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Synthesis of Modified Polyisoprene Based Viscosity Index Improvers for Lubricants

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Abstract

A number of polyisoprenes (PI) and their modified star-branched polymers (PISB) have been synthesised by anionic polymerization technique using butyl litium (BuLi) as catalyst and divinyl benzene(DVB) as coupling agent. Synthesised polymers and a commercial product have been comparatively studied in a mineral lubricant for thickening and viscosity index (VI) improving behaviour. Star-branched polymers have shown better thickening and VI improving properties.

Introduction

VI improver are added to lubricants (mineral as well as synthetic oils) to maintain optimum levels of viscosity for minimising frictional losses in hydrodynamic lubrication regime over wide operating temperatures during their service (1). Of the three classes of commerially accepted VI improvers viz. diene copolymers, polymethacrylates and olefin copolymers diene based polymers/copolymers occupy a prominent place in the market as it is possible to tailor their structure, molecular weight and molecular weight distribution by anionic polymerisation techniques. Amongst diene based polymers, styrene-isoprene copolymers and styrene-butadiene copolymers are commerically used. Isoprene/butadiene polymers are reported to be potential VI improvers (2,3): however, they are not commercially significant.

In spite of considerable work on synthesis of diene polymers and copolymers for application as VI improvers (4-6), relatively less is known about their structure-performance relationship. The present paper reports the synthesis and evaluation of a number of polyisoprenes and their modified star-branched polymers as VI improvers. Data on thickening and VI improving behaviour of twelve synthesised polymers determined in a mineral lubricant have been presented.

Experimental

Materials : Isoprene (Fluka make), DVB (Aldrich, 55% solution in ethylvinyl benzene), n-BuLi (Aldrich, 2.5 M solution), cyclohexane

(GSFC, Baroda) and molecular sieves type 5A and alumina grade G-87 (IPCL,Bombay) were used.

Purification : Cyclohexane was purified by refluxing and distilling over sodium-benzophenone catalyst followed by refluxing and distilling from n-BuLi and finally percolation through activated alumina and molecular sieve (for removal of inhibitor and moisture at trace level (7,8). Isoprene was purified by treatment with freshly sublimed maleic anhydride at 0-5°C followed by stirring and distilling from n-BuLi, percolation through activated alumina and molecular sieves and finally stirring and distilling over n-BuLi (7,8). DVB was purified by percolation through activated alumina followed by distillation at reduced pressure from n-BuLi. The moisture content of the purified solvent and monomers was maintained below 10 ppm level.

Synthesis of polymers : Homo and star branched isoprene polymers were synthesised by anionic polymerization technique using varying concentrations (0.05-0.2 wt %) of n-BuLi. For the synthesis of star branched polymers, DVB was used with varying molar ratio of DVB to n-BuLi between 1 and 6. In a typical polymerization reaction, required quantity of cyclohexane was charged to a 250 ml 4-necked flask equipped with condenser, addition funnel, thermo well, magnetic stirrer, heating oil bath and gas inlet tube. When the reaction flask had attained the desired temperature, required amount of isoprene and n-BuLi (premixed in the addition funnel) were added slowly under stirring. Rise in reaction temperature by 12-15°C indicated the formation of polymer. The temperature of the bath was then raised by about 20°C and the reaction was allowed to run for another half an hour. The polyisoprene was recovered from the reaction mixture by methanol treatment followed by drying in vacuum at 50-60°C.

The synthesis of star branched polyisoprenes was carried out in a similar manner. Required quantity of DVB was added to the living polymers after achieving desired level of conversion. The reaction was continued for additional 1-2 hrs. Appearance and persistence of red colour in the reaction flask indicated formation of star branched product.

In all, two polyisoprenes and ten star-branched polyisoprenes were synthesised. Characterisation of polymers was done by determination of molecular weight ($\bar{M}w$, $\bar{M}n$), molecular weight distribution ($\bar{M}w/\bar{M}n$) and number of arms for the star branched polymers with the help of GPC technique using linear-polyisoprene standards. Intrinsic viscosity measurements of polymers in cyclohexane at 30°C were also determined to study possible relationship between molecular weight properties and thickening tendency (Table 1).

