



Physico-chemical studies on Novel Terpolymers for Viscosity Index Improvers

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Abstract

Petroleum can refine to yield lubricants and high energy fuels, such as diesel oil, gasoline and jet fuels. The petroleum stock limited, and therefore other methods have been sought. Polymers having high molecular weight find use as lubricating oil additives in three application areas of: viscosity-index improvers (VII), pour-point depressants and polymeric detergents. The present works aim to find new applications of terpolymers as viscosity-index improvers (VII) in the field of lubricants. Overwhelming utilization of natural petroleum resources may be a problem in the future. Therefore, such of higher molecular weight terpolymers can used as a VI improver (or Thickeners) and low molecular weight terpolymers can also used as synthetic base oil. The easily made vinyl esters obtained in good yield from readily available, inexpensive raw materials; also the vinyl esters are conceivably low cost monomers. The study opens up new routes of multi-functional synthetic lubricants.

Keywords: Viscosity index improvers, terpolymers, second virial coefficient, contour length.

Introduction

Petroleum can be refined to yield lubricants and high energy fuels, such as diesel oil, gasoline, and jet fuels. The petroleum stock is limited, and therefore other methods have been sought. Polymers having high molecular weight find use as lubricating oil additives in three application areas of: polymeric detergents, pour-point depressants, and viscosity-index improvers. Viscosity-index improvers(VII) are oil-soluble polymers having a molecular weight between the range of 4.5×10^4 to 1.7×10^6 . The conduct of viscosity-index (VI) improver depends on the department of polymer in lubricants^{1, 2-4}. The viscosity-index, a number calculated by Dean et.al.⁵ from observed viscosities of an oil at 100oF and 210oF for the measurement of the viscosity change of the oil relative to temperature changes. By definition, high viscosity-index oil is less affected by temperature change than low viscosity-index oil. Aside from the high viscosity-index, lubricating oil should also induce anti-wear property and detergent-dispersant action and also should be used at very low temperatures, i.e. Should have very low pour-point. Chemical and thermal stability are also equally significant for good viscosity-index improver. The viscosity-index improvers are polymers that contract and dilate with changes in temperature. They are very compacting at low temperatures and affect the viscosity of a lubricant very little. But, "expand" at higher temperatures into much larger long-chain polymers which significantly increase the viscosity of their mineral white-oil. Then, as the mineral white-oil with increases in temperature loses viscosity, VI improver prevents the viscosity drop by increasing their size. The thickening power of lubricants is increasing with the increase in molecular weight of the polymers used. But the polymer additives

must be soluble in base oil throughout the use. Copolymers of esters of methacrylic acid with a C10-18 alkanol and Copolymers of C₁₋₂₄ alkyl containing (meth) acrylates, N, N-dialkyl-amino alkyl (meth) acrylates and N-vinylpyrrolidene and/or morpholioalkyl (meth) acrylates are useful as VI improvers for lubricating oil for driving systems^{6,7}. The VI improvers are basically contained five main classes of polymers: Olefin copolymers, polymethylmethacrylates, hydrogenated poly (isoprene or styrene-co-butadiene), combination of polymethylmethacrylates / Olefin copolymers and polystyrene-co-maleic anhydride systems are also used to enhance thickening power of lubricating oils⁸. The terpolymers derived from octadecyl methacrylate / styrene /dodecyl methacrylate are giving properties as VI improvers of lubricating oils⁹. Butyl acrylate copolymers with various α -olefins like octene, dodecene, tetradecene, and octadecene behaves as a VI improvers and pour-point depressants¹⁰.

Material and Methods

Materials: The following substances were purchased from CDH lab reagents and Chiti-Chem Corporation, Gujarat, India, and employed without further purification: p-formaldehyde, Zinc chloride, Acetic acid, Methyl ethyl ketone (MEK), triethyl amine (Et₃N), Sodium iodide, Hydroquinone (HQ), Benzoyl peroxide (BPO), Benzene, acrylic acid, Sodium hydroxide, Hydrochloric acid, Sulfuric acid etc., Vinyl acetate (VAc) was washed with dilute sodium hydroxide solution to remove the stabilizers. Linear alkyl benzene (LAB) dioctyl maleate (DOM) and white oil were purchased from industries and utilized without further refining.

