Synthesis, Characterization, and Evaluation of Poly[n-alkyl(oxy)-n-hexyl acrylates]

G. PRATAP,[*,1] K. L. SHANTHA,[†,2] D. V. MOHAN RAO, and V. S. BHASKAR RAO[‡,2]

[1]New Mexico Petroleum Recovery Research Center, Socorro, New Mexico 87801, and [2]Organic Coatings and Polymers Division, Indian Institute of Technology, Hyderabad 500 007, India

SYNOPSIS

Oxoalkyl acrylates of long-chain 7-oxo alcohols were synthesized as intermediate monomers for the preparation of poly[n-alkyl(oxy)-n-hexyl acrylates] for the first time. These polymers have wide applications as fluidity improvers (pour point depressants) for petroleum crude oils. Characterization of all the intermediate monomers was done by IR, ^{1}H-NMR, and MS, and that of polymers by IR, ^{1}H-NMR, and GPC. These polymers were systematically investigated for their efficacy as pour point depressants on three types of high waxy Bombay High (Indian) crudes. In addition to establishing the pour points, relevant rheological parameters of the untreated and the additive-treated crude oils were determined in the laboratory with a rotational viscometer. Results of the crude oils that were pre- and posttreated with these new polymers have shown enhanced activity of flow properties as compared to the crudes that were treated with poly(n-alkyl acrylate) flow improver.

INTRODUCTION

The transportation of waxy crude oil from production site to refineries, especially through subsea pipelines, poses serious problems.[1,2] Of the many alternatives available for the transportation of such high waxy crude oils, pretreatment with polymeric additives (known in the oil industry as flow improvers or pour point depressants) has received the greatest acceptance due to its simplicity and economy.[3,4] Some macromolecules, containing long-chain pendent groups, have shown the interesting property of affecting the rheological behavior of non-Newtonian high waxy petroleum oils when treated with appropriate polymeric additive at ppm levels. These polymers remarkably improve the fluidity of petroleum oils by lowering their pour points (the lowest temperature at which crude oil ceases to flow), viscosities, and yield values. A substantial number of patents[5-8] and published articles[9-11] are available

that deal with the use of polymeric additives for lowering the pour point of specific hydrocarbon fractions such as middle distillates, fuel oils, lubricating oils, and crude oils. Most of the successful flow improvers are derived from vinyl monomers such as acrylate and methacrylate, ethylene, vinyl alcohol esters, esters of polysaccharides, styrene-maleic anhydride esters, etc. Although crude oils show high specificity with respect to flow improvers, there are some common structural features among these polymeric additives. For instance, there is some relationship between the wax carbon distribution of the petroleum oil and the length of the pendent chains of polymeric additive. The complex nature of the interactions among various precipitating high molecular weight species such as asphaltenes, maltene, or resin fractions, in addition to the waxes covering a wide range of carbon numbers, has resulted in specific additives being effective only with very specific types of crudes. Theories regarding the mechanism of the action of polymeric additives were propounded at a macrolevel with extensive crystallographic studies to establish the influence of the additive on the habitat of the crystallizing waxes.[12,13] It is, however, generally acknowledged that the transition from the platelike forms of the waxes to dendritic or spheruletic crystal

---

structures accompanies the lowering of the pour point.

In this study, we report the synthesis and spectroscopic characterization of novel 7-oxoalkyl acrylate monomers and of the corresponding poly[n-alkyl(oxy)-n-hexyl acrylates]. Also, a comparative performance evaluation of these polymers with poly(n-docosanyl acrylate) was made by measuring the pour points and the rheological properties, such as viscosities and yield values, of the pre- and post-treated high waxy Bombay High (Indian) crude oils called BHN, BHS, and SHD and the results are presented.

EXPERIMENTAL

Materials

Stabilized acrylic acid, p-toluenesulfonic acid (TsOH), 1-docosanol, and hydroquinone (HQ) were used as supplied for the synthesis of 7-oxoalkyl acrylates and n-docosanyl acrylate. Benzoyl peroxide (Bz$_2$O$_2$), purified[14] by recrystallizing from methanol and vacuum drying, was used as a free radical initiator for polymerization. While toluene was used for the syntheses of monomers, dry and sulphur-free xylene was used for the polymer synthesis.

A homologous series of 7-oxo alcohols ranging in carbon numbers from C$_{12}$ to C$_{22}$, required for the preparation of 7-oxoalkyl acrylates monomers, were synthesized by the facile acylation of 1-morpholino-1-cyclohexene with acid chlorides as shown in Scheme I for the first time by these authors.[15]

Bombay High (BHN, BHS, and SHD) crude oils, collected from different regions of Bombay High offshore after degassing, deemulsification but before the additive treatment, were used to evaluate the efficacy of the synthesized polymers. These crude oils were well characterized and the results were documented in several publications.[16-18] The physico-chemical characteristics of these crude oils are given in Table I.