Table 1 Synthesis and characterization data of synthesized polymers

Sr. No	Polymer code	n-BuLi %	DVB/n-BuLi molar ratio	$\bar{M}w$	$\bar{M}w/\bar{M}n$	No.of arms	[h] dl/g
1	PI-1	0.05	-	131000	1.21	-	1.120
2	PI-2	0.10	-	75000	1.15	-	0.740
3	PISB-1	0.05	1	650000	1.10	5	-
4	PISB 2	0.05	2	580000*	-	-	2.410
5	PISB-3	0.05	3	701000	1.25	5	2.740
6	PISB-4	0.05	6	744000	1.26	5	2.400
7	PISB-5	0.10	1	468000	1.09	6	1.590
8	PISB-6	0.10	3	600000*	-	5	1.840
9	PISB-7	0.15	1	377000	1.07	6	1.275
10	PISB-8	0.15	3	400000	1.10	6	1.440
11	PISB-9	0.20	1	350000*	-	5	0.745
12	PISB-10	0.20	3	371000	1.08	6	1.150

Performance evaluation : Performance of the synthesised polymers as well as a commerical product (CP) was studied in a mineral lubricant of 10.6 cSt viscosity at 100°C in terms of thickening and VI improvement for purposes of achieving viscosity targets of multigrade oils.

Results and Discussion

Polymer synthesis : Table 1 gives data on catalyst, DVB:BuLi ratio, molecular weight,intrinsic viscosity for twelve synthesised polymers. It is observed that polydispersity ($\bar{M}w/\bar{M}n$) of the polymers obtained was satisfactory; values remained below 1.2 except in two cases. As expected, molecular weights were found to decrease with increase in catalyst concentration. No significant increase in molecular weight and number of arms in the star-branched polymers was noticed with increase in DVB to BuLi molar ratio from 1 to 6. Although intrinsic viscosity values, in general, were found to increase with increase in molecular weight no linear relationship between the two properties was observed as reported earlier (9).

Thickening and VI improving behaviour of polymers : Effect of twelve synthesised polymers and a commercial product coded as CP on the thickening and VI improving behaviour of a mineral lubricant at 0.5 wt percent concentration is given in Table 2. All the products increased the viscosity and VI of the mineral lubricant (thickening at 100°C by 1.6 - 5.4 cSt and VI by 6-24 units). The degree of increment in thickening and VI improvement was found to depend on molecular weight and type of polymer; star-branched products,

in general, showed higher thickening and VI improvement effect than the homopolymers. It was also observed that a number of synthesised star-branched products showed comparatively better performance than CP.

Table 2 Effect of synthesised polymers and commercial product on thickening and VI improving behaviour in a mineral lubricant at 0.5 wt. percent concentration

Sr.No.	Polymer code	KV at 100°C, cSt[a]	Thickening, cSt[b]	VI[c]
0	None	10.59	-	103
1	PI-1	13.06	2.47	114
2	PI-2	12.23	1.64	109
3	PISB-1	14.21	3.62	118
4	PISB-2	15.34	4.75	122
5	PISB-3	15.93	5.34	127
6	PISB-4	16.00	5.41	127
7	PISB-5	14.17	3.58	119
8	PISB-6	14.67	4.08	124
9	PISB-7	13.36	2.77	114
10	PISB-8	13.68	3.09	117
11	PISB-9	12.20	1.61	109
12	PISB-10	13.14	2.55	116
13	CP	13.57	2.98	117

a Kinematic Viscosity (KV) at 100°C as per ASTM D-445 method
b Thickening : KV of polymer treated oil - KV of untreated oil determined at 100°C. c VI : As per ASTM D-2270 method

Figs 1 and 2 show effect of concentration (0.1-0.5%) of six selected synthesised polymers and CP on thickening and VI improvement of a mineral lubricant. As expected, the thickening and VI improving effect was found to depend on polymer concentration; increase in polymer concentration resulted in increase in thickening and VI. In general, the improvement was pronounced beyond 0.3 wt% concentration of polymer. Amongst all the products studied, star-branched polymer, PISB-3 exhibited the best performance both in thickening and VI improving characteristics and appeared to be a potential candidate for formulating multigrade oils at a lower treat level.