Synthesis of linear alkyl benzyl chloride (LABC)¹¹: LABC is synthesized by chloromethylation of Linear Alkyl Benzene (LAB) (Scheme-1). Dry HCl gas was drawn through a mixture of 0.08 moles of LAB, 0.16 moles p-formaldehyde, 0.15 moles ZnCl₂ and 1.67 moles glacial acetic acid for 6-8 hours, at 80°C, with stirring. After removal of catalysts, the chlorine content was determined by ASTM STD. I. P. -118/48¹².

Synthesis of Linear Alkyl Benzyl Acrylate (LABA)¹³: A mixture of 2 moles of LABC, 2 moles of sodium salt of acrylic acid, 0.7 moles of methyl ethyl ketone, 0.05 moles of triethylamine, 0.03 moles of sodium iodide and 1.5% hydroquinone with respect to the total weight of LABC and sodium salt of acrylic acid was charged into a 1-liter medium pressure apparatus. The content was refluxed with stirring for 2 hours. After removal of catalysts and byproduct, sodium chloride, the reaction content was distilled under low pressure. Thus LABA was obtained with the yield value of 60-70%, unsaturations of 90-95% (determined by Iodine value) and boiling point 270-75°C/3 mm (Scheme-I). The structures of LAB, LABC and LABA were confirmed by Infra Red Spectroscopy, figure-1.

IR Spectroscopic analysis: Nicolet Impact 400D Fourier Transform Infra Red Spectrophotometer was used to identify the commercial grade LAB, synthesized LABC and LABA monomer, using KBr disk. The infra-red spectra of these materials are displayed in figure-1.

Terpolymersation: The different feed ratios of LABA, DOM and VAc are given in table-1; the terpolymers were obtained by free radical polymerization. Monomers were dissolved in benzene and taken in a three-necked flask. At the beginning, the contents were subjected to nitrogen flushing for fifteen minutes, and then gradually heated to 85°C. When the temperature of the reaction reached 85°C, benzoyl peroxide (1.5%) dissolved in benzene as

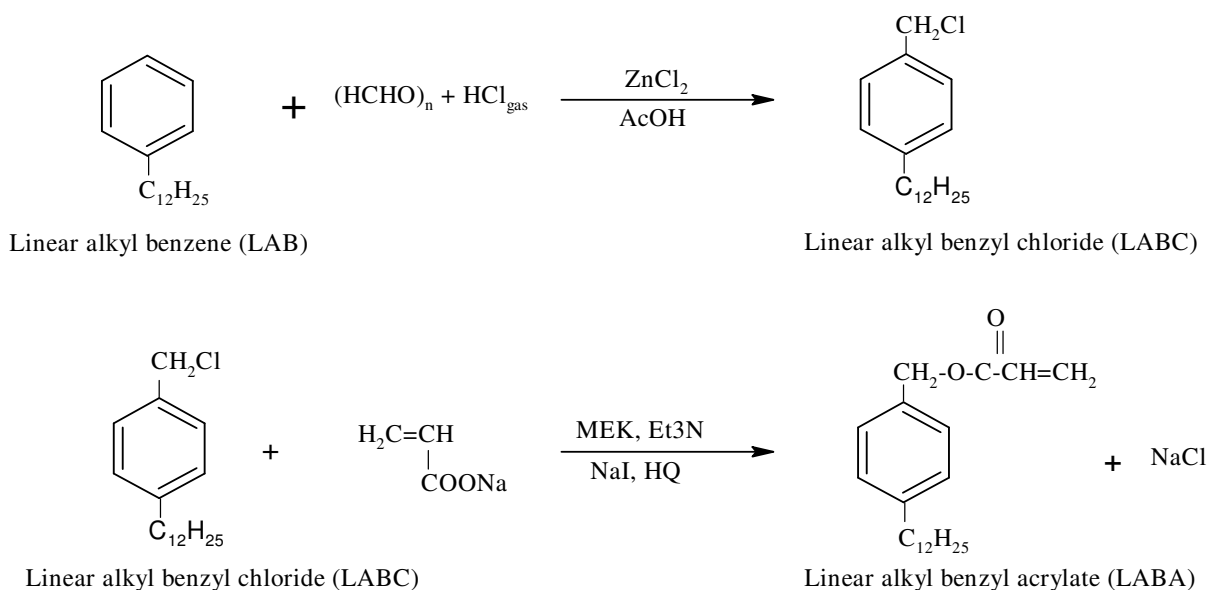
an initiator was added drop by drop. The whole content was refluxed for 12 h. Ultimately, the viscous or gel product was distilled under reduced pressure (~3mm), followed by precipitation in excess ethanol and vacuum dried for 24 hours. The white mineral oil equal in weight of the monomers is added as an additive (terpolymers-white oil, 50:50, w/w) for series IB, while for series IA white mineral oil was not added.

