

Synthesis and Evaluation of Poly- α -olefins for Improving the Flow Properties of Gas Oil

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SYNOPSIS

Polymers of individual and mixed normal C₁₂, C₁₄, C₁₆, and C₁₈ α -olefins are synthesized, purified, and then characterized. The performance of poly- α -olefins is assessed for improving the cold flow properties of a local gas oil in terms of cloud-point and pour-point depression. Results show that poly- α -olefins have great potency in decreasing the pour point of the distillate fuel, whereas a slight effect is observed in decreasing the cloud point. Efficiency of the polymeric pour-point depressants is discussed on the basis of their structure and average molecular weight. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Wax-bearing distillate fuels are known to set a semiplastic mass on cooling below the temperature of the crystallization point of their wax content. This change is measured in terms of cloud point and/or pour point. The problem is that the wax content in distillate fuels, particularly those of a high final boiling point that are composed mainly of normal paraffins of a high carbon number, will crystallize at relatively high temperatures when the fuel is cooled. Networks of wax crystals will then be formed on further cooling, leading to clogging of fuel lines and filters.¹

Many different types of pour-point depressants have been used to overcome this problem, e.g., condensation products of chlorinated paraffins and naphthalene, polyacrylates, polymethacrylates, copolymers of ethylene and vinyl esters, copolymers of fumarates/maleates and vinyl acetate, copolymers of styrene and maleates, and copolymers of α -olefins and maleates and poly- α -olefins.²

These polymeric additives function by nucleation, adsorption, and/or cocrystallization with the formed wax crystals in such a way as to be less prone to

each other, thus modifying their size and shape into compact fine crystals, i.e., crystal growth is not prohibited; it is simply directed or channeled along different routes.³ Poly- α -olefins have long been used as an important class of pour-point depressants for lubricating oils,⁴⁻⁶ distillate fuels,^{7,8} and residual fuel oils.⁹

Some investigators have synthesized high molecular weight poly- α -olefins from high carbon number α -olefins using the Ziegler-Natta catalyst in the presence of H₂ (Won and Maplewood¹⁰; Heilman and Wilburn³; Chong⁴). Others have oligomerized high α -olefins (C₁₀—C₁₆) in the presence of the AlBr₃/HBr catalytic system (Fontana et al.¹¹). Other workers (Thomas and David⁷; Morduchowitz and Bialy⁹; and Harold et al.⁸) used anhydrous AlCl₃ solely for the oligomerization of high α -olefins.

The present work was aimed at synthesizing high molecular weight poly- α -olefins that could be utilized as pour-point depressants for the Egyptian waxy western desert gas oil. This object was realized by developing a proposed catalytic system of AlCl₃/HCl so as to avoid numerous side reactions that occur during cationic polymerization when using AlCl₃ only and lead to oligomerization. The performance of the prepared polymers on the basis of their structure and average molecular weight is also discussed.

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Table I Physicochemical Characterization of the Investigated Gas Oil

Test	Method	Value
Sp. gr. 60/60°F	IP 160/87	0.8527
Aniline point, °C	IP 2/78	92
Flash point, °C	ASTM D 93/85	108
Kinematic viscosity at 40°C, cSt	IP 71/80	8.91
Cloud point, °C	ASTM D 2500	13
Pour point, °C	ASTM D 97	6
<i>n</i> -Paraffin content, wt %	Urea adduction ¹²	12.5
Average carbon no. of <i>n</i> -paraffin content	Gas chromatography	18
Distillation, °C	ASTM D 86	
IBP %		167
10%		236
20%		255
30%		285
40%		299
50%		310
60%		333
70%		351
75%		359
79%		362
FBP		362
Recovery		79 vol %
Residue		20 vol %
Loss		1 vol %

EXPERIMENTAL

Materials

Four commercial pure long-chain C₁₂, C₁₄, C₁₆, and C₁₈ α -olefins (NEODENE α -olefins) were supplied by Shell Chemical Co. The other chemicals are of technical grade. A local waxy gas oil of the physicochemical characteristics (listed in Table I) is used for evaluating the performance of the prepared additives.