Synthesis of 7-Oxoalkyl Acrylates

The synthesis of long-chain 7-oxoalkyl acrylate monomers (1a–1f) ranging from C$_{12}$ to C$_{22}$ was accomplished[19] according to Scheme II.
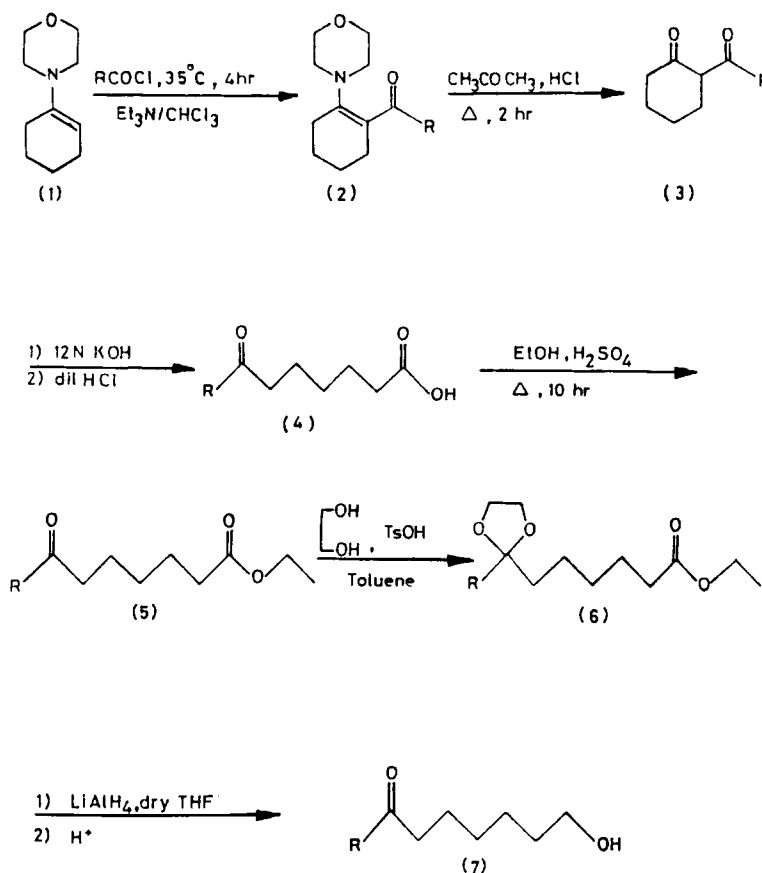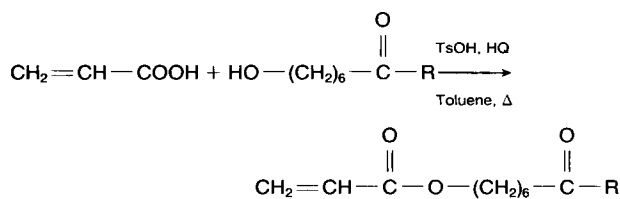

Scheme I

Table I   Physico-Chemical Characteristics of Bombay High Crude Oils

Characteristics	BHN[a]	BHS[a]	SHD[a]
Density	0.8264	0.8306	0.8341
API gravity	39.6	38.8	38.1
Pour point (°C)	+30.0	+30.0	+30.0
Kinematic viscosity			
At 40°C	2.84	3.04	3.64
At 50°C	2.33	2.36	2.67
Wax content (wt %)	12.6	11.2	12.0
Asphaltenes	1.2	1.5	1.3

[a] Refers to the platforms of Bombay High off-shore from where the crude oil samples were collected.

$$CH_2=CH-COOH + HO-(CH_2)_6-\overset{\overset{\textstyle O}{\|}}{C}-R \xrightarrow[\text{Toluene, }\Delta]{\text{TsOH, HQ}}$$

$$CH_2=CH-\overset{\overset{\textstyle O}{\|}}{C}-O-(CH_2)_6-\overset{\overset{\textstyle O}{\|}}{C}-R$$

Scheme II

where R = $-(CH_2)_n-CH_3$ and n = 4, 6, 8, 10, 12, and 14.

7-Oxo alcohol/1-docosanol (0.3 mol), acrylic acid (0.4 mol), hydroquinone (0.5 g), p-toluene–sulfonic acid (0.5 g), and toluene (250 mL) were refluxed until the expected amount of water of dehydration was collected azeotropically in a Dean and Stark trap. At the end of the reaction, the solvent was distilled off. The contents of the reaction mixture was then extracted with hexane and washed free of the catalyst and of any unreacted acid with water until the washings were neutral. Removal of the solvent under reduced pressure gave the crude ester monomer in quantitative yields (95–97%). The crude ester, chromatographed on silica gel (finer

than 200 mesh) using hexane as the eluent, afforded 80–85% of the pure monomer. The purity of these monomers was checked by gas chromatography using a 10% SE-30 column of 8 × $\frac{1}{6}$ in. length and 6 mm in diameter. The analytical data of these monomers are listed in Table II.

Characterization of 7-Oxoalkyl Acrylates

Infrared Spectroscopy

The IR spectra of these monomers were recorded using a Perkin-Elmer (model 221) spectrophotometer. The IR spectra of 7-oxoalkyl acrylates (a) and n-docosanyl acrylate (c) monomer are quite similar, except in the carbonyl stretching region where the oxo-group ($\overset{\diagdown}{\diagup}C=O$) and the ester carbonyl of 7-oxoalkyl acrylates absorbed strongly and appeared as a characteristic mixed doublet while the ester carbonyl of n-docosanyl acrylate appeared as a strong absorption as shown in Figure 1. The presence of the ester functionality in both the monomers was further supported by the appearance of C—O stretching vibration at 1180 cm^{-1}.

The characteristic C=C stretching and C—H in-plane deformation vibrations of these acrylic ester monomers appeared as doublets at 1635–1615 cm^{-1} and at 1295–1265 cm^{-1}, respectively. In addition, a weak absorption corresponding to $CH_2=CH-$ stretching vibration of these acrylic esters appeared at 3010 cm^{-1}. The characteristic C—H out-of-plane deformation vibration corresponding to $CH_2=C\underline{H}$ and $C\underline{H}_2=CH$ of these monomers appeared as a doublet at 970–965 cm^{-1} and 805–715 cm^{-1}, respectively. While the C—H stretching vibration of methylenes ($-CH_2-$) absorbed strongly at 2925–2855 cm^{-1} because of larger alkyl substituent, the C—H deformation vibration of methylenes appeared at 1465 cm^{-1} and that of C—CH$_3$ occurred at 1375 cm^{-1}.