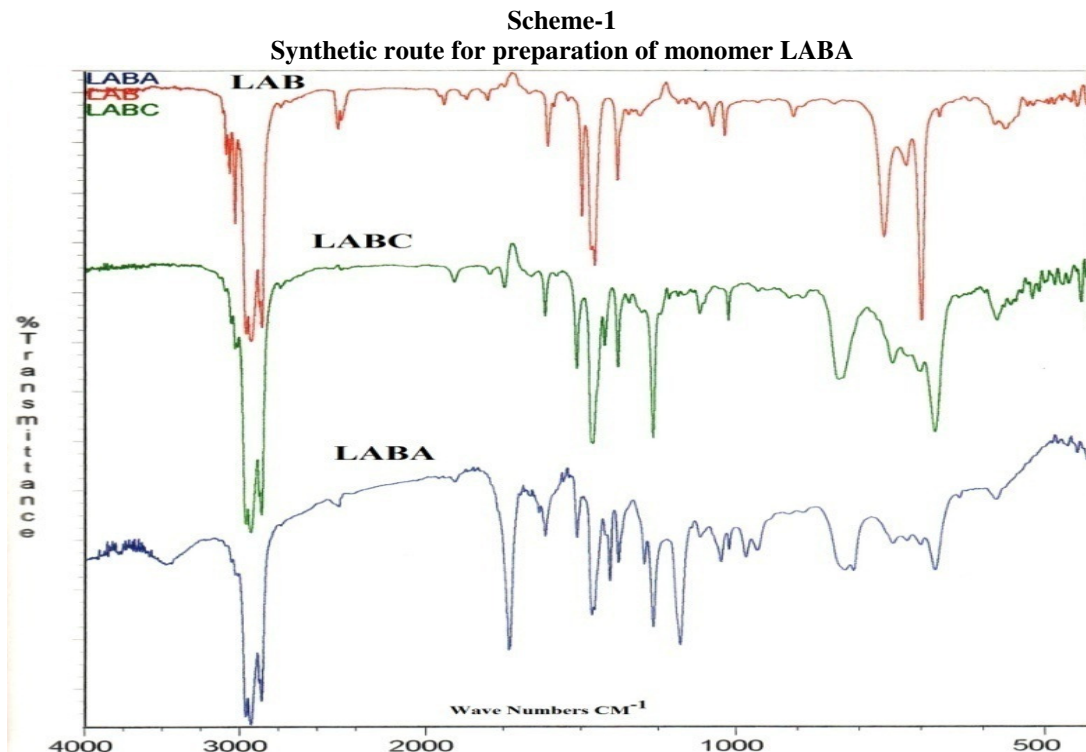
Determinations of absolute Molecular weight and Second Virial constants of the synthesized terpolymers: The number average molecular weights (\bar{M}_n) of the synthesized terpolymers were found out by using High-Speed Membrane Osmometry (Hewlett-Packard-502) equipped with constant temperature device. The second virial coefficients (A_2) were experimentally calculated from the slope of the plot π/c versus c , concentration, at different temperatures. The asymmetry data on terpolymers of the series-IA in toluene and series-IB in white oil at different temperatures are shown in table-2.

Determination of Rheological properties and Viscosity Index (VI): The shear stress-shear rate measurements were carried out on LABA: DOM: VAc, series-IB terpolymers at 100°F and 210°F using Rheometer model Rheostat-II (Germany), concentric cylinder geometry and cone-plate shear elements (with cone angle 3° having a 36mm diameter). The viscosity values at 100°F and 210°F are used to estimate the viscosity-index (VI) of the terpolymers solution in white-oil, ASTM D-2270-64¹⁴. Since the VI of the oil employed is more than 75, the following relation has been employed to estimate VI of some terpolymers solution in oil:

$$VI = [(\text{anti-log } N) - 1/0.0075] + 100$$

Where N relates to the kinematic viscosity at 210°F and other constants





Results and Discussion

Fourier transform infra-red (FTIR) Spectral analysis: The FTIR spectra confirmed that the compositions of the synthesized LABC and LABA. This brings out that the esterification reactions were successfully made out and the desired product formed. The IR spectrum of LABC, observed in figure 2, which can prove the following: 1620, 1518, and 1465 cm^{-1} bands may be assigned to aromatic ring vibrations. 1465-1430 cm^{-1} band may be assigned for CH_3/CH_2 deformation modes, 1378 cm^{-1} is attributed for CH_3 umbrella mode. The para substituted benzene ring has a strong absorption around 840 cm^{-1} , the band observed at 730 cm^{-1} for four or more CH_2 groups. A strong band at around 690 cm^{-1} is attributed for C-Cl stretching mode. For LABA, a strong band obtained at 1731 cm^{-1} due to C=O stretching mode while $\nu_{\text{C-H}}$ (out of plane banding) of vinyl moiety observed at 980-960 cm^{-1} . A medium strong 1405 cm^{-1} band is probably due to in-plane C-H deformation mode of vinyl group. Medium band at 1300 cm^{-1} may be due to C-O stretching.

Determinations of absolute Molecular weight and Second Virial coefficients (A_2) of the terpolymers: The osmotic pressure measurement were carried out for various concentration of each of the samples of series IA in toluene at room temperature, and some of the samples of series IB in white mineral oil at room temperature, 33°C and 70°C to determined the \bar{M}_n (number average molecular) weight and polymer-solvent interaction, thereby, it is possible to obtained

thermodynamic parameter of polymer solutions according to Mc Millan and Mayer¹⁵.

The molar proportion of monomers as indicated in table-1 reveal that the initial samples of A, B and C are associated with large numbers of side groups of LABA and DOM, probably offering strong steric hindrance to the growth of polymer chains resulting in low-molecular weight materials. The other terpolymers with varying the composition of DOM and VAc with a constant proportion of LABA show different nature of polymers which does not permit the correlation of \bar{M}_n with A_2 . It should be pointed out that individual samples of terpolymers are not fractionated thus the observed derived properties are associated with inherent heterogeneity. Nevertheless, the second virial coefficient changes with molecular weight taking cognizance of varying chemical composition of monomeric units in the sample.

The second virial coefficient at 33°C is significantly smaller than IA in toluene at the same temperature as observed by comparing the data of table-2. It may be inferred grossly that white-oil is a weak solvent for the terpolymers and toluene, the good solvent. As the temperature is raised to 70°C, the solvent-polymer interaction increases (becomes more favorable) resulting into increased values of A_2 . Some typical osmometric plots of π/c (cm.lit./g) Versus c (g./Lit.) for series-IA in toluene at room temperature are shown in figure.2, and Series-IB in white-oil at 70°C are shown in figure-3.

