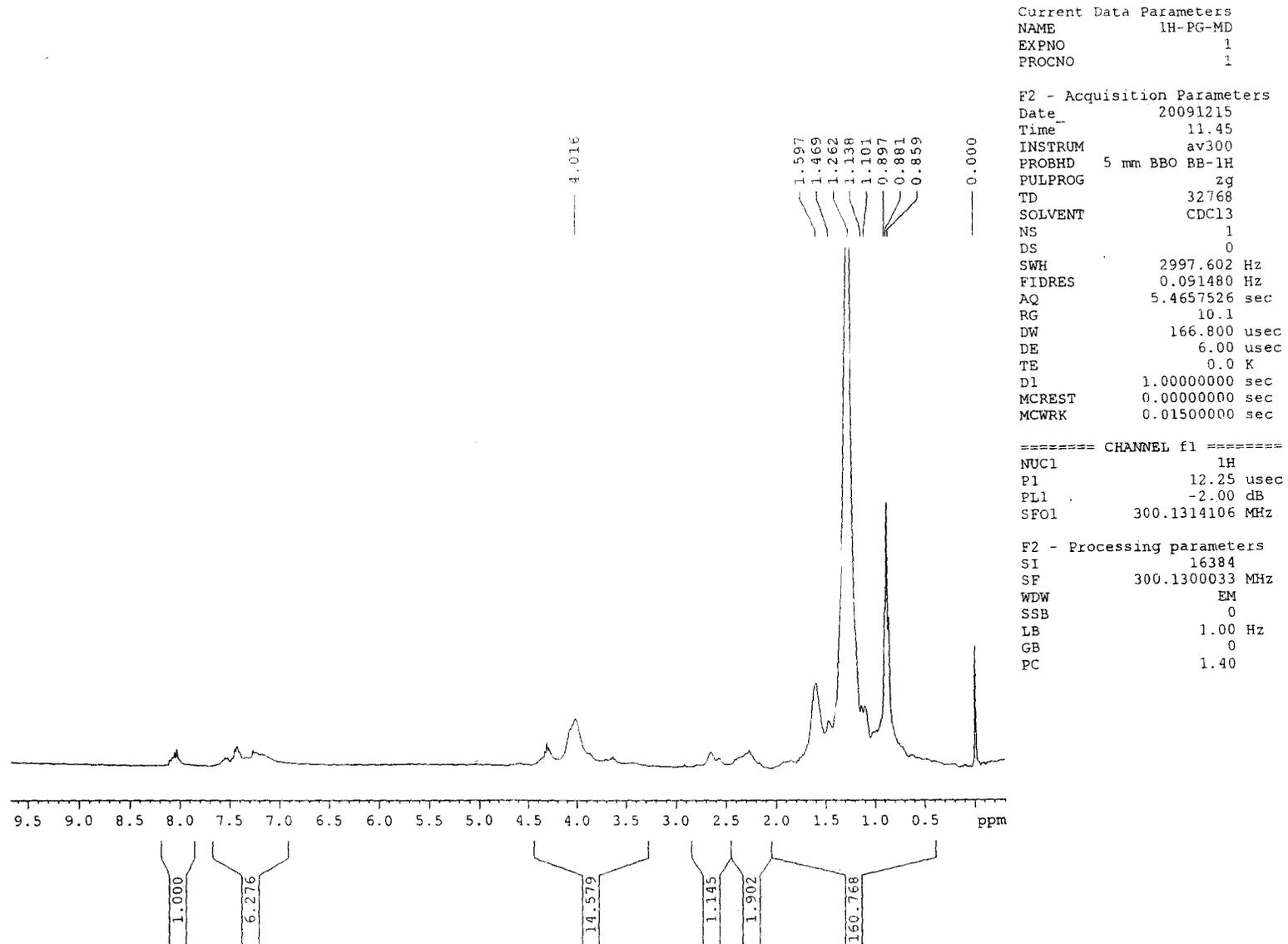


Figure 13. ^1H NMR spectra of poly(dodecylacrylate)