Polymerization of α -Olefins

Polymerization reactions were conducted by applying cationic polymerization using the proposed catalytic system, AlCl₃/HCl (catalyst/cocatalyst) where the cocatalyst HCl functions as the proton-donating compound. The defined quantity of individual or mixed α -olefins and *n*-pentane as an inert diluent are charged into a two-neck flask equipped with a mechanical stirrer and a contact thermometer. In addition, anhydrous AlCl₃ is added in a molar ratio of 0.1 mol AlCl₃ : 1 mol monomer. The calculated quantity of AlCl₃ is added periodically in four equal

batches every 0.5 h from the beginning of the reaction. HCl is added in an equimolar ratio with respect to AlCl₃ in every batch while vigorously stirring at 25–27°C for 3–6 h.

The crude poly- α -olefins were purified by pouring into distilled water for the washing of the catalyst and the separation of the organic layer, then quenched in isopropanol, left for 0.5 h for decantation, and then dried by vacuum distillation at 80°C. The purified poly- α -olefins showed either a viscous clear light orange or a viscous white gelatinous appearance. The reaction conditions of polymerization of the prepared poly- α -olefins are listed in detail in Table II.

Polymerization Reaction

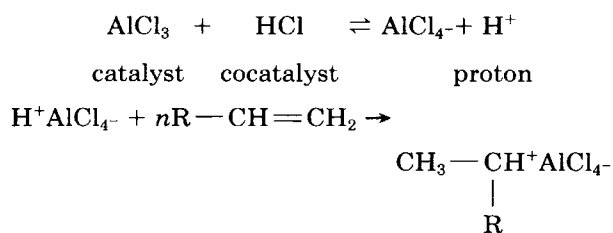
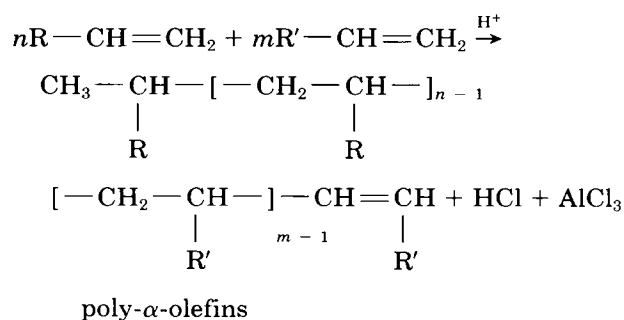


Table II Reaction Conditions for Polymerization of α -Olefins (C_{12} – C_{18})

Reaction Symbol	Reaction Components			Reaction Conditions		
	Monomers	Average Side-chain Carbon Length (C_{av})	Diluent	Catalyst System	Temp (°C)	Time (h)
R0-1	30 g α -dodecene	10	100 g <i>n</i> -pentane	2.4 g anhydrous $AlCl_3$ 0.6 mL HCl	25	6
R0-2	30 g α -tetradecene	12	100 g <i>n</i> -pentane	2.0 g anhydrous $AlCl_3$ 0.5 mL HCl	25	4
R0-3	30 g α -hexadecene	14	100 g <i>n</i> -pentane	1.8 g anhydrous $AlCl_3$ 0.5 mL HCl	27	3
R0-4	30 g α -octadecene	16	100 g <i>n</i> -pentane	1.6 g anhydrous $AlCl_3$ 0.4 mL HCl	27	3
R0-5	7 g α -dodecene 53 g α -octadecene	15	200 g <i>n</i> -pentane	3.4 g anhydrous $AlCl_3$ 0.8 mL HCl	27	3
R0-6	10 g α -tetradecene 35 g α -octadecene	15	150 g <i>n</i> -pentane	2.5 g anhydrous $AlCl_3$ 0.6 mL HCl	27	3
R0-7	30 g α -hexadecene 30 g α -octadecene	15	200 g <i>n</i> -pentane	3.4 g anhydrous $AlCl_3$ 0.8 mL HCl	27	3
R0-8	7 g α -dodecene 8 g α -tetradecene 15 g α -hexadecene 30 g α -octadecene	14	200 g <i>n</i> -pentane	3.6 g anhydrous $AlCl_3$ 0.8 mL HCl	27	3
R0-9	15 g α -dodecene 15 g α -tetradecene 10 g α -hexadecene 5 g α -octadecene	12	150 g <i>n</i> -pentane	3.0 g anhydrous $AlCl_3$ 0.7 mL HCl	27	3



where R and R' are linear alkyl chains of C_{10} – C_{16} .