Table II   Analysis of 7-Oxoalkyl Acrylates

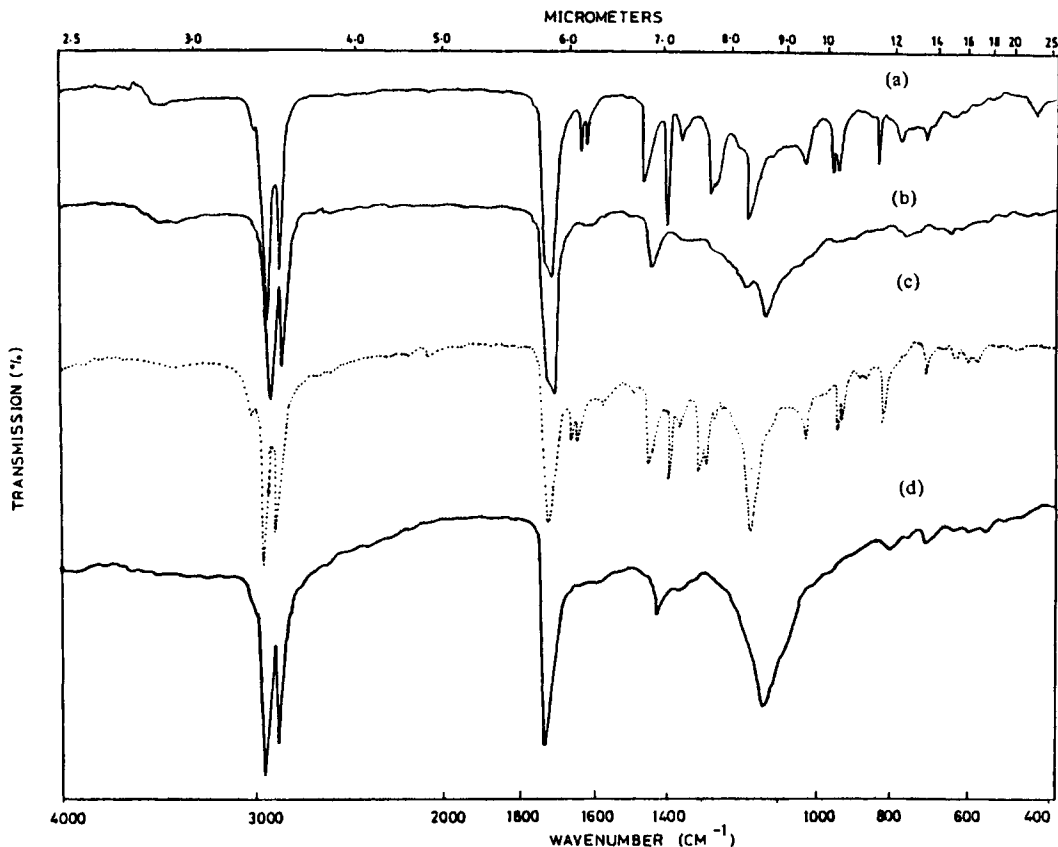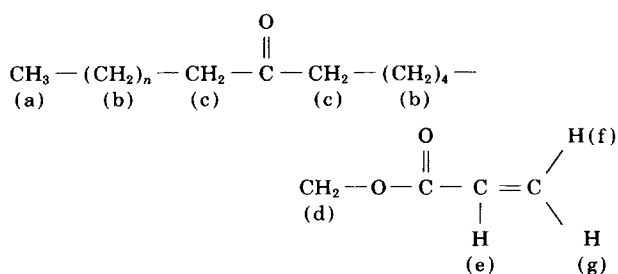| Monomer	R	Yield (%)	mp (°C)	Refractive Index, n_D (°C)	Purity[a] (%)
1a	$-(CH_2)_4CH_3$	85	—	1.4492 (30)	100.0
1b	$-(CH_2)_6CH_3$	82	—	1.4502 (30)	100.0
1c	$-(CH_2)_8CH_3$	83	26	1.4522 (30)	99.9
1d	$-(CH_2)_{10}CH_3$	82	32	1.4533 (35)	100.0
1e	$-(CH_2)_{12}CH_3$	84	37	1.4534 (40)	99.9
1f	$-(CH_2)_{14}CH_3$	81	44	1.4527 (45)	100.0

[a] GC analysis.

Figure 1 IR spectra of (a) 7-Oxodocosanyl acrylate monomer, (b) Poly[n-pentadecyl(oxy)-n-hexyl acrylate], (c) n-Docosanyl acrylate monomer, and (d) Poly(n-docosanyl acrylate).

Proton Magnetic Resonance Spectroscopy

^{1}H-NMR spectra of the pure monomers in carbon tetrachloride were recorded using a JEOL-FX-90Q NMR spectrophotometer. The chemical shifts were recorded in δ values (ppm) from the internal standard, tetramethylsilane (TMS). For all 7-oxoalkyl acrylates, the spectra are consistent with the structures and only the essential features are discussed here. The general structural formula of 7-oxoalkyl acrylates may be represented as follows:

$$
\begin{array}{c}
\text{O} \\
\|\\
CH_3 - (CH_2)_n - CH_2 - C - CH_2 - (CH_2)_4 - \\
\text{(a)} \quad \text{(b)} \quad \text{(c)} \quad \quad \text{(c)} \quad \text{(b)}
\end{array}
$$

$$
\begin{array}{c}
\text{O} \quad \quad \quad \quad \text{H(f)} \\
\|\quad \quad \quad \quad \quad / \\
CH_2 - O - C - C = C \\
\text{(d)} \quad \quad \quad \quad | \quad \quad \backslash \\
\quad \quad \quad \quad \quad \text{H} \quad \quad \text{H} \\
\quad \quad \quad \quad \quad \text{(e)} \quad \quad \text{(g)}
\end{array}
$$

The chemical shifts of methyl protons (a) registered as a distorted triplet at 0.88δ owing to the coupling with the adjacent methylene (b) protons

that, in turn, appeared as a multiplet between 1.2–1.54δ by coupling with methyl (a) and other methylene (c, d) protons. A fine triplet was registered at 2.4δ corresponding to methylenes (c), flanked to oxo group and as a result of coupling with adjacent methylenes (b). The methylenes (d), bonded to the ester oxygen and by coupling with adjacent methylenes (b), registered as a triplet in the downfield region between 4.08 and 4.2δ. The protons corresponding to (e), (f), and (g) appear to constitute an ABC system resulting in multiplets as shown in Figure 2. The protons (e) registered as a doublet at 6.5δ owing to *trans* and *cis* allylic couplings with the protons (f) and (g), respectively. Those corresponding to (f) and (g) protons appeared as nonidentical multiplets at 5.7–5.9δ and 6.1–6.3δ because of *cis*-geminal and *trans* allylic-geminal couplings, respectively, with proton (e) and with each other.