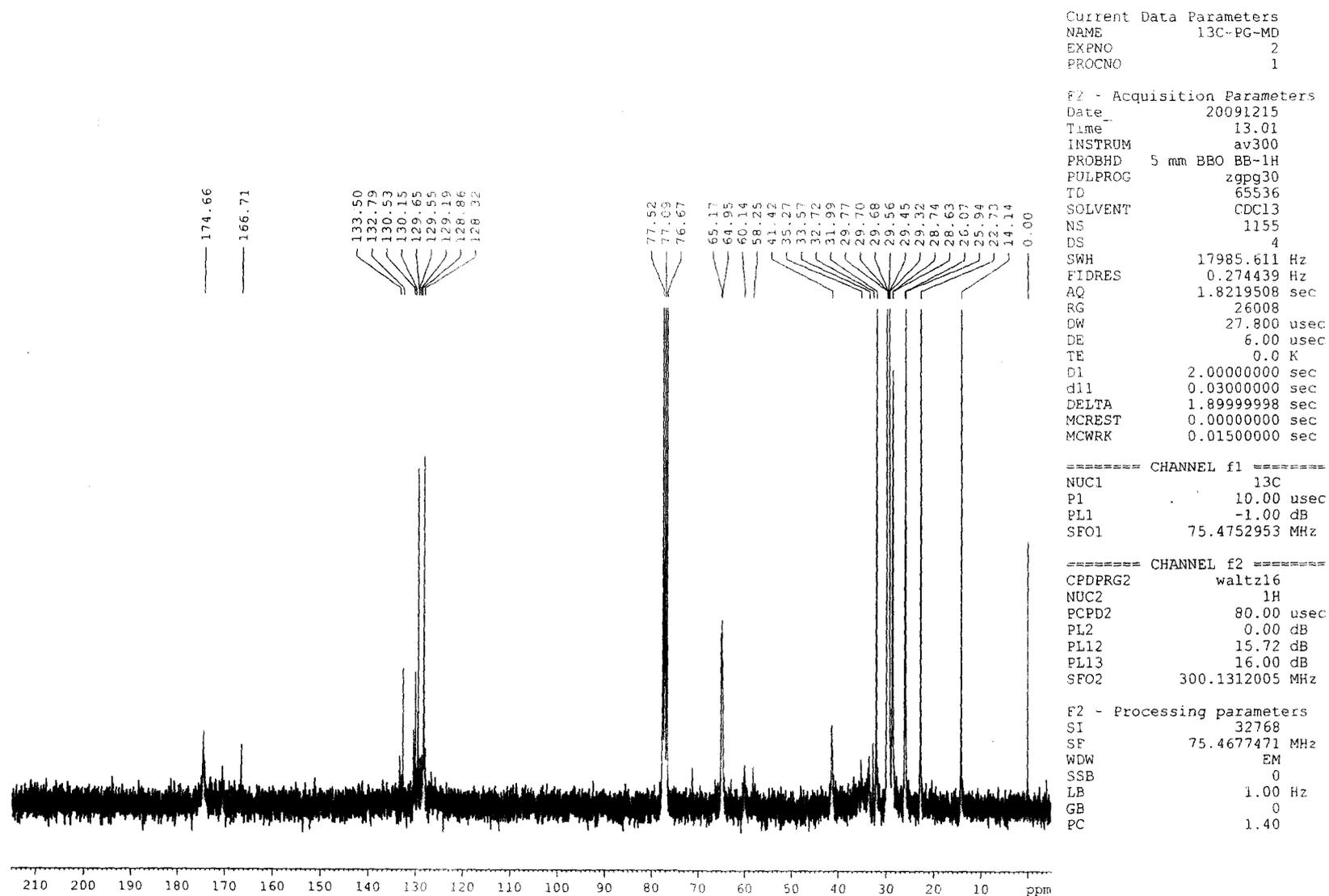


Figure 14. ^{13}C NMR spectra of poly(dodecylacrylate)