Characterization of the Synthesized Poly- α -olefins

The synthesized poly- α -olefins were characterized in terms of kinematic viscosity, average molecular weight, and molecular weight distribution as given in Table III and illustrated in Figure 1. The average molecular weight of the polymers was measured by a high-performance liquid chromatography (HPLC)

apparatus (Waters Model 510) using a gel permeation chromatographic technique against polystyrene molecular weight standards. The following conditions were applied during measurement:

Solvent: Toluene, HPLC grade

Column: Ultrastyrigel 500, 1000, 10000, 100000 Å

Temperature: 25°C

Flow speed: 18 cm³ min⁻¹

The structure of the prepared poly- α -olefins was studied through infrared (IR) spectral analysis. The IR spectra showed similar patterns as shown in Figure 2, curves (b), (c), and (d), for α -dodecene homopolymers, α -dodecene- α -octadecene copolymers, and an α -dodecene- α -tetradecene- α -hexadecene- α -octadecene terpolymer, respectively. Curve (a) represents the IR spectral pattern of the monomer α -dodecene which illustrates the C–H stretching

Table III Characterization of the Synthesized Poly- α -olefins

Polymer Designation	Composition	Average Side-chain Carbon Length (C_{av})	Kinematic Viscosity at 100°C, cSt	M_w	Appearance
P ₁	Poly- α -dodecene	10	27.5	56,000	Viscous clear light yellow
P ₂	Poly- α -tetradecene	12	48.3	77,400	White gelatinous viscous
P ₃	Poly- α -hexadecene	14	35.2	60,200	Viscous clear light yellow
P ₄	Poly- α -octadecene	16	65.7	89,400	White gelatinous viscous
P ₅	Poly(α -dodecene-co- α -octadecene)	15	28.7	57,700	Viscous clear light yellow
P ₆	Poly(α -tetradecene-co- α -octadecene)	15	38.5	69,200	Viscous clear light yellow
P ₇	Poly(α -hexadecene-co- α -octadecene)	15	29.8	57,500	Viscous clear light yellow
P ₈	Poly(α -dodecene, α -tetradecene, α -hexadecene, α -octadecene)	14	27.6	55,500	Viscous clear light yellow
P ₉	Poly(α -dodecene, α -tetradecene, α -hexadecene, α -octadecene)	12	28.4	58,000	Viscous clear light yellow

vibration of $=CH_2$ and CH_2 and CH_3 absorbed strongly at 3079 and 2836 cm^{-1} , respectively, whereas the C—H out-of-plane bending vibration of $=CH_2$ appeared strongly at 994 and 909 cm^{-1} for the vinyl group and as a weak absorption of the in-plane bending vibration at 1415 cm^{-1} . The C=C stretching vibration of unsaturation gives rise to a strong absorption band at 1642 cm^{-1} . A strong absorption of the bending vibration appeared at 754 cm^{-1} for $(CH_2)_n$. The structure of the synthesized polymers was confirmed by the three typical identical curves, (b)–(d), in which a total absence of the C=C stretching vibration at 1642 cm^{-1} , the $=CH_2$ stretching vibration absorbed at 3079 cm^{-1} , the C—H out-of-plane bending vibration of the vinyl group at 994 and 909 cm^{-1} , and absence of the C—H in-plane bending vibration of the vinyl group at 1415 cm^{-1} , i.e., there is no contamination of the polymers with the monomer.

Evaluation Tests

The nine synthesized polymers were assessed for their effectiveness in improving the cold-flow properties of a local gas oil in terms of a pour-point test

according to the ASTM D-97 procedure and a cloud-point test according to the ASTM D-2500 procedure.

RESULTS AND DISCUSSION

The performance of the pour-point depressants is known to be dependent on their structure. The following factors are discussed in the case of the present synthesized poly- α -olefins:

Average Molecular Weight and Molecular Weight Distribution

The prepared poly- α -olefins P₁–P₉ were added individually to the investigated gas oil at concentrations of 2000 and 5000 ppm successively for each. The treated samples were tested for their pour point and cloud point. Results are listed in Table IV, from which it is obvious that P₄ has achieved the optimum effectiveness of the pour-point depression ($>24^\circ C$) at a 2000 ppm concentration, followed by P₃ and P₆, which attained 12 and 9°C consecutively. This result can be accounted for by the higher average molecular weights of the three poly- α -olefins ($M_w > 60,000$).