Mass Spectroscopy

The mass spectra of 7-oxoalkyl acrylates (1a–1f) have not been reported earlier. These were recorded on a Micromass VG 7070H spectrometer at 70 eV.
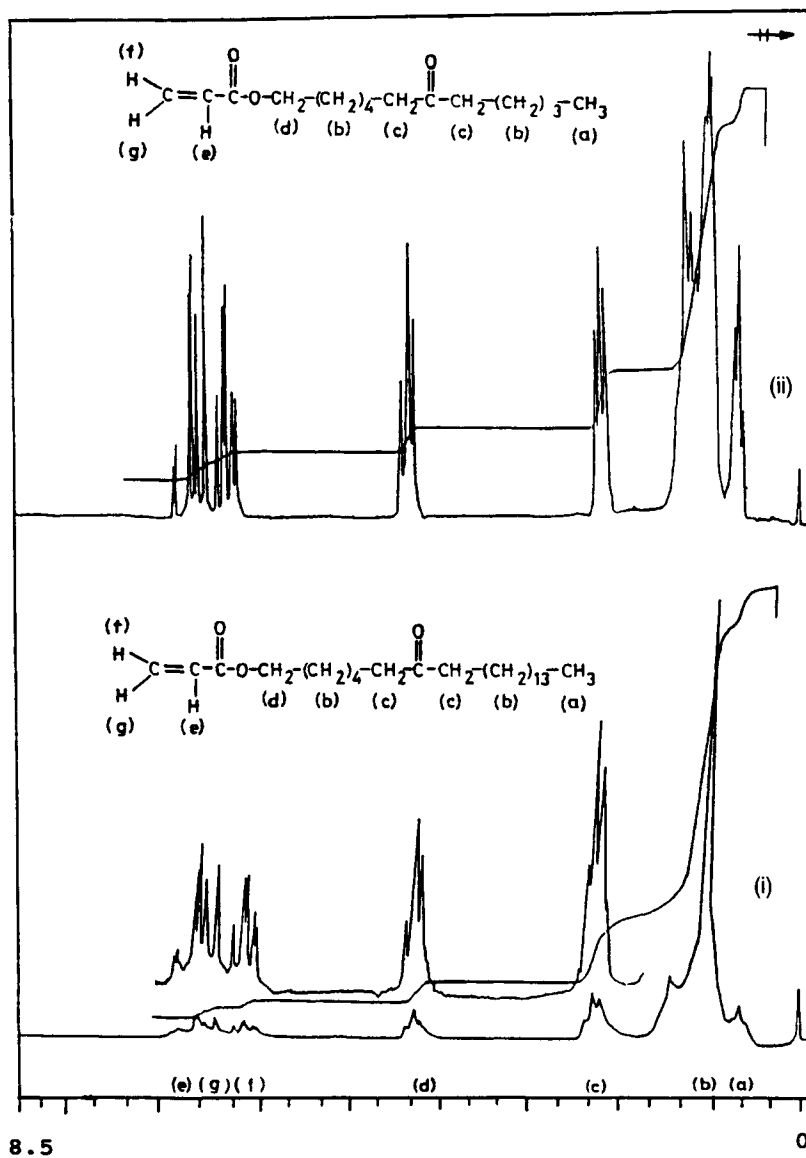
Figure 2 ^{1}H NMR spectra of (i) 7-Oxodocosanyl acrylate and (ii) 7-Oxododecyl acrylate.

The typical mass spectra of 7-oxodocosanyl acrylate (1f) and n-docosanyl acrylate are shown in Figures 3 and 4, respectively. 7-Oxoalkyl acrylates fragment in a specific manner, which may be represented as shown in Figure 5 and the results are discussed with respect to their fragmentation pattern.
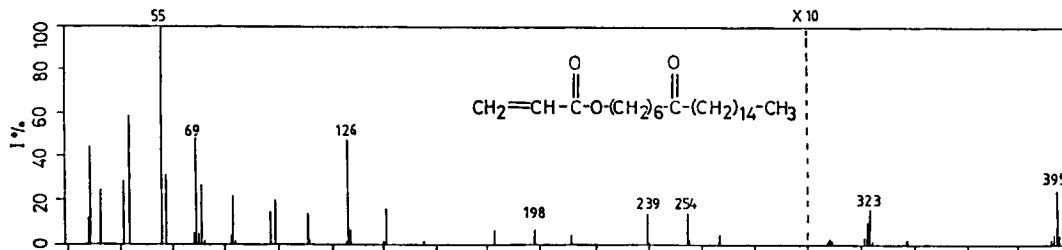

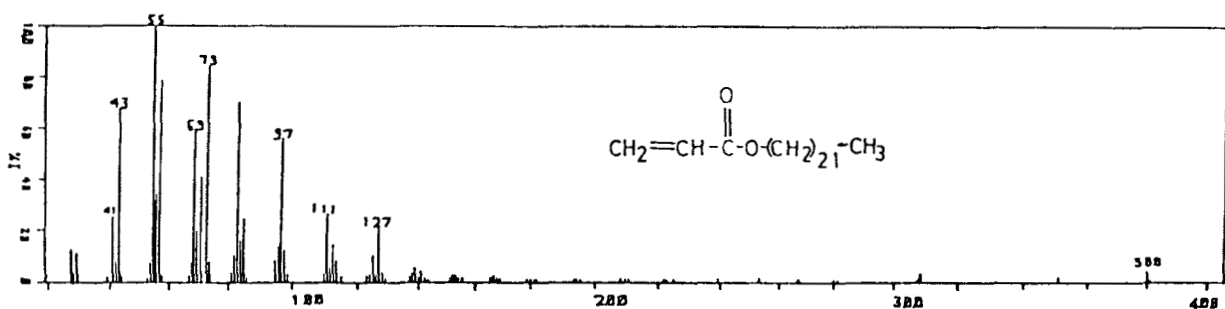**Figure 3** Mass spectrum of 7-Oxodocosanyl acrylate.

Figure 4 Mass spectrum of n-Docosanyl acrylate.