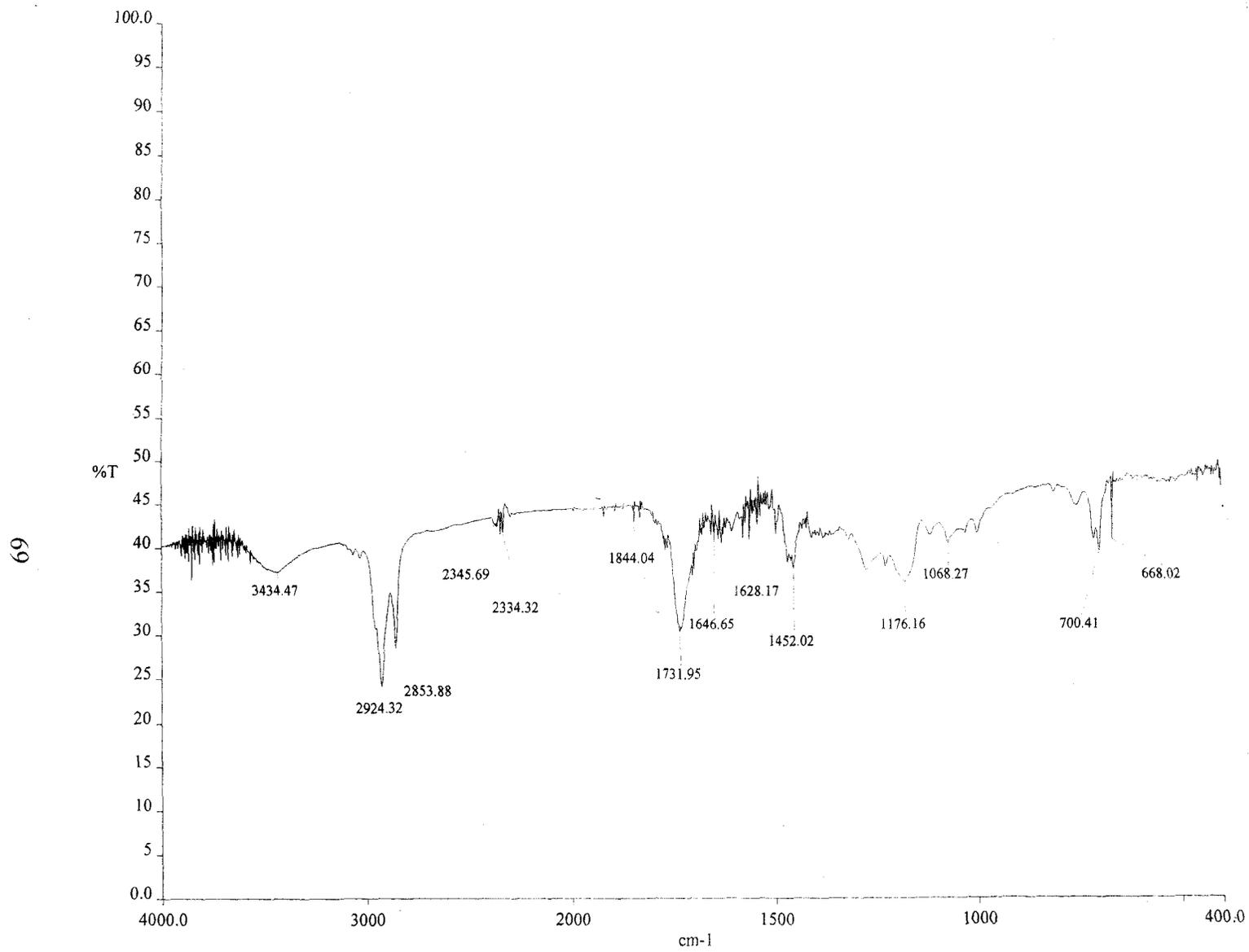


Figure 15. IR spectra of copolymer of dodecylacrylate + styrene

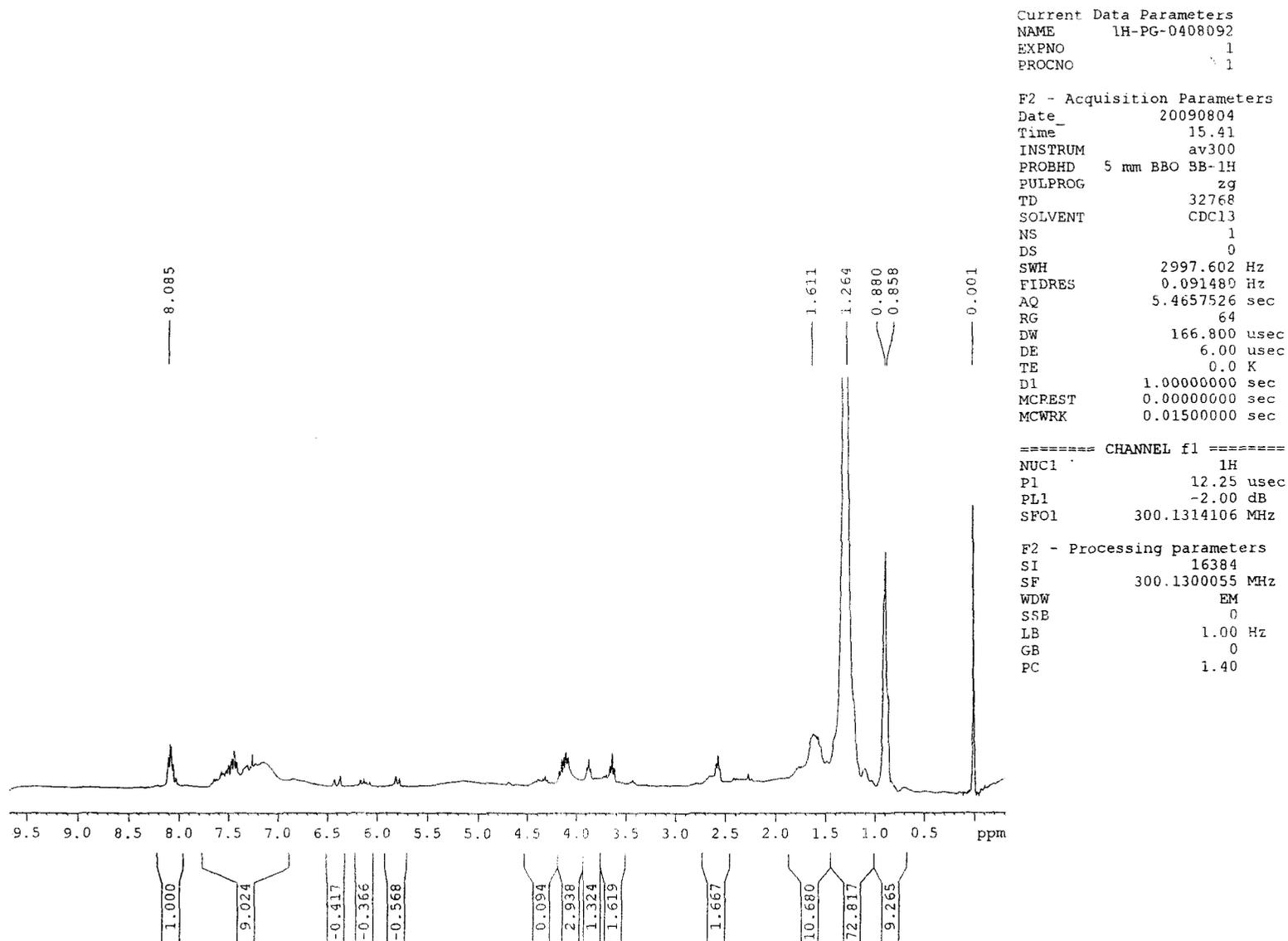
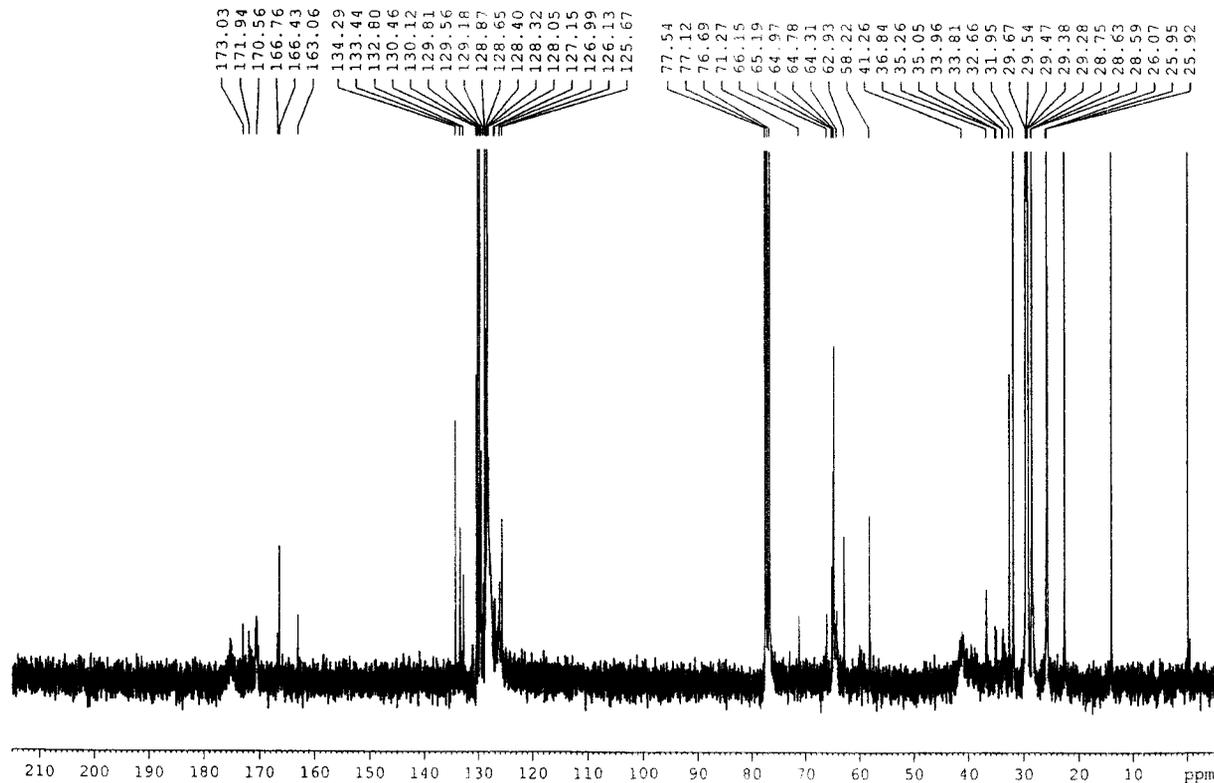


Figure 16. ^1H NMR spectra of copolymer of dodecylacrylate + styrene



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Figure 17. ^{13}C NMR spectra of copolymer of dodecylacrylate + styrene

Except copolymer of decyl acrylate (P-2 to P-4), comparison among the copolymers of PIDA- Styrene and PDDA- styrene indicated that although there is a sudden drop in the $[\eta]$ values at a 5% styrene concentration but beyond that a gradual increase of $[\eta]$ values with the increase of styrene content in the monomer composition is observed. This may be because of the flexibility of the respective homopolymer chain by the incorporation of styrene in the copolymer. However, beyond the concentration of 5% of styrene the hydrodynamic volume exceeds that of PIDA and PDDA and thus the gradual increase of $[\eta]$ values is observed [19, 20]. The abnormalities as are observed with PDA styrene system may be because of the fact that increase in styrene concentration in the feed of PDA- Sty composition does not have contribution towards the $[\eta]$ value of the copolymer. This may be because of the loss of flexibility of the polymer chain with incorporation of the styrene in PDA.