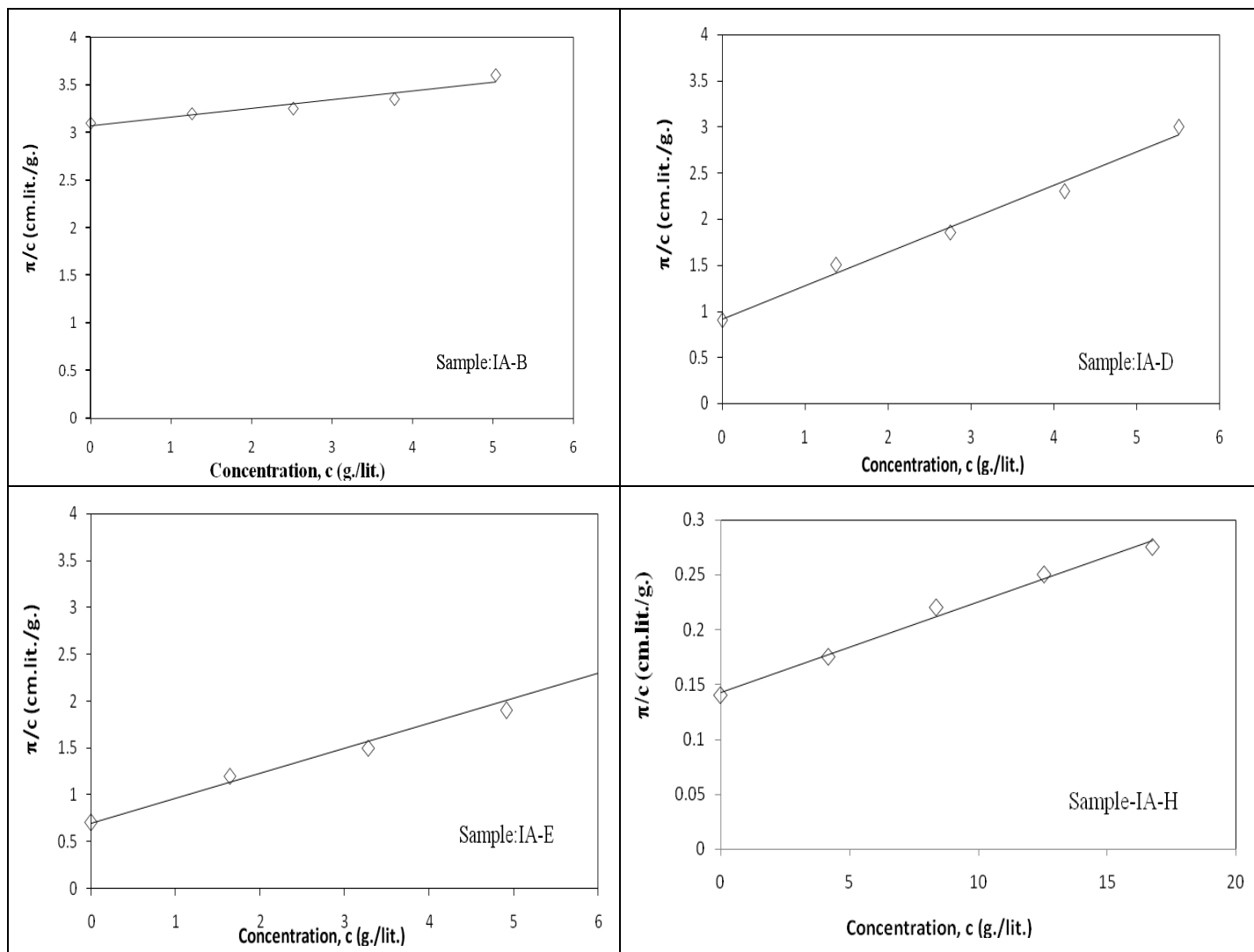


Figure-2

Reduced osmotic pressure, π/c versus concentration c , of series -IA in toluene at 33°C temperature

The backbone length of the terpolymers molecules in terms of contour length (L) was calculated by assuming the average character of the repeat unit in the terpolymers and considering the C-C bond length as 1.54 \AA . For example, consider sample-A of IA series having $\bar{M}_n = 7.5 \times 10^3$ and molar proportion of monomers as LABA:DOM:VAc: 0.1:0.8:0.1; the average monomer weight (\bar{m}_0) comes out to be 313.6 and hence the average number of repeat units (\bar{n}) in the polymer chains assumes the value 23.9, the contour length (L) of the terpolymers is 73.6 \AA ($=3.08 \times 23.9$), and the number of pendent octyl groups (branches) in the chain (p), amounts to be 43 [$=23.9 (0.1 \times 2 + 0.8 \times 2)$]. These parameters for all other terpolymers samples of IA and IB series are calculated and tabulated in table-3.

Determination of Kinematic Viscosity and Viscosity-index (VI): The effect of the polymeric compounds as viscosity index

improvers depends mainly on the behavior of polymer molecules in the dispersed phase (base oil or white oil). It was found that a polymeric solution viscosity depends on the polymer chain size and the extent of their intermolecular and intramolecular interactions, also dependent on the interactions between polymer and solvent molecules, concentration of polymer and the solvent nature.

The terpolymers were tested for their effectiveness towards viscosity index improvers for the base oil. In this respect, the kinematic viscosities were determined at 100°F and 210°F for the undoped oil contains 50% concentration of the tested additives. \bar{M}_w (weight average molecular weights) are obtained from GPC analysis and the computed values of Viscosity Index (VI) for all sample studies are included in Table-4. The values of VI vary from 48 to 374, respectively, from samples A to H of the series-IB terpolymers. The data

obtained reveal that viscosity-index increases with rise in MW (molecular weight) of terpolymers. More precisely viscosity-index increases in the polymer samples with decreasing proportion of DOM, that is, by decreasing the number of pendent groups in a long polymer chain. This would be exonerated if we examine the data of table-3 with respect to \bar{n} and p values. Each repeat unit possesses more than one pendent group from sample A to D; Hence the contribution of pendent group is more than the backbone contribution. It should be clear therefore that for a successful VI improver there should be a significant length of the chain, owing to the influence of the molecular weight on the effective coil radius and hence the VI. This measure is not satisfied by initial samples and thus they are poor VI improvers. They may be treated as base oils.