All these monomers were characterized by the appearance of molecular M^+ and $M + 1$ ions. Both types of monomers showed the base peak m/z 55 (a), characteristic of acrylates owing to the $CH_2=CH-CO^+$ fragment ion furnished by the α- cleavage of the acrylic ester functionality. The major ion peaks were usually furnished by the initial cleavage of bonds adjacent to the oxo and ester groups and also by the rearrangement of radical ions and are listed in Table III. In contrast to n-docosanyl
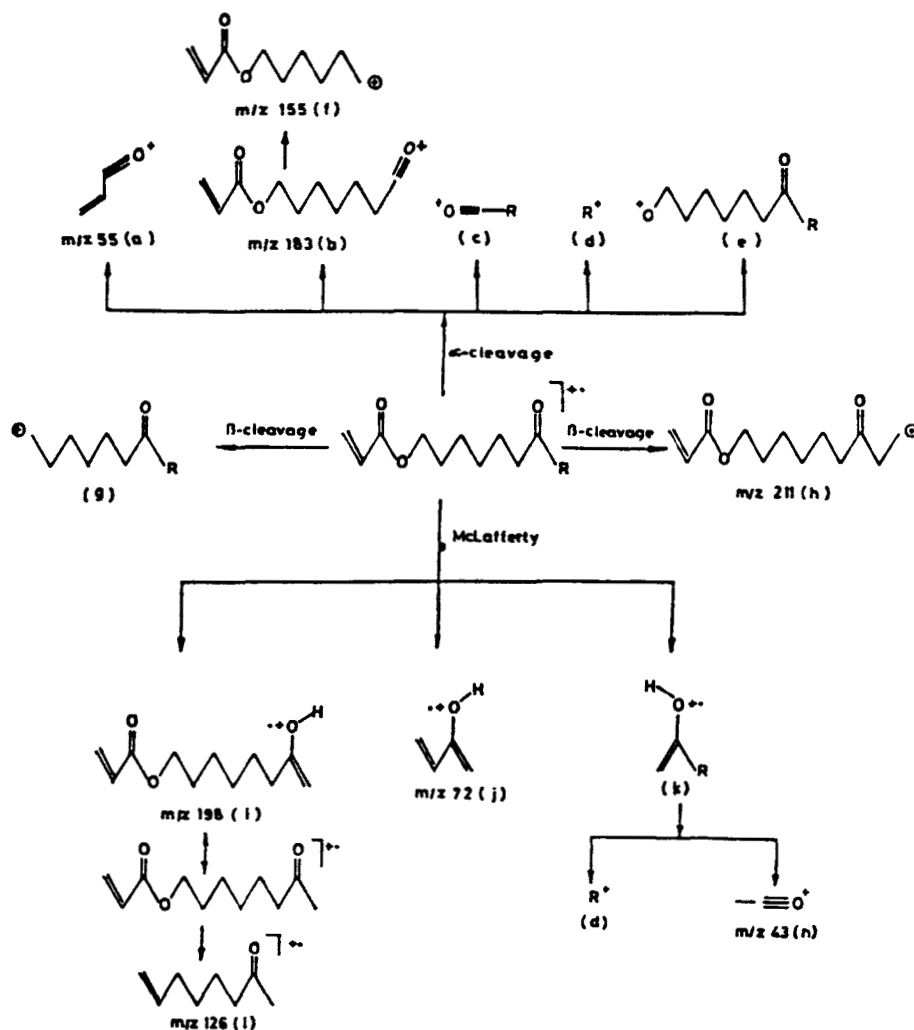

**Figure 5** Mass spectral fragmentation pattern of 7-Oxoalkyl acrylates.

Table III   Mass Spectral Analysis of 7-Oxoalkyl Acrylates

Monomer	Diagnostic and Fragmented Ions (m/z)						
	M + 1	M^+	c	d	e	g	k
(1a) 7-Oxododecyl acrylate	255	254	99	71	199	183	114
(1b) 7-Oxotetradecyl acrylate	283	282	127	99	227	211	142
(1c) 7-Oxohexadecyl acrylate	311	310	155	127	255	239	170
(1d) 7-Oxooctadecyl acrylate	339	338	183	155	283	267	198
(1e) 7-Oxoeicosanyl acrylate	367	366	211	183	311	295	226
(1f) 7-Oxodocosanyl acrylate	395	394	239	211	339	323	254

acrylate, 7-oxoalkyl acrylates showed more oxygen containing ion peaks, that dominated over other ion peaks. The site-specific McLafferty rearrangement ions, resulting by the cleavage of bond beta to oxo and ester carbonyl groups with the rearrangement of γ hydrogen, were noticeable in all these monomers at m/z 198 (i), 72 (j) and M-140 (k). Of these ions, the rearranged M-140 (k) ion was the diagnostic peak of these monomers. The ion m/z 198 (l) suffered the loss of 72 amu ($C_3H_4O_2$) to yield m/z 126 (m) ion. The intensity of another diagnostic ion $R-C{\equiv}O^+$ (c), resulting from α-cleavage, increased with the increase in alkyl chain length. Furthermore, all these spectra showed ion peaks at m/z 29, 43, 57, 71, 85, etc. corresponding to alkyl moiety R^+ (d) and the peaks corresponding to R^+-2H at m/z 41, 55, 69, 83, etc. together with noticeable olefinic rearrangement ions of R^+-1 at m/z 42, 56, 70, and 84.

Polymer Synthesis

7-Oxoalkyl acrylate monomers (1a–1f) and n-docosanyl acrylate were polymerized by free-radical polymerization technique using benzoyl peroxide initiator as shown in Scheme III.
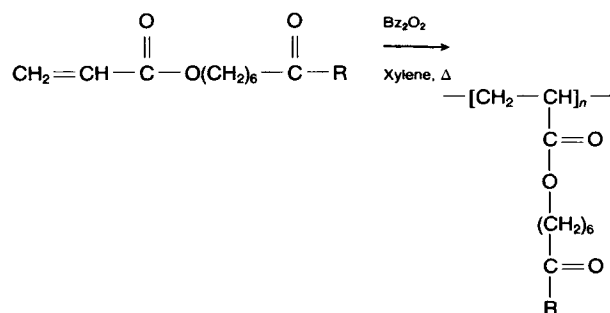
Scheme III

where R = $(CH_2)_n{-}CH_3$.

Solution polymerization[20] of these monomers was carried out in a three-necked flask fitted with a stir-

rer, thermometer, and a three-way stop cock that made it possible to sparge the flask with nitrogen. Monomer, sulphur-free xylene, and benzoyl peroxide were introduced into the flask. It was then sparged with nitrogen and the polymerization was conducted at 90°C. At the end of the reaction period, the polymer was precipitated with methanol. The resulting polymer was then filtered and dried in a vacuum oven at 40°C. The polymerization conditions and the analytical data of these polymers are given in Table IV.