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kraemer, Martin and SB equation (eq 2 to 5), but in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. Values obtained by single point determination method were higher than the values obtained by graphic extrapolation method as was observed earlier [19].

Both homopolymer and copolymers in toluene medium indicating poor solvations (Table 4) as is evident from the respective viscometric constant values, and thus points towards the formation of micelle or spherical structures as discussed earlier [19]. However, it is interesting to notice that for all the polymers in toluene, k_{sb} values were not close to 0.28 except few cases and $k_h + k_k$ values were not found to close to 0.5 in most of the cases. But negative value of Kraemers coefficient for all copolymeric sample did not put any restriction to explain better solubility of copolymer in toluene.

Table 5 presents the percentual differences ($\Delta \% = 100 ([\eta]/ [\eta]_h) - 100$) of intrinsic viscosity $[\eta]$ values of homopolymers and the copolymers determined through graphic extrapolation using Kraemer, Martin and SB equations with respect to Huggins equation. It can be noticed that the range was narrow when compared to the values obtained through a single point using SB, SC and DC equation. Again, the percentage differences in case of polymers of dodecyl acrylate are higher than those of polymers of isodecyl acrylate both in graphic extrapolation and single point determination method (except P-3 and P-7).

Table 6 presents the percentual difference ($\Delta \% = [100(M/M_h)] - 100$), obtained for viscometric molecular weight values. These values were calculated considering Huggins equation as a reference. Martin equation showed the smallest Δ differences except P-1.

Viscometric molecular weight (M_v) obtained by using Mark - Houwink equation, is presented in Table 7. As was reflected in the respective $[\eta]$ values, the homopolymer showed higher Viscometric Molecular weight (M_v) compared to the copolymers.

Performance of the polymeric samples as pour point depressant (PPD)

Pour point of the different levels of additive doped lube oils were tested and tabulated in Tables 8. It indicated that the prepared copolymer samples are more efficient as pour point depressant than the homopolymer and the efficiency increases with the increase in concentration of additive up to a certain limit.

The greater hydrodynamic volume of the copolymer may restrict the formation of wax deposition network in the base oil, which is responsible for their poor flow ability at a lower temperature [21].

This is further supported by the intrinsic viscosity $[\eta]$ and viscometric molecular weight (M_v) values obtained by viscometric analysis with the copolymer and homopolymer samples. Both the parameters showed lesser values in case of copolymer than that of the homopolymer. Since the structure and morphology of the polymer chain plays a significant role for an additive to act as an effective PPD [17], incorporation of aromatic ring in the acrylate chain may be responsible for this encouraging PPD performance of the copolymer. The greater hydrodynamic volume, not only made the polymer less compatible with the solvent (less $[\eta]$ values) but at the same time prevents the formation of wax crystal network, which is responsible for reducing flow ability of the base oils.

2.1.3 Conclusion

Incorporation of styrene in the acrylate back-bone raises the thermal stability of the copolymer and extent of styrene incorporation directly proportional to the thermal stability of the copolymer.

Intrinsic viscosity values of the copolymer are less than the corresponding homopolymer and the values obtained by single point determination method are higher than the values obtained by graphical extrapolation method.

Viscometric molecular weight of the copolymer is less than the homopolymer of acrylate.

Pour point depressant (PPD) performance of the copolymer is always better than the homopolymer in the entire base oils studied. Increase in styrene concentration in the copolymer (up to a certain limit) induces better PPD performance into the additive.

Table 1: Composition of the monomers in the copolymers 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-4 is the copolymer of DA+ different mass fractions of styrene ; P-5 is homopolymer of isodecyl acrylate (IDA); P-6 to P-8 is the copolymer of IDA+ different mass fractions of styrene; P-9 is homopolymer of dodecyl acrylate (DDA); P-10 to P-12 is the copolymer of DDA+ 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	1	-	-	-
P-2	0.975	0.025	0.01	0.015
P-3	0.95	0.05	0.02	0.023
P-4	0.925	0.075	0.035	0.037
P-5	1	-	-	-
P-6	0.975	0.025	0.01	0.015
P-7	0.95	0.05	0.02	0.023
P-8	0.925	0.075	0.035	0.037
P-9	1	-	-	-
P-10	0.975	0.025	0.01	0.015
P-11	0.95	0.05	0.02	0.023
P-12	0.925	0.075	0.035	0.037

Table 2: Thermal Gravimetric Analysis Data of all prepared samples

Sample	Decomp.Temp.	PWL
P-1	250/340	23/86
P-2	300/400	45/84
P-3	320/430	60/85
P-4	320/440	62/85
P-5	180/300	15/86
P-6	200/340	25/80
P-7	230/400	29/90
P-8	240/410	32/92
P-9	230/330	32/91
P-10	230/340	30/70
P-11	230/380	15/60
P-12	240/400	15/60

Table 3: Intrinsic viscosity values of all prepared samples calculated by using different equation (eq 2 to eq 7) a- extrapolation of graph, b- single point determination

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1	4.335	5.004	4.180	5.368	6.490	6.697	7.340
P-2	2.677	3.538	3.375	3.760	4.106	4.105	4.350
P-3	2.445	3.248	3.087	3.430	3.768	3.758	3.963
P-4	2.401	3.225	3.001	3.38	3.634	3.619	3.8
P-5	3.774	3.845	3.881	3.945	4.02	3.983	4.119
P-6	2.737	2.876	2.846	2.930	3.074	3.046	3.110
P-7	2.877	3.167	3.099	3.229	3.505	3.474	3.573
P-8	3.004	3.287	3.222	3.378	3.561	3.529	3.623
P-9	4.059	4.361	4.336	4.512	4.637	4.599	4.773
P-10	2.621	2.752	2.724	2.772	2.882	2.857	2.933
P-11	3.211	3.522	3.452	3.626	3.784	3.750	3.876
P-12	3.424	3.859	3.766	4.016	4.128	4.091	4.230

Table 4. Viscometric constants obtained for all prepared homo and copolymer samples. k_h , k_k , k_m and k_{sb} Huggins, Kraemer, Martin and Schulz- Blaschke coefficients respectively