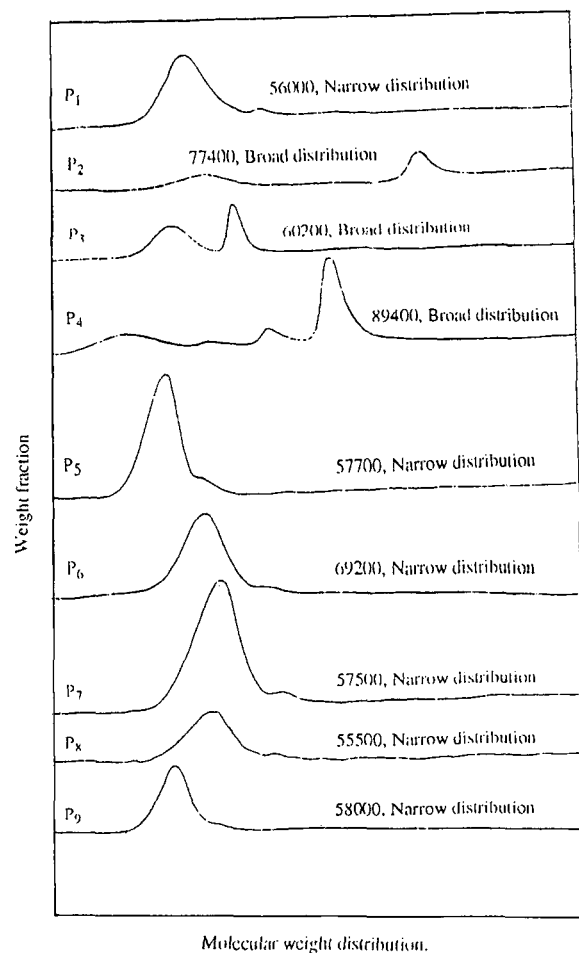


Figure 1 Molecular weight distribution of the prepared poly α -olefins P_1 - P_9 .

On the other hand, P_2 does not have a pour-point depression despite its higher molecular weight ($M_w = 77,400$). This may be due to its relatively short side-chain moiety C_{12} which is incapable of mutual interaction with the average carbon number of n -paraffin content in the tested gas oil composition C_{18} . As for the cloud point, the nine prepared poly- α -olefins do not have any significant effect except a 3°C depression at most.

In addition, it is also realized that the molecular weight distribution of the prepared poly- α -olefins plays an important role in defining their effectiveness as pour-point depressants. It is obvious from Table IV and Figure 1 that the two efficient poly- α -olefins P_3 and P_4 exhibit a broad molecular weight distribution, while the rest have a narrow distribution. P_2 showed no efficiency in spite of its higher average molecular weight and broad molecular weight distribution owing to the lack of interaction

with the n -paraffin content in the gas oil as previously mentioned.

Side-chain Length

The influence of the side-chain length of the prepared poly- α -olefins on their effectiveness as pour-point depressants was studied through the evalua-