The kinematic viscosity calculations were carried out on dilute solutions (1 to 10%) of Series-IA, sample-E and F terpolymers using white-oil as solvent, employing concentric cylinder

rotational viscometer, at room temperature, 100⁰F and 210⁰F. The typical plots of kinematic viscosity versus concentration and VI versus concentration at different temperatures for IA-E and IA-F terpolymers in white-oil are shown in figure-4. The high values of the VI are obtained even at 2-3% concentration of terpolymers in oil.

Determination of pour-point, cloud-point and freezing point: In order to characterize the behavior of the terpolymers as pour-point depressant of the base oil, the terpolymers-oil solutions (50:50 w/w) were subjected to the test as per the ASTM D97-39¹⁶ method using the specified equipment and thermometers. The observed values of cloud-point, pour-point and freezing-point for terpolymers of the series-IB are tabulated in Table-5. It was found that the prepared compounds were efficient as Pour-point depressant and the efficiency increases by decreasing the concentration of the vinyl acetate (VAc) monomer.

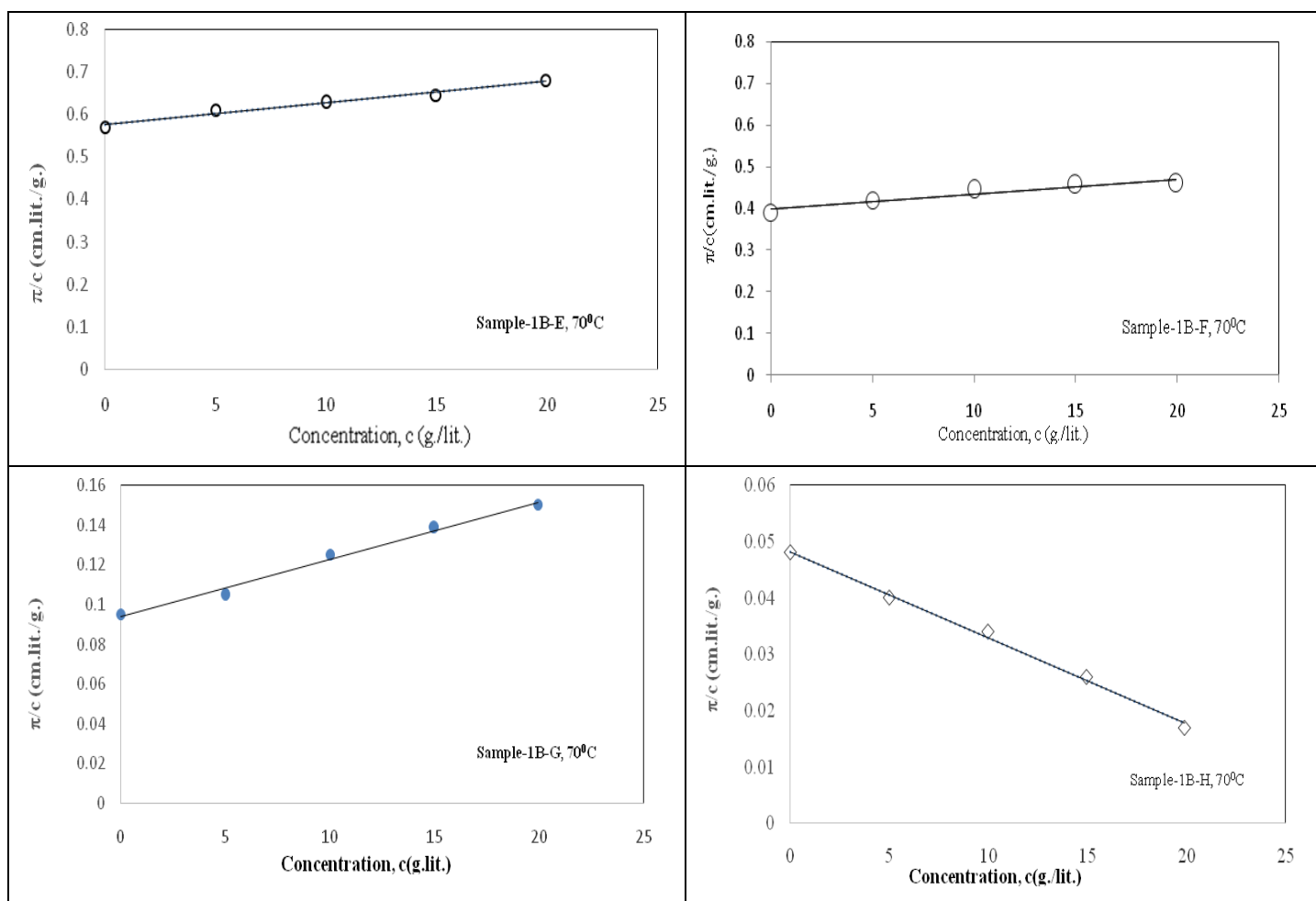


Figure-3

Reduced osmotic pressure, π/c versus concentration c , of Series-IB (Sample-E, F, G and H) in white oil, at 70°C