Sample	k_h	k_k	k_m	k_{sb}	k_h+k_k
P-1	1.572	-0.134	2.079	0.462	1.438
P-2	1.167	-0.045	2.078	0.371	1.122
P-3	2.183	-0.084	-4.084	0.452	2.099
P-4	2.085	-0.076	-3.085	0.450	2.009
P-5	0.475	0.107	0.359	0.294	0.582
P-6	0.850	-0.044	0.604	0.462	0.806
P-7	1.140	-0.089	0.694	0.501	1.051
P-8	1.103	-0.084	0.683	0.480	1.019
P-9	0.76	0.044	0.478	0.347	0.804
P-10	0.802	-0.017	0.572	0.465	0.785
P-11	1.057	-0.057	0.649	0.453	1.000
P-12	1.194	-0.065	0.670	0.441	1.129

Table 5. Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values, Huggins equation taken as a reference. a- data from extrapolation; b – data from single point determination

Sample	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
P-1	15.432	-3.575	23.829	49.711	54.486	69.319
P-2	32.162	26.074	40.455	53.380	53.343	62.495
P-3	32.842	26.257	40.286	54.110	53.370	62.085
P-4	34.319	34.989	40.774	51.135	50.728	58.267
P-5	1.881	2.835	4.531	6.518	5.538	9.141
P-6	5.079	3.982	7.052	12.313	11.290	13.628
P-7	10.080	7.716	12.235	21.828	20.751	24.192
P-8	9.421	7.257	12.450	18.542	17.477	20.606
P-9	7.440	6.824	11.160	14.240	13.304	17.591
P-10	5.074	3.930	5.761	9.958	9.004	11.904
P-11	9.685	7.505	12.924	17.845	16.786	20.710
P-12	12.704	9.988	17.290	20.561	19.480	23.540

Table 6. Determination of molecular weight by Mark - Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl.g}^{-1}$ 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	16051	19563	15264	21554	28004	29244	33186
P-2	8255	12128	11364	13190	14893	14888	16127
P-3	7285	10778	10048	11623	13229	13180	14182
P-4	7105	10673	9664	11387	12584	12513	13384
P-5	13,270	13,616	13,792	14,107	14,478	14,295	14,972
P-6	8,520	9,122	8,991	9,359	10,000	9,874	10,162
P-7	9,127	10,419	10,112	10,702	11,984	11,838	12,306
P-8	9,687	10,968	10,670	11,389	12,249	12,097	12,544
P-9	14,672	16,199	16,071	16,977	17,630	17,431	18,347
P-10	8,026	8,593	8,464	8,671	9,149	9,039	9,373
P-11	10,620	12,064	11,734	12,558	13,319	13,154	13,768
P-12	11,603	13,684	13,232	14,458	15,017	14,473	15,531

Table 7. Percentual differences obtained for viscometric molecular weight values ($\Delta \% = [100(M/M_h)] - 100$)

Sample	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	21.880	-4.903	34.284	74.468	82.194	106.75
P-2	46.917	37.662	59.782	80.411	80.351	95.360
P-3	47.948	37.927	59.547	81.592	80.114	94.674
P-4	50.218	36.016	60.267	77.114	76.115	88.374
P-5	2.607	3.934	6.307	9.103	7.724	12.826
P-6	7.066	5.528	9.847	17.371	15.892	19.272
P-7	14.156	10.792	17.256	31.303	29.703	34.831
P-8	13.224	10.148	17.570	26.448	24.879	29.493
P-9	10.408	9.535	15.710	20.161	18.805	25.048
P-10	7.065	5.457	8.036	13.992	12.621	16.783
P-11	13.597	10.490	18.249	25.414	23.861	29.642
P-12	17.935	14.039	24.606	29.423	24.735	33.853

Table 8. Pour point of additive doped base oils

Sample	Base oils		Pour point of Base oil	Pour point of additive doped Base oil		
				2.5%	5%	10%
P-1	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-12
	BO2	S1	-6	-9	-9	-12
		S2	-6	-9	-9	-12
P-2	BO1	S1	-3	-12	-15	-15
		S2	-3	-12	-15	-15
	BO2	S1	-6	-15	-21	-24
		S2	-6	-15	-24	-21
P-3	BO1	S1	-3	-12	-21	-21
		S2	-3	-15	-21	-24
	BO2	S1	-6	-12	-21	-21
		S2	-6	-15	-21	-24
P-4	BO1	S1	-3	-15	-24	-24
		S2	-3	-15	-21	-24
	BO2	S1	-6	-15	-24	-24
		S2	-6	-15	-21	-24

P-5	BO1	S1	-3	-6	-6	-9
		S2	-3	-6	-9	-9
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-12
P-6	BO1	S1	-3	-9	-9	-6
		S2	-3	-9	-9	-12
	BO2	S1	-6	-12	-12	-9
		S2	-6	-9	-12	-12
P-7	BO1	S1	-3	-9	-12	-15
		S2	-3	-9	-15	-18
	BO2	S1	-6	-12	-15	-21
		S2	-6	-15	-15	-15
P-8	BO1	S1	-3	-12	-15	-15
		S2	-3	-15	-12	-12
	BO2	S1	-6	-15	-15	-18
		S2	-6	-15	-18	-24
P-9	BO1	S1	-3	-6	-12	-15
		S2	-3	-9	-12	-15
	BO2	S1	-6	-12	-12	-12
		S2	-6	-12	-15	-18
P-10	BO1	S1	-3	-9	-15	-18
		S2	-3	-12	-15	-21
	BO2	S1	-6	-12	-15	-15
		S2	-6	-15	-18	-21
P-11	BO1	S1	-3	-9	-12	-18
		S2	-3	-12	-12	-15
	BO2	S1	-6	-15	-15	-18
		S2	-6	-12	-15	-21
P-12	BO1	S1	-3	-9	-12	-15
		S2	-3	-12	-15	-18
	BO2	S1	-6	-12	-15	-18
		S2	-6	-12	-18	-21

2.2 SECTION B: Evaluation of Poly(acrylates) and their Copolymer as Viscosity Modifiers

2.2.1 Introduction

The development of modern engine and transmission technologies would be impossible without lubricant additives. From its conception in the early 1900s, the lubricant additive industry has worked in partnership with the oil and the automotive industries to enhance durability and performance of engine and drive line systems through lubricant design [22]. Additives are synthetic chemicals that can improve or add performances of lubricants. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life. One of the important types of additive is viscosity index improvers commonly known as viscosity modifier [23].

The viscosity index is an indicator of the change in viscosity as the temperature is changed. The higher the viscosity index (VI), the lesser the viscosity of an oil changes for a given temperature change. Viscosity index improvers are used to limit the rate of change of viscosity with temperature. These improvers have little effect on oil viscosity at low temperatures. However, when heated the improvers enable the oil viscosity to increase within the limited range permitted by the type and concentration of the additive. This quality is most apparent in the application of multigrade motor oils.