Polymer Analysis

Infrared Spectroscopy

Infrared spectra of these homopolymers were taken in chloroform. The representative IR spectra of poly[n-pentadecyl(oxy)-n-hexyl acrylate] and poly(n-docosanyl acrylate) are shown in Figure 1 for comparison and the essential features are discussed here. The structures of these polymers were ascertained by the total absence of the doublet absorptions at 1635 and 1615 cm^{-1} corresponding to the C=C stretching vibrations. Furthermore, the total disappearance of C−H in-plane and C−H out-of-plane deformation bands of $CH_2{=}CH-$ confirmed the polymerization of these monomers. Other absorptions corresponding to the ester carbonyl were seen in both acrylates with the appearance of oxo group absorption in oxoalkyl acrylate polymers.

Proton Magnetic Resonance Spectroscopy

The characterization of polymers by high-resolution spectroscopy has received much attention.[21] The ^{1}H-NMR spectra of poly[n-alkyl(oxy)-n-hexyl acrylate] (I) and poly(n-docosanyl acrylate) (II) were recorded in $CDCl_3$. The ^{1}H-NMR spectra of these polymers (I) are not reported earlier and the essential features are discussed here.

Table IV Homopolymerization of 7-Oxoalkyl Acrylates

Monomer	Bz₂O₂ (mol %)	Temp. (°C)	Time (h)	Conversion (%)	$M_n \times 10^4$	$M_w \times 10^4$
1a	0.5	90	24	90	2.47	9.38
1b	0.5	90	25	87	2.68	10.12
1c	0.5	90	24	90	2.91	11.04
1d	0.5	90	24	89	3.32	13.78
1e	0.5	90	26	90	3.62	16.10
1f	0.5	90	24	91	3.94	19.21
n-Docosanyl acrylate	0.5	90	25	90	3.72	18.44
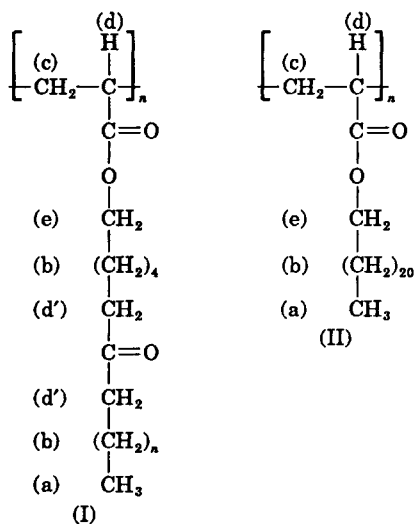
The methyl protons (a) in (I) and (II) registered as a distorted triplet at 0.88δ. The methylene protons (b) could be noticed as a multiplet at 1.1–1.4δ and those corresponding to (c) and (d) appeared as a distorted triplet at 1.54δ. The (d') group protons, flanked to the oxo functionality, registered as a triplet at 2.36–2.4δ in (I) and were not seen in (II) as shown in Figure 6. A much distorted down-field triplet at 4.2δ corresponds to the methylene protons (e) bonded to the ester carbonyl ($-CO_2-CH_2-$).

Gel Permeation Chromatography

These polymers were characterized by using a high-speed Shimadzu HPLC equipped with GPC attachment provided with a styragel column of 7.9 mm ID and 500 mm long. Tetrahydrofuran (THF) was the mobile phase with a flow rate of 1 mL/min. Column inlet pressure was 30 kg/cm² while the column temperature was 30°C. A UV photometric detector (254 nm) with a sensitivity of 0.64 AUFS, 16×10^{-1}, was used for detection. Samples (10-μL) of 1% polymer
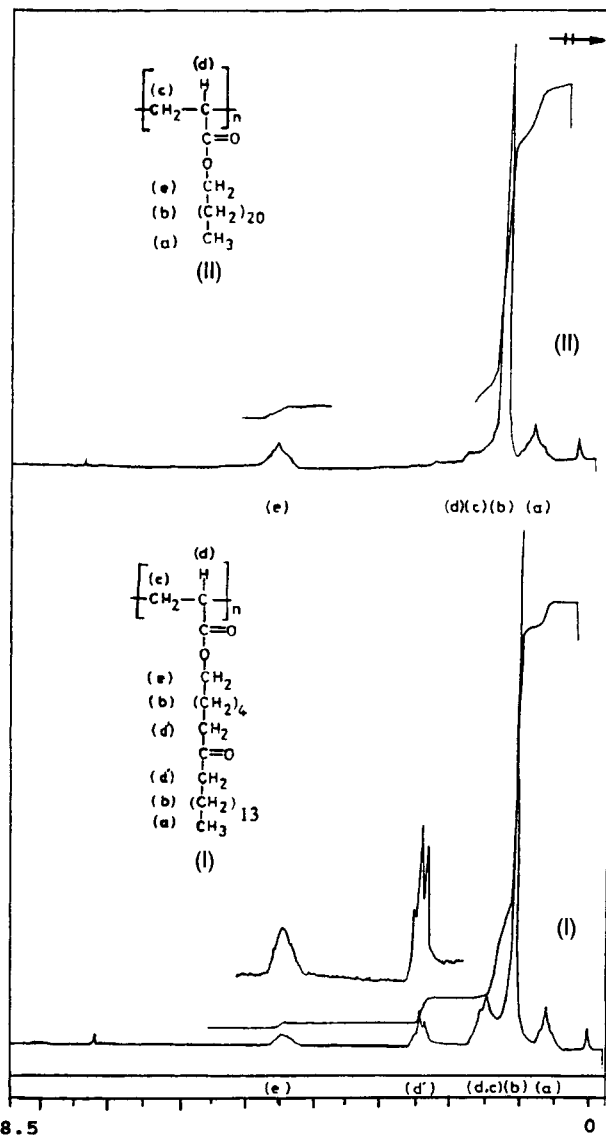
Figure 6 ¹H NMR spectra of (I) Poly[n-pentadecyl(oxy)-n-hexyl acrylate] and (II) Poly(n-docosanyl acrylate).

solutions in THF were injected into the column. The weight (M_w) and number averages (M_n) of these polymers are listed in Table IV.

EVALUATION OF THE POLYMERS

All the polymers were evaluated for their efficacy as flow improvers on Bombay High crude oils by determining the pour points and the rheological properties such as viscosities and yield values of the untreated and the additive-treated oil samples under identical conditions.