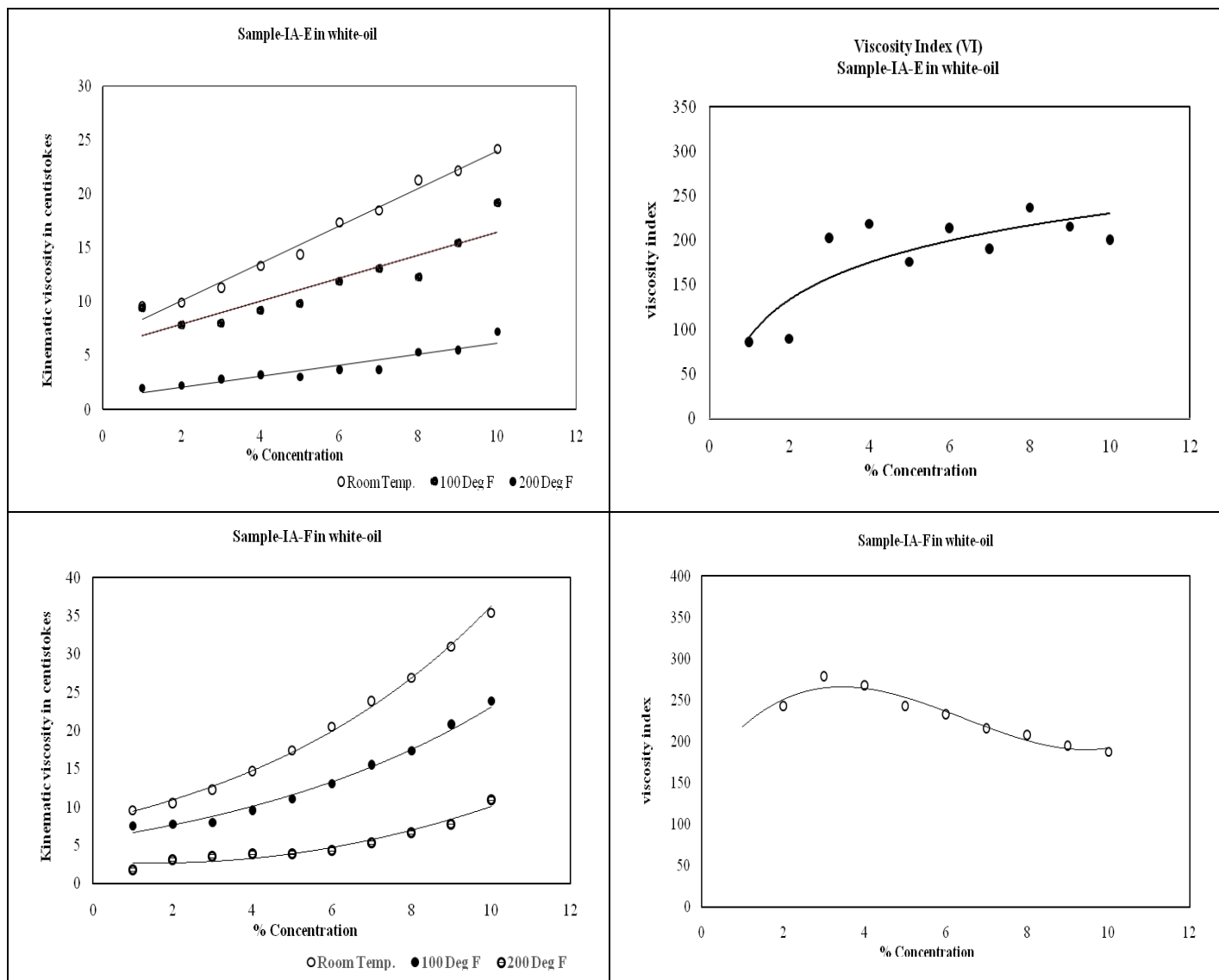


Figure-4

Plots of dilute solution kinematic viscosity and VI versus concentration (%) at several temperatures of series IA using white-oil as a solvent