Viscosity index improvers function by increasing the relative viscosity of oil more at high temperatures than at low temperatures [3-5]. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is believed that the polymer molecule in solution exists as a random coil, which is swollen by the lube oil solvent. The volume of this molecule determines the viscosity increase. In cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules, having greater volume and the oil produces a proportionally greater thickening effect which in turn raises the VI of the oil.

An ideal lubricant for most purposes would possess the same viscosity at all temperatures [8]. Viscosity index improvers (VII) are added to lubricating oils to make them conform more closely to the ideal lubricant. Although a few non-polymeric substances such as metallic soaps exhibit VI improving properties [9], all commercially important VI improvers today are oil-soluble organic polymers. Suitable polymers exert a greater thickening effect (percent increase in viscosity of the base oil for unit weight of polymer) on oil at higher temperatures than they do at lower temperatures [10] and thus improve the VI of lube oil.

Considering the above discussion and the past literature reports (as elaborated in Chapter I of this Part), present investigation comprises the synthesis, characterization and evaluation of poly(decyl acrylate), poly(dodecyl acrylate), poly(isodecyl acrylate) and their copolymer with styrene as a potential viscosity index improver (VII) for lube oil.

2.2.2 Result and Discussion

The prepared polymers were tested for their effectiveness as viscosity index improvers for base oil (BO1 and BO2) according to ASTM D-2270. In this respect, the kinematic viscosity of the oil doped with different concentrations of the tested additives was determined at 313 K and 373 K. The concentrations were ranging from 1% to 6% (w/w), which is used to study the effect of the additives concentration on VI of lube oils.

It is clear from the VI data tabulated in Table 2 to Table 13 and also from Figure 1 and Figure 2, as evaluated in present investigation indicated that irrespective of the polymer (homo and copolymer) and nature of the base oil VI values increases with the increase in additive concentration in the base oils studied. A critical observation of the VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. It is also observed that branching in the carbon chain of the alcohol deteriorates its performance when used as a VII in the lube oil. Thus, the chain length and its arrangements play a significant role when added in the lube oil to act as a VII.

As the temperature is raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands due to the increase in the solvation power and the increased size of the micelle. This increase in micelle size counterbalances the reduction of the viscosity of the

lube oil and, hence, decreases the changes of viscosity with temperature of the mixture [24-26]. The increase in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution and thus exerting greater thickening effect and so as to VII.

2.2.3 Conclusion

Irrespective of the polymers (homo and copolymer) and nature of the base oils, VI values increases with the increase in additive concentration in the base oils studied.

VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. Again, branching in the carbon chain of the alcohol, deteriorates the performance of the acrylate when used as a VI improver in the lube oil. Thus, the chain length and its arrangements in the polymer of a viscosity modifier play a significant role when added in the lube oil to act as a VI improver.

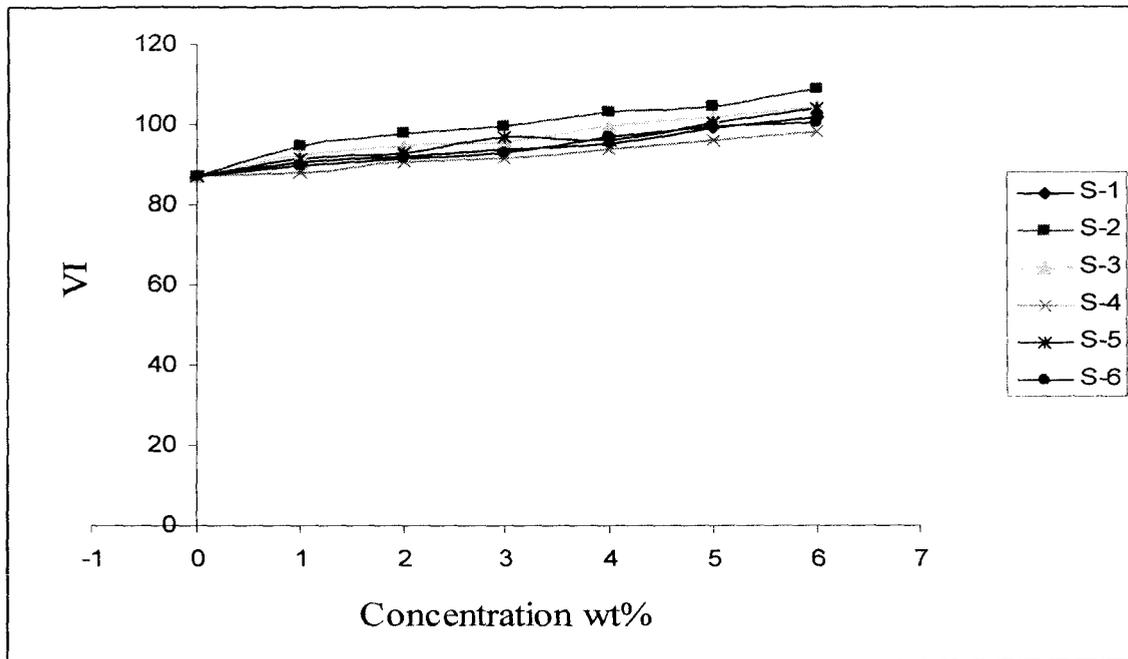


Figure 1. Plot of Viscosity Index (VI) vs polymer concentration in BO1 base oil, where S-1 poly(decyl acrylate), S-2 poly(isodecyl acrylate), S-3 poly(dodecyl acrylate).