Pour Point Determination

In a 250-mL flask fitted with a condenser and a magnetic stirrer, 100 mL of crude oil sample was taken. The flask was then placed in a constant-temperature bath maintained at $50 \pm 2°C$ for 15 min. At the end of this period, 150 ppm of the polymer additive was added to the crude oil and heating was continued for about 30 min with stirring. The flask was taken out of the water bath and the contents were allowed to cool down to $35 \pm 1°C$. The additive-treated crude oil was then loaded in a pour point tube, and the pour point was determined as per ASTM D 97-66 modified method.[22] The pour points of the treated BHN, BHS, and SHD crude oils were determined in a similar manner and that of the untreated crude oils, also determined in a similar way without the polymer additive, are listed in Table V.

Viscosity Measurements

Viscosity measurements of both the untreated and the treated BHN, BHS, and SHD crude oil samples

were carried out on a Haake RV-12 rotational viscometer with an NV (double gap) coaxial sensor system.[10,23] It is also equipped with a PG-142 programmer operating at shear rates ranging from 5.41 to 2769.92 s^{-1} and x-y-t recorder for continuous scanning and recording.

The experimental procedure consists of loading the viscometer cup, which was preheated to $50°C$, with 12 mL of the untreated/additive-treated crude oil sample. The temperature of the sample was then brought down to the required temperature ($20°C$) at the lowest shear rate (dynamic cooling). Shearing was continued for 10 min at the test temperature, and the rheogram was recorded using the external programmer PG-142. Viscosities of the crude oil samples were calculated at various shear rates using the following equations.

Shear rate, D (s^{-1}) depends linearly on the number of revolutions of rotor, n:

$$D = M \times n$$

Shear stress, τ (Pa) is linearly related to torque at the rotor:

$$\tau = A \times S$$

Viscosity, η (mPa s) is the ratio of shear stress to shear rate:

$$\eta = \tau/D = AS/Mn \text{ (Pa s)}$$

$$\eta = G \times S/n \text{ (mPa s)}$$

where M, A, and G are the instrument constants and the values are

Table V Pour Point Data of Treated Crude Oils

| Polymer[a] (flow improver)	Pour Point (°C)		
	BHN	BHS	SHD
Untreated crude oil	30	30	30
Poly[n-pentyl(oxy)-n-hexyl acrylate]	30	30	30
Poly[n-heptyl(oxy)-n-hexyl acrylate]	30	30	30
Poly[n-nonyl(oxy)-n-hexyl acrylate]	30	30	30
Poly[n-undecyl(oxy)-n-hexyl acrylate]	30	30	30
Poly[n-tridecyl(oxy)-n-hexyl acrylate]	21	24	24
Poly[n-pentadecyl(oxy)-n-hexyl acrylate]	12	15	15
Poly(n-docosanyl acrylate)	18	18	18

[a] Dosage = 150 ppm and doping temp. = $50°C \pm 1$.
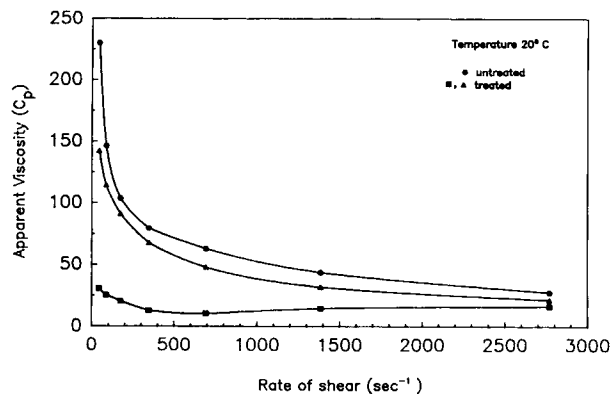
Figure 7 Apparent viscosity of BHN crude oil as a function of shear rate at 20°C: (●) Untreated, (■) Treated with poly[n-pentadecyl(oxy)-n-hexyl acrylate], and (▲) Treated with poly(n-docosanyl acrylate).

M = 5.41 (min/s)
A = 1.78 (Pa/scale grad.)
G = 329 = $10^3 \times A/M$ (mPa s/scale grad. min)
S = measuring value (scale grad.)
n = actual speed (min^{-1})

The viscosities of the untreated and the additive-treated BHN, BHS, and SHD crude oils were determined at 20°C to evaluate the effect of the polymer on viscosity of these crudes and the results are shown in Figures 7–9. The yield values of the untreated and of the additive-treated crude oils were determined using a Faan VG viscometer at 20 and 25°C and the results are given in Table VI.

The preceding results of pour points, viscosities, and yield values of the treated crudes with these polymers indicate the superior performance of
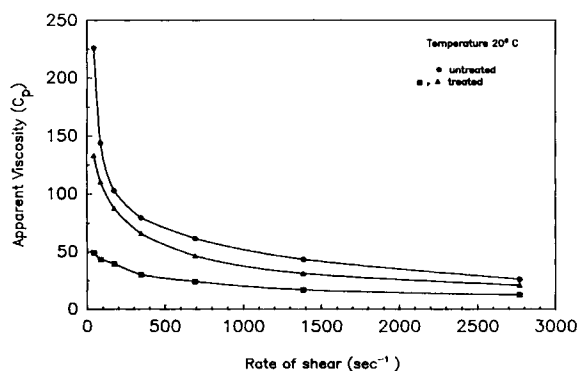

Figure 8 Apparent viscosity of BHS crude oil as a function of shear rate at 20°C: (●) Untreated, (■) Treated with poly[n-pentadecyl(oxy)-n-hexyl acrylate], and (▲) Treated with poly(n-docosanyl acrylate).
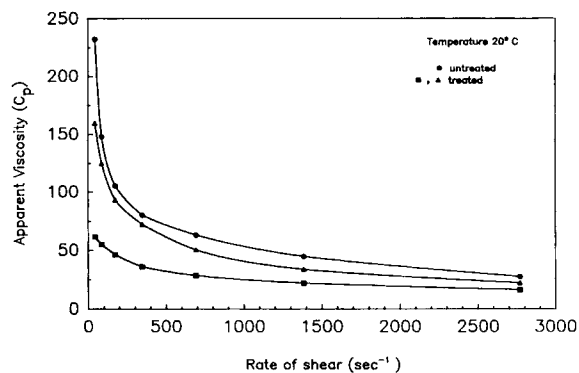

Figure 9 Apparent viscosity of SHD crude oil as a function of shear rate at 20°C: (●) Untreated, (■) Treated with poly[n-pentadecyl(oxy)-n-hexyl acrylate], and (▲) Treated with poly(n-docosanyl acrylate).

poly[n-pentadecyl(oxy)-n-alkyl acrylate] as flow improver when compared to poly(n-alkyl acrylate).