Table-1
 Terpolymers designation and Monomer feed

Terpolymers Designation SAMPLE	MONOMER RATIO	
	SERIES-IA LABA:DOM:VAc	SERIES-IB LABA:DOM:VAc
A	0.1:0.8:0.1	0.1:0.8:0.1
B	0.1:0.7:0.2	0.1:0.7:0.2
C	0.1:0.6:0.3	0.1:0.6:0.3
D	0.1:0.5:0.4	0.1:0.5:0.4
E	0.1:0.4:0.5	0.1:0.4:0.5
F	0.1:0.3:0.6	0.1:0.3:0.6
G	0.1:0.2:0.7	0.1:0.2:0.7
H	0.1:0.1:0.8	0.1:0.1:0.8

Table-2
Osmometry results of LABA: DOM: VAc terpolymers

Series IA in toluene at room temperature (33 ⁰ C)			Series IB in white-oil at different temperatures			
Sample	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$ cc.mole/g ²	Sample	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$ cc.mole/g ²	
A	0.75	40.0			33 ⁰ C	70 ⁰ C
B	1.00	66.6	D	9.6	5.13	1.87
C	1.16	85.6	E	10.1	0.49	1.43
D	4.00	138.9	F	15.9	0.7	2.14
E	6.66	111.2	G	33.6	0.89	0.68
F	8.6	0.85	H	40.8	0.49	-0.68
G	12.20	0.98	-	-	-	-
H	20.05	2.6	-	-	-	-

Table-3

The average monomer weight (\bar{m}_o), the number of average repeat units (\bar{n}), the contour length (L) and the number of branches (p) in the terpolymers molecules of series-I based on Table-1 and 2.

Series-IA in Toluene				
Sample	\bar{m}_o	\bar{n}	L, A^0	p
A	313.6	23.9	73.6	43.0
B	288.2	34.7	106.9	55.6
C	262.8	44.0	135.5	61.6
D	237.4	168.4	518.6	202.1
E	212.0	314.3	968.0	314.3
F	186.6	460.7	1418.9	368.6
G	161.2	756.9	2331.3	454.1
H	135.8	1476.8	4548.5	590.7
Series-IB in white-oil				
Sample	\bar{m}_o	\bar{n}	L, A^0	p
D	237.4	404.4	1245.6	485.0
E	212.0	476.4	1467.3	476.0
F	186.6	852.1	2624.5	681.0
G	161.2	2084.4	6419.9	1250.0
H	135.8	3004.4	9253.6	1201.0

Table-4

Viscosity-index (VI) data derived for Series-IB terpolymers in white-oil

Sample	Device	$\bar{M}_w \times 10^{-4}$	Viscosity (η) cps		VI
			100 ⁰ F	210 ⁰ F	
A	RC	4.62	7.78	1.85	48
B	RC	2.13	13.7	3.1	129
C	RC	3.19	19.3	4.46	169
D	RC	7.37	100	9.62	89
E	RC	6.53	215.7	34.26	214
F	CP	10.97	307.7	47.1	223
G	CP	16.35	411	63.16	236
H	CP	18.53	998.8	243.48	374

Where, RC: Rotational cylindrical device, spindle S1, CP: Cone and plate device, CP-3⁰ 36mm

Table-5
The pour-point, cloud-point and freezing-point data (ASTM D97-39) of Series-IB terpolymers

Sample	Appearance at room	Cloud-point	Pour-point	Freezing-point
A	Clear viscous liquid	17	8	6
B	Clear viscous liquid	19	8	6
C	Clear viscous liquid	22	11	7
D	Clear viscous liquid	23	11	8
E	Clear viscous liquid	24	11	8
F	Clear viscous liquid	27	12	9
G	Clear highly viscous	28	12	9
H	Slight hazy highly	29	13	10

Conclusion

i. Linear alkyl benzyl acrylate monomer derived from linear alkyl benzene via chloromethylation was synthesized, purified and characterized. ii. A series of terpolymers derived from linear alkyl benzyl acrylate, dioctyl maleate and vinyl acetate were prepared and characterized. iii. The introduction of long-chain alkyl group from LABA and DOM provides little or no variations in viscosity with temperature, which is one of the significant characteristics of good viscosity index improvers. iv. Thus, the novel terpolymers derived from LABA,DOM and VAc are very good Viscosity Index improvers giving very high value (200-240) at even 2% concentration of the terpolymers in white-oil.

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