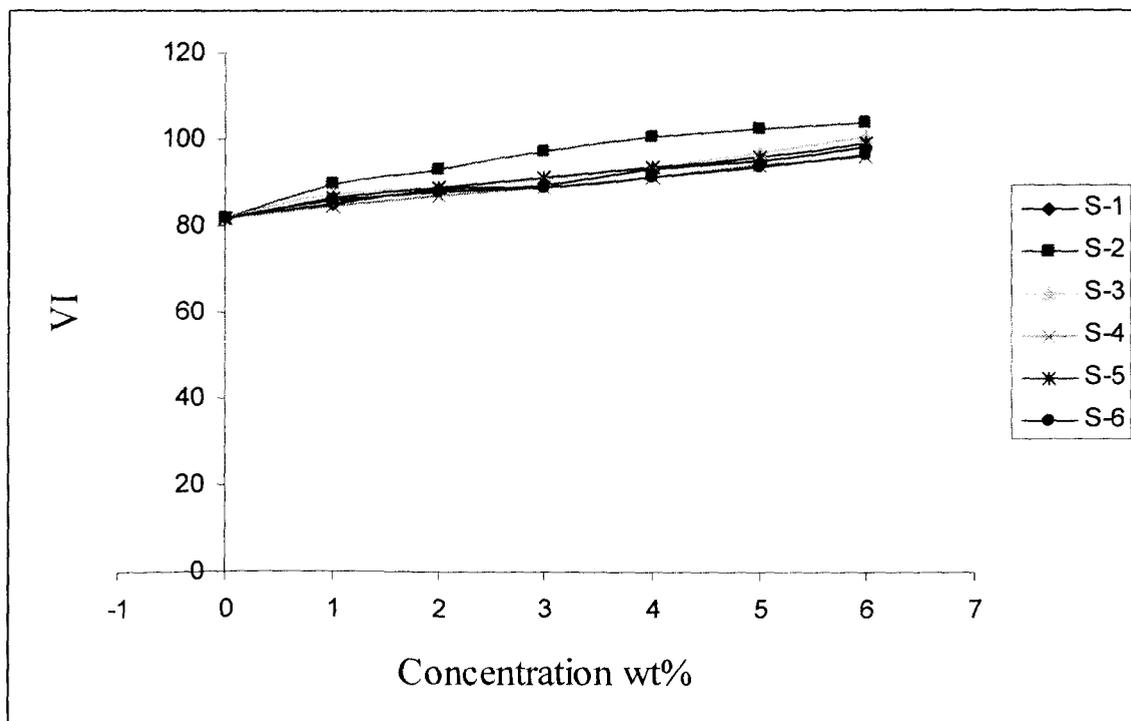


Figure 2. Plot of Viscosity Index (VI) vs polymer concentration in BO2 base oil, where S-1 poly(decyl acrylate), S-2 poly(isodecyl acrylate), S-3 poly(dodecyl acrylate).

Table 1. Base oil properties

Base oil properties	Base oils	
	BO1	BO2
Viscosity at 40 ⁰ C in cSt	7.202	23.609
Viscosity at 100 ⁰ C in cSt	1.872	3.951
Cloud point, ⁰ C	-8	-10
Pour point, ⁰ C	-3	-6

Table 2. VI values for poly(decyl acrylate) (S-1) in BO1 oil

Solution Conc. Wt %	Kinematic Viscosity at 40 ⁰ C	Kinematic Viscosity at100 ⁰ C	VI
0	7.202	1.872	87.00
1	7.262	1.891	90.48
2	7.298	1.901	91.93
3	7.345	1.914	93.66
4	7.403	1.928	95.08
5	7.440	1.946	98.98
6	7.479	1.962	101.95

Table 3. VI values for poly(decyl acrylate) (S-1) in BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40 ⁰ C	Kinematic Viscosity at100 ⁰ C	VI
0	23.609	3.951	81.68
1	23.982	4.032	85.09
2	24.070	4.080	88.41
3	24.125	4.099	89.30

4	24.232	4.157	92.80
5	24.303	4.189	94.80
6	24.393	4.248	98.15

Table 4. VI values for poly(isodecyl acrylate) (S-2) in BO1 oil

Solution Conc. Wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.302	1.903	92.51
2	7.340	1.915	94.52
3	7.382	1.925	95.36
4	7.424	1.945	99.52
5	7.460	1.959	101.95
6	7.502	1.975	104.58

Table 5. VI values for poly(isodecyl acrylate)(S-2) in BO2 oil

Solution Conc. wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1%	24.026	4.060	87.21
2%	24.083	4.087	88.71
3%	24.156	4.116	90.48
4%	24.248	4.164	93.38
5%	24.335	4.223	96.77
6%	24.402	4.284	100.34

Table 6. VI values for poly(dodecylacrylate)(S-3) in BO1 oil

Solution Conc. Wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.357	1.918	94.52
2	7.422	1.938	97.60
3	7.474	1.953	99.52
4	7.546	1.977	103.00
5	7.603	1.993	104.58
6	7.682	2.022	108.68

Table 7. VI values for poly(dodecyl acrylate)(S-3) in BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
	24.070	4.097	89.59
2	24.147	4.149	93.09
3	24.236	4.217	97.32
4	24.311	4.270	100.34
5	24.371	4.310	102.48
6	24.419	4.338	103.80

Table 8. VI values for copolymer of DA+ styrene (S-4) BO1 oil

Solution Conc. Wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.246	1.882	88.11
2	7.310	1.900	90.77
3	7.385	1.914	91.35
4	7.451	1.932	93.66
5	7.529	1.952	95.93
6	7.610	1.972	98.15

Table 9. VI values for copolymer of DA+ styrene (S-4) BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.899	4.017	84.78
2	23.986	4.054	86.91
3	24.092	4.092	89.00
4	24.159	4.125	91.06
5	24.267	4.174	93.95
6	24.357	4.214	95.93

Table 10. VI values for copolymer of IDA+ styrene (S-5) in BO1 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.284	1.893	89.89
2	7.334	1.905	91.35
3	7.410	1.923	93.09
4	7.498	1.949	96.77
5	7.606	1.976	99.52
6	7.673	1.991	100.61

Table 11. VI values for copolymer of IDA+ styrene (S-5) BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.949	4.040	86.00
2	24.020	4.067	87.81
3	24.084	4.088	89.00
4	24.158	4.124	91.06
5	24.234	4.166	93.66
6	24.342	4.214	96.21

Table 12. VI values for copolymer of DDA+ styrene(S-6) BO1 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.339	1.906	91.35
2	7.422	1.925	93.09
3	7.510	1.951	96.77
4	7.608	1.965	95.93
5	7.684	1.992	100.34
6	7.738	2.014	104.06

Table 13. VI values for copolymer of DDA + styrene (S-6) in BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.987	4.050	86.61
2	24.080	4.087	88.71
3	24.171	4.128	91.35
4	24.250	4.165	93.38
5	24.364	4.215	95.93
6	24.478	4.275	99.25

2.3 SECTION C: Comparison of Viscometric Parameters of the Homo and Copolymer of Poly(decyl acrylate) in Lubricating Oil

2.3.1 Introduction

Lubricating oil (also known as base oil), is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and naphthenic 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.

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

They added to impart specific property to the oil. Some of them impart new and useful properties to the lubricant, and others enhance properties already present [27, 28]. 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. Thus a comparative study in terms of chemistry of the additive and composition of the base oil is very much pertinent to be included in our investigation.

Recent research [29] 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 [a brief introduction is given in Part 1, Chapter 1, sec A] 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 [30].

Therefore, the study, which is most probably the first report of such an investigation, may be very useful for predicting the performance of the additive in base oils of different compositions.