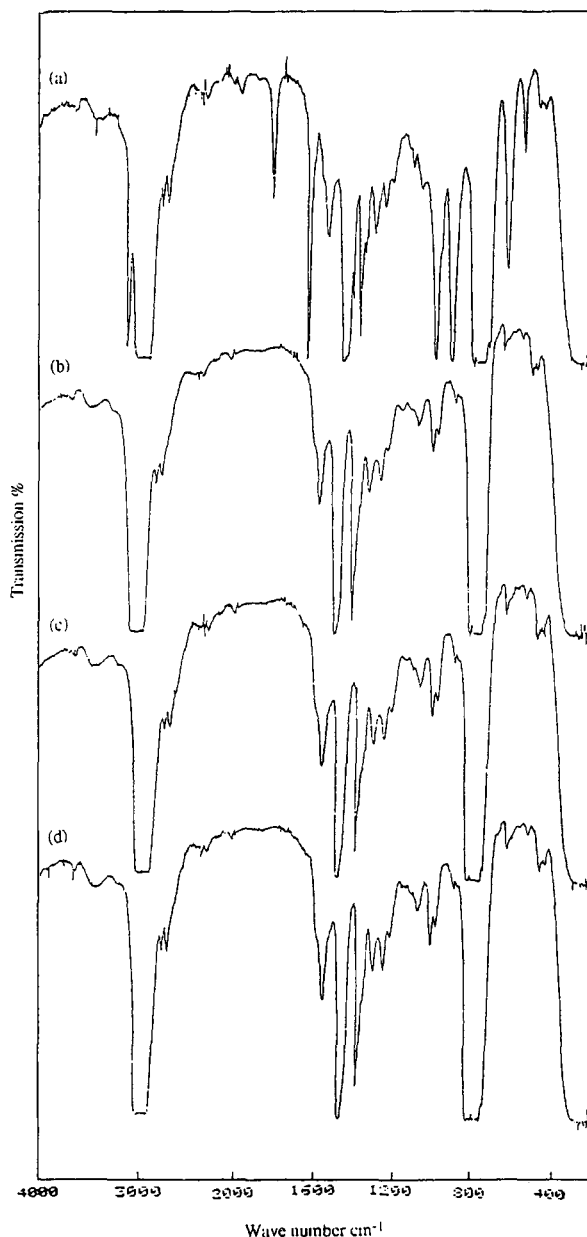


Figure 2 IR spectra of (a) α -dodecene, (b) poly α -dodecene, (c) poly (α -dodecene-co- α -octadecene), and (d) poly (α -dodecene-co- α -tetradecene-co- α -hexadecene-co- α -octadecene).

Table IV Activity of Poly- α -olefins in Improving the Flow Properties of the Tested Gas Oil Blend

Polymer Designation	Average Side-chain Carbon Length (C_{av})	M_w	Concentration (ppm)					
			Pour Point ($^{\circ}\text{C}$)			Cloud Point ($^{\circ}\text{C}$)		
			Nil	2000	5000	Nil	2000	5000
P ₁	10	56,000	6	3	0	13	12	10
P ₂	12	77,400	6	6	3	13	13	11
P ₃	14	60,200	6	-6	-6	13	11	11
P ₄	16	89,400	6	< -18	< -18	13	12	10
P ₅	15	57,700	6	6	0	13	13	11
P ₆	15	69,200	6	-3	-3	13	12	12
P ₇	15	57,500	6	3	-6	13	11	10
P ₈	14	55,500	6	0	-3	13	13	12
P ₉	12	58,000	6	6	6	13	13	13

tion of poly- α -olefins P₁, P₂, P₃, and P₄ of side-chain length C₁₀, C₁₂, C₁₄, and C₁₆, respectively. Experimental results shown in Table IV revealed that side-chain lengths of C₁₀-C₁₂ have no effect on the pour point. Increasing the side-chain length more than C₁₂ enhances the pour-point depression effect. The longer the side chain, the more depression could be realized. Table IV shows that poly- α -olefins P₃ and P₄ of side-chain length C₁₄ and C₁₆ have attained pour-point depressions of 12 $^{\circ}\text{C}$ and >24 $^{\circ}\text{C}$, respectively. This behavior could be explained on the basis that the side-chain length of a carbon number up to C₁₂ is unable to interact with the average carbon number chain of the *n*-paraffin content in the gas oil composition (C₁₈). Increasing the side chain to C₁₄ and more leads to mutual interaction between the side-chain moiety of the polymer via cocrystallization and various carbon chain lengths of *n*-paraffins at a wide cooling temperature range, leading, in turn, to greater pour-point depression. This is in good agreement with that previously mentioned in the literature.¹³

Difference in Chain Carbon Length of Pendant Moieties of Copolymers

Results listed in Table V show that by decreasing the difference between carbon chain length of pendant moieties of the synthesized copolymers the efficiency of the copolymer increases until the difference vanishes in the case of the homopolymer P₄ (poly- α -octadecene homopolymer). This effect is probably dependent on the extent of cocrystallization of the pendant moieties of polymers with the average carbon number (C₁₈) of *n*-paraffins in the fuel composition. This effect is increased by increasing the concentration of C₁₄ and C₁₆ pendant side chains in the order P₄ > P₇ > P₆ > P₅.