CONCLUSIONS

7-Oxoalkyl acrylate monomers were prepared in high purity and their characterization by IR, ¹H-NMR, and mass spectroscopic methods was reported for the first time. Their mass spectra revealed an interesting fragmentation pattern. The intensity of the characteristic fragment ion M-140 (k) decreased with the increase in the chain length.

Poly[n-alkyl(oxy)-n-hexyl acrylates] were prepared from 7-oxoalkyl acrylates and their characterization by IR and ¹H-NMR was also reported. Of the series of poly[n-alkyl(oxy)-n-hexyl acrylates], the most pronounced activity on three different Bombay High crudes was exhibited by poly[n-pentadecyl(oxy)-n-hexyl acrylate]. This is attributed to the cocrystallization of the waxes with the pendent groups of the polymer due to the close similarities of these pendent groups with the waxes of the crude oils, which are rich in C_{22} hydrocarbons as evidenced by the wax analysis.[24] The pour point data of the crude oils treated with these polymers showed improved activity with the increase of pendent chain length of the polymer.

Our apprehension that the incorporation of an "oxo" group in the pendent chain might affect their activity was unfounded. Instead, this incorporation led to the enhanced activity of these flow improvers on Bombay High crude oils. Introduction of an oxo group in the pendent chains of these polymers resulted in increased polarity as evidenced by TLC. We assume that this slight increase in polarity led

Table VI   Yield Values (Pa) of Untreated and Treated Crude Oil Samples

Flow Improver	BHN		BHS		SHD	
	20°C	25°C	20°C	25°C	20°C	25°C
Untreated crude oil	4.45	1.48	5.34	1.78	6.23	2.67
Poly[n-pentadecyl(oxy)-n-hexyl acrylate]	0.90	0.35	1.01	0.43	1.12	0.51
Poly(n-docosanyl acrylate)	1.72	0.73	1.83	0.87	1.97	0.95

to better dispersion of asphaltic materials of crude oil. This observation is supported by the low yield values, pour points, and viscosities of the crude oils treated with these flow improvers as compared to the relatively high pour points, viscosities, and yield values of the same crude oils treated with poly(n-docosanyl acrylate).

In addition to the efficacy of these polymers as flow improvers for crude oils, this approach offered an excellent method for obtaining fatty acids and fatty alcohols in the range of C_{20-22} that are scarcely available from natural sources.

REFERENCES

1. B. Smith and C. E. Crest, Oil Gas J., 111 (May, 1979).
2. A. Uhde and G. Kopp, J. Inst. Pet., **57**, 63 (March, 1971).
3. R. C. Price, J. Inst. Pet., **57**(554), 106 (1971) and references cited therein.
4. T. R. Stifferman, SPE paper 7409 (Sept. 1978).
5. N. V. Maatschappij, Neth. Pat. 7,202,748 (1972); U.S. Pat. 3,957,659 (1976); Chem. Abstr., **78**, 74,539q (1973).
6. P. G. Pappas, W. C. Edmisters, and H. S. Von Levern, U.S. Pat. 3,846,092 (1974); Chem. Abstr., **82**, 158,562n (1975).
7. A. H. Wagenaar and P. H. Vander Meij, Ger. Offen. 1,963,567 (1970); Br. Pat. 1,282,946 (1968); Chem. Abstr., **73**, 89,548k (1970).
8. P. Y. Gee and H. J. Andrus, Jr., Mobil Oil Co., U.S.
Pat. 3,574,575 (1971), Chem. Abstr., **75**, 8,255f (1971).
9. H. H. Abou El Naga, W. M. Abd El Azim, and M. M. Ahmed, J. Chem. Tech. Biotechnol., **35A**, 241 (1985).
10. C. Irani, J. Zajac, J. Pet. Tech., 289 (Feb, 1982).
11. G. P. van Engelen, C. L. Kaul, B. Vos, H. P. Arantha, J. Pet. Tech., 2539 (1981).
12. G. A. Holder and J. Winkler, J. Inst. Pet., **51** (499), 228 (1965); G. A. Holder and J. Winkler, Nature, **207**, 719 (1965).
13. D. A. Shock, J. D. Sudbury, and J. J. Crockett, J. Pet. Tech., 23 (Sept, 1955).
14. A. I. Vogel, Practical Organic Chemistry, 3rd ed., Longmane and Green, London, p. 807 (1978).
15. G. Pratap, K. L. Shantha, and V. S. Bhaskar Rao, Org. Prep. Pro. Int., **20**(6), 593 (1988).
16. V. Ramaswamy, S. L. S. Sarowha, and I. D. Singh, Fuel, **65**, 1281 (1986).
17. D. Chandra and V. K. Bhatia, J. Chem. Tech. Biotechnol., **34A**, 203 (1984).
18. P. L. Gupta, P. V. Dogra, R. K. Kuchhal, and Pradeep Kumar, Fuel, **65**, 515 (1986).
19. C. E. Rehberg, Org. Syn., **26**, 18 (1946); C. E. Rehberg and C. H. Fisher, Ind. Eng. Chem., **40**, 1429 (1948).
20. R. C. L. Chow and C. S. Marvel, J. Appl. Polym. Sci., **13**, 1545 (1969).
21. F. A. Bovey, ^1H NMR Resolution of Macromolecules, Academic Press, New York, 1972.
22. Standard Methods of Test for Pour Point of Petroleum Oils, ASTM D 97-66, part 17, Annual Book of ASTM Standards, pp. 81–84 (1974).
23. J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, Viscosity and Flow Measurement, Interscience Publishers, New York, 1963.
24. Annual reports of Council of Scientific & Industrial Research consultancy to Oil & Natural Gas Commission, India (1985–1987).