Studies on other performance properties which are essentially requirement for a VI improver such as shear stability, low temperature viscosity, rheological characteristics etc. are in progress. Preliminary results indicate that synthesised polymers possess good shear stability characteristics.

Conclusion

Two homo and ten star branched polyisoprenes of varying molecular weight were synthesised using BuLi as catalyst and DVB as coupling agent. No significant change in number of arms with varying molar ratio of DVB to BuLi was observed.

FIG 1: EFFECT OF SYNTHESISED POLYMER CONCENTRATION ON THICKENING BEHAVIOUR IN A MINERAL LUBRICANT AT 100 DEG C

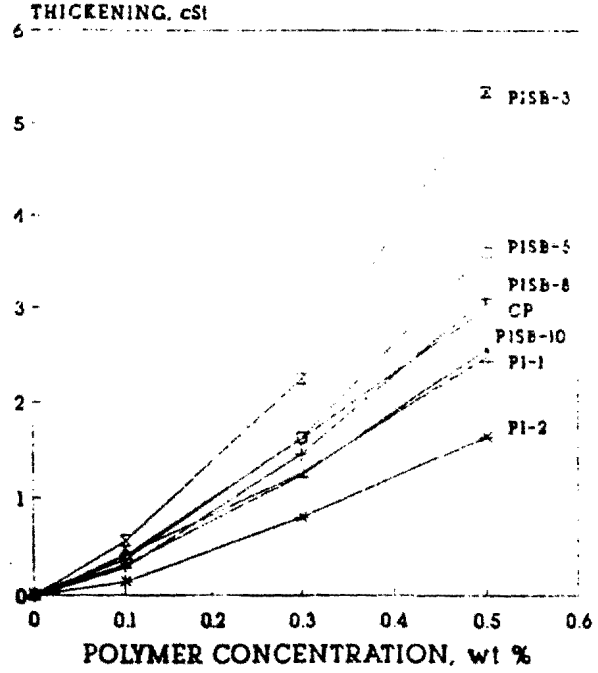
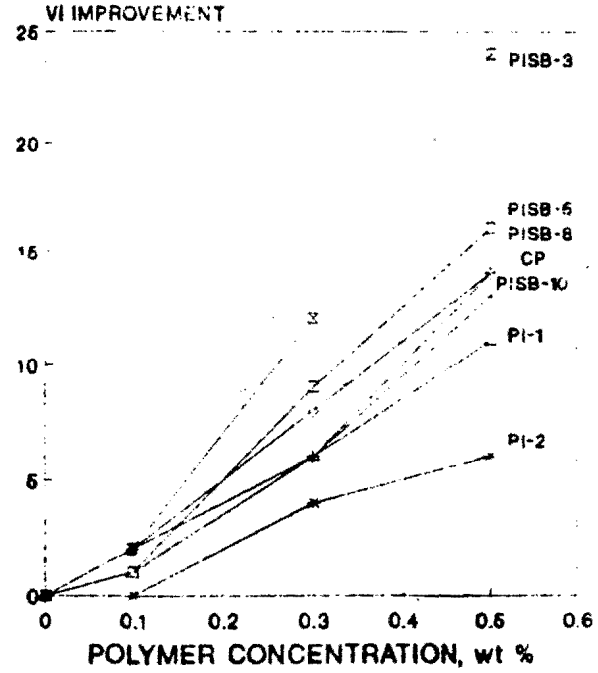


FIG 2: EFFECT OF SYNTHESISED POLYMER CONCENTRATION ON VI IMPROVEMENT IN A MINERAL LUBRICANT



Synthesised products in a mineral lubricant exhibited good effect in thickening and VI improving characteristics. Star-branched polymers showed superior performance.

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