Average Side-chain Length of Terpolymers

The method of calculating the average side-chain length of pendant moieties of the polymer is disclosed in U.S. Patent 3,814,690, which illustrates the method for calculating "mol equivalent average

Table V Effect of Difference in Chain Carbon Length of Pendant Moieties of Copolymers on Their Efficiency

Polymer Designation	Composition of Side-chain Carbon Length	C_{av}	Difference in Chain Carbon Length	M_w	Pour-point Depression ($^{\circ}\text{C}$) at 5000 ppm
P ₅	C ₁₀ -C ₁₆	15	6	57,700	6
P ₆	C ₁₂ -C ₁₆	15	4	69,200	9
P ₇	C ₁₄ -C ₁₆	15	2	57,500	12
P ₄	C ₁₆	16	0	89,400	> 24

Table VI Effect of Average Side-chain Carbon Length of Terpolymers on Their Efficiency

Polymer Designation	Composition	Average Side-chain Carbon Length (C_{av})	M_w	Pour-point Depression ($^{\circ}\text{C}$) at	
				2000 ppm	5000 ppm
P ₈	Poly(α -dodecene, α -tetradecene, α -hexadecene, α -octadecene)	14	55,500	6	9
P ₃	Poly(α -hexadecene)	14	60,200	12	12
P ₉	Poly(α -dodecene, α -tetradecene, α -hexadecene, α -octadecene)	12	58,000	0	0
P ₂	Poly(α -tetradecene)	12	77,400	0	3

chain length," which is the same as "average side-chain length." The following formula is used:

$$C_{av} = \frac{(CN_1)(MP_1) + (CN_2)(MP_2) + (CN_3)(MP_3)}{MP_1 + MP_2 + MP_3}$$

where CN_1 is the number of chain carbons in the first chain; CN_2 , the number of chain carbons in the second chain; CN_3 , the number of chain carbons in the third chain; MP_1 , the mol % of the first component; MP_2 , the mol % of the second component; and MP_3 , the mol % of the third component, and mol % is equal to the mol fraction times 100%.

The influence of the average side-chain length of pendant moieties of the synthesized poly- α -olefins on their performance was studied through the two terpolymers P₈ and P₉ whose average side-chain carbon length are C_{14} and C_{12} , respectively. Experimental data listed in Table VI illustrate that P₈ ($C_{av} = 14$) has a pour-point depression = 6°C , while P₉ ($C_{av} = 12$) has no effect. At the same time, the homopolymer P₃ ($C_{av} = 14$) has a better performance

than has P₈, while P₂ ($C_{av} = 12$) has no effect. These results indicate that the terpolymer P₈ of the specified average chain carbon length C_{14} achieve generally the same performance as that of the homopolymer of the same side-chain carbon length P₃ except that efficiency increases in the case of the homopolymer. This may be due to the increased concentration of the carbon chain length (C_{14}) which is capable of interaction with more n -paraffin content of the fuel composition. The terpolymer P₉ has no effect, the same as with the homopolymer P₂ of the same side-chain carbon length, possibly due to a complete lack of interaction.

Effect of Concentration of the Synthesized Poly- α -olefins vs. Commercial Pour-point Depressants

The two effective synthesized poly- α -olefins P₃ and P₄ were assessed in decreasing the pour point in comparison with two commercial pour-point depressants, viz., Lubrizol (L6682) and Servo (CW 250). Results listed in Table VII and illustrated in Figure 3 show that the two synthesized polymers P₃

Table VII Effect of Concentration of the Efficient Poly- α -olefins in Comparison with Commercial Pour-point Depressants

	Additive Type	Pour Point ($^{\circ}\text{C}$) at Concentration (ppm)						
		Nil	200	400	600	800	1000	2000
Synthesized	P ₃	6	3	3	3	3	0	-6
	P ₄	6	-3	-3	-6	-12	-15	< -18
Commercial	L 6682	6	6	6	6	6	6	6
	CW 250	6	3	0	-1	-1	-1	-2