In the present case we have undertaken poly(decyl acrylate) as the additive and base stocks of two different compositions for the present investigation.

2.3.2 Results and discussion

Viscometric data were obtained using the seven equations as mentioned in Chapter I of Part I. A linear relation for the plot of $\log \eta_{sp}$ vs $\log C[\eta]$ obtained for all samples [Figure 1a & 1b] indicated that measurements were performed in Newtonian flow [31,32]. 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–Blascke (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–Blascke (SB) equation is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems [33-36]. In this work, this value was used.

Table 1-2 presents intrinsic viscosity $[\eta]$ 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 $[\eta]$ 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 additives in this oil. Variation of $[\eta]$ 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 .

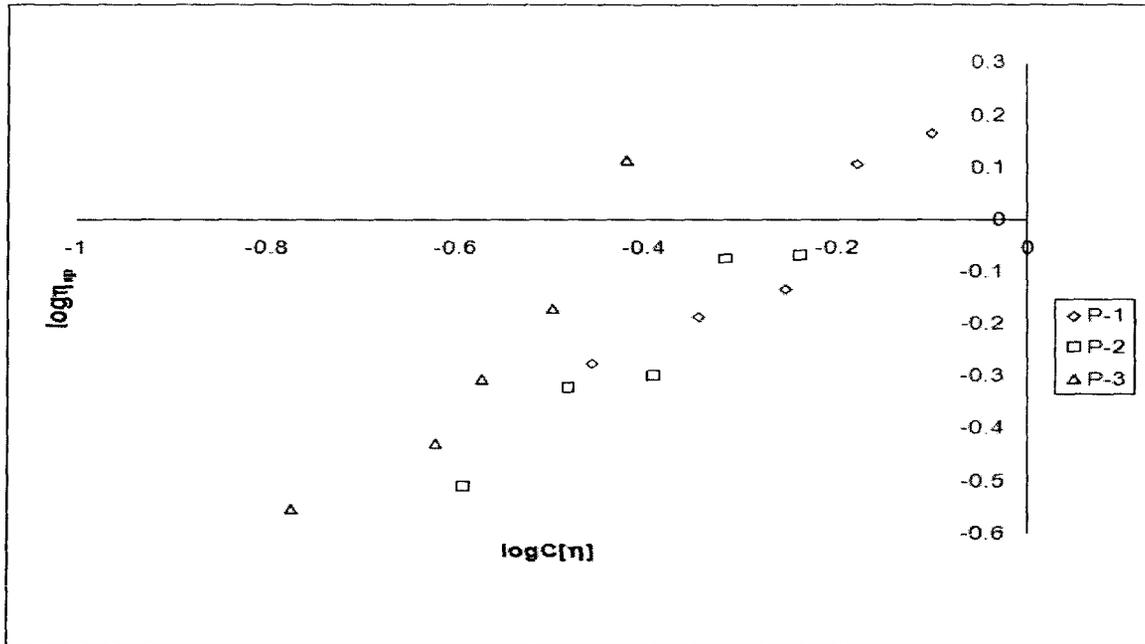


Figure 1a. Plot of $\log \eta_{sp}$ vs $\log C[\eta]$ for BO1.

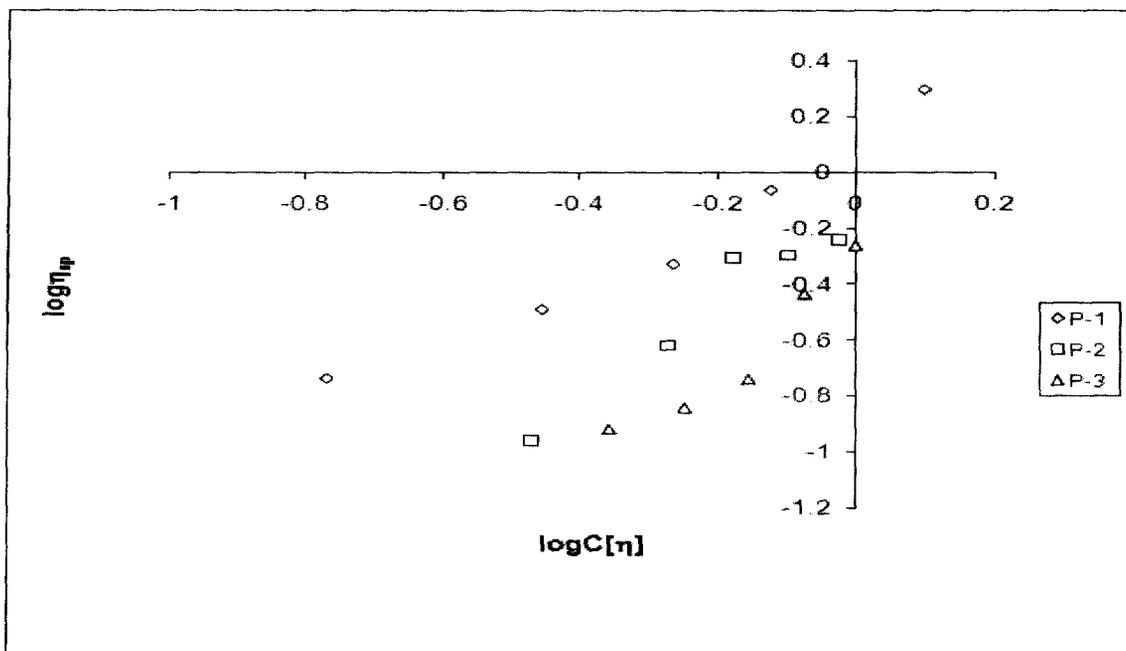


Figure 1b. Plot of $\log \eta_{sp}$ vs $\log C[\eta]$ for BO2.

It is also observed that $[\eta]$ values decrease with the incorporation of styrene, but increases with increases in styrene concentration in case of oil BO2 and decreases in oil BO1. Intrinsic viscosities $[\eta]$ 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.

Table 3 & 4 presents values of viscometric constants calculated for homo and copolymers 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 5 - 6 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 are smaller in oil BO2 compared to oil BO1.

Table 7 – 8 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.

2.3.3 Conclusions

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. Properties like intrinsic viscosity, viscosity average molecular weight of the polymeric additives are influenced by the compositions of the base oils. This work is probably the first report of viscometric studies of polymeric additives in base oils.

Table 1. 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. P-1 poly(decyl acrylate), P-2 and P-3 are copolymer of decyl acrylate with different % ratio of styrene.

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 2. 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

Table 3. 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 4. 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 5. 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 6. 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 7. 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

Table 8. Viscometric molecular weight of all prepared sample in BO2 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	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