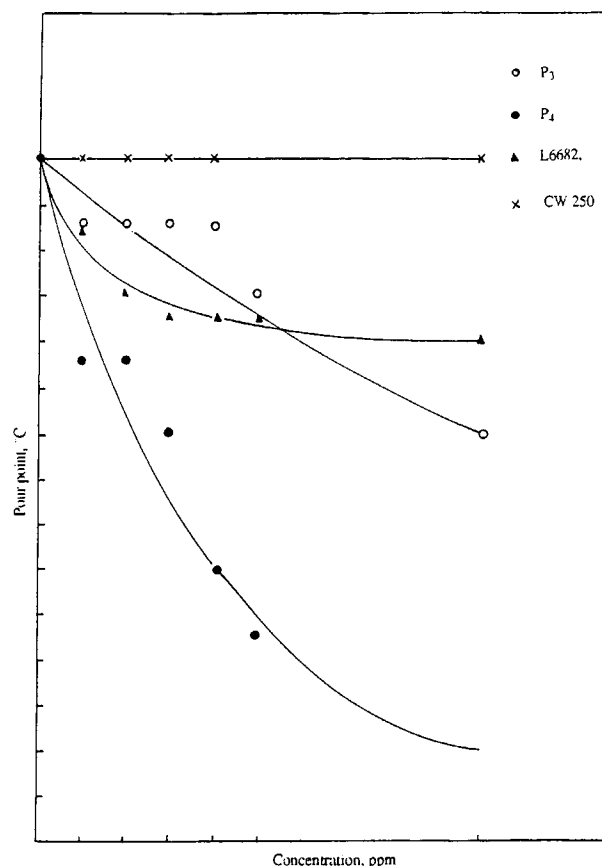


Figure 3 Effect of efficient synthesized poly α -olefins in comparison with commercial pour point depressants.

and P₄ are more efficient than are the two commercial pour-point depressants. The commercial pour-point depressant L6682 has no effect at all.

CONCLUSION

The average molecular weight, molecular weight distribution, and average side-chain length of the polymeric structure of poly- α -olefins substantially control their effectiveness as pour-point depressants. However, copolymers of the same average side-chain

length may have different performance due to the difference in the weight percent of the olefin monomer composition. Poly- α -olefins of average side-chain carbon length $\geq C_{14}$, weight average molecular weight $> 60,000$, and broad molecular weight distribution are effective pour-point depressants for the tested local gas oil. The cloud point is slightly improved by the prepared poly- α -olefins. The use of substantially higher concentrations of poly- α -olefins for inducing pour-point depression indicates that the polymeric structure of poly- α -olefins is of relatively low efficiency for the tested local gas oil.

REFERENCES

1. S. R. Lebedev, R. M. Berezina, and Y. B. Chertkov, *Chem. Tech. Fuels Oils*, **11** (10), 811 (1975).
2. M. W. Ranney, *Fuel Additives for Internal Combustion Engines*, Noyes Data Corp., New Jersey, 1978, pp. 121-155.
3. W. J. Heilman and B. E. Wilburn, Eur. Pat. 0,498,549 A1 (1992).
4. X. X. Chong, *J. Lub. Eng.*, **49**(3), 196-200 (1993).
5. W. A. Hewett, R. C. Jones, and L. E. Lorensen, U.S. Pat. 2,895,915 (1959).
6. W. J. Heilman and T. J. Lynch, U.S. Pat. 4,132,663 (1979).
7. J. C. Thomas and W. Y. David, U.S. Pat. 3,252,771 (1966).
8. N. M. Harold, J. W. Max, and P. R. Richard, U.S. Pat. 4,255,159 (1981).
9. A. Morduchowitz and J. J. Bialy, U.S. Pat. 4,022,590 (1977).
10. R. S. Won and N. J. Maplewood, U.S. Pat. 3,920,622 (1975).
11. C. M. Fontana, G. A. Kidder, and R. J. Herold, *Ind. Eng. Chem.*, **44**, 1688 (1952).
12. J. R. Marquat, G. B. Dellow, and E. R. Freitas, *Anal. Chem.*, **40**(11), 1633 (1968).
13. R. Vipradas and M. C. Dwivedi, in *5th Internationale Kolloquium*, Esslingen, Germany, January 14-16, 1986, Vol. II, pp. 8-11.

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