

Synthesis of 6- and 7-Oxo Poly(vinyl Ester)s and Their Evaluation

K. L. SHANTHA, G. PRATAP, and V. S. BHASKAR RAO,
Regional Research Laboratory, Hyderabad-500 007, India

Synopsis

Long chain vinyl esters of 6- and 7-oxoaliphatic acids are synthesized as intermediate monomers for the preparation of poly 6-oxo and 7-oxo vinyl esters. These comblike polymers have wide applications as fluidity improvers. Detailed characterization of all the intermediates is done by IR, PMR, and MS for the first time. Their evaluation is done on high waxy Bombay high crude.

INTRODUCTION

Some comblike polymers, especially those with long chain pendent groups, have shown the interesting property of affecting the rheological behavior of high wax containing petroleum oils such as diesel oils, lubricating oils, fuel oils, and crude oils. They show marked improvement in their fluidity when treated with appropriate polymeric additives of the above type.¹⁻⁴ Although these oils show high specificity with respect to the above polymers, there are some common structural features among these additives. For example, there is some relationship between the wax carbon distribution of the petroleum oil and the length of the pendent side chain of the comblike polymer. Several theories regarding the mechanism of action of these comblike polymers were propounded at a macrolevel and some conclusions were drawn.⁵ But the mechanism of their action at the molecular level appears to be still uncertain.

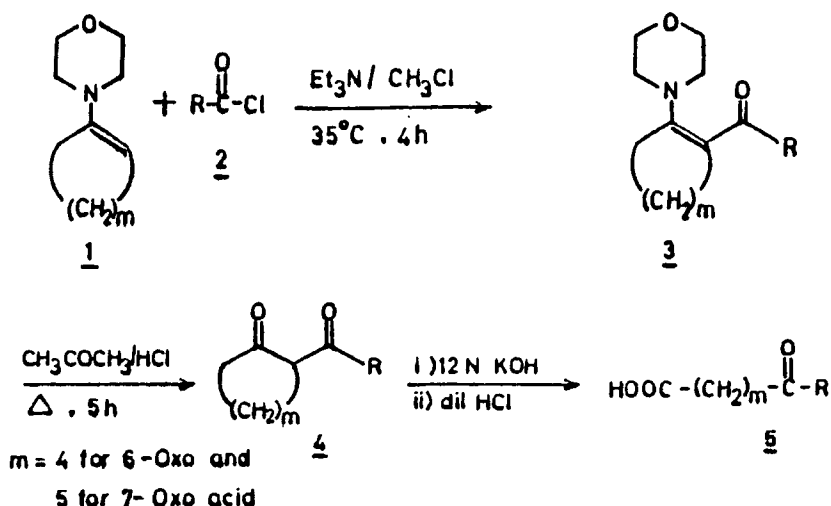
In the present paper, we describe the synthesis and spectroscopic characterization of a number of poly (6-oxo) and poly (7-oxo) vinyl esters and their evaluation on high wax containing Bombay High (Indian) crude oil.

EXPERIMENTAL

Materials

Vinyl acetate was purified by washing with 5% aqueous sodium hydroxide thrice and then with distilled water. It was then dried over anhydrous sodium sulfate and distilled.

6- and 7-oxoaliphatic acids with carbon numbers ranging between 16-24 were prepared by reacting cyclopentanone enamine and cyclohexanone enamine with appropriate acid chloride as reported earlier.⁶⁻⁹



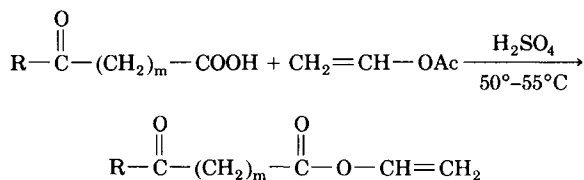
Scheme 1.

Mercuric acetate and sodium acetate trihydrate obtained from E-Merck (AR grade) were directly used.

Distilled solvents were used for TLC. Solvents used for spectroscopic measurements were of spectral grade. Composite Bombay high crude after demulsification and degassing was used to establish the activity of the series of compounds synthesized.

Synthesis of Vinyl Esters

The long chain oxo vinyl esters with carbon numbers ranging from C_{16} to C_{24} were prepared by transesterification using vinyl acetate:^{10,11}



Scheme 2.

Oxoacid (0.015 mol) and stabilized vinyl acetate (0.16 mol) were taken in a 100-mL round bottomed flask fitted with a condenser mounted on a water bath. The bath temperature was maintained at 50–55°C for 1 h. After the solution became clear, mercuric acetate (500 mg) dissolved in small amounts of vinyl acetate (10–15 ml) was added dropwise. After 45 min of addition of $\text{Hg}(\text{OAc})_2$, about three to four drops of 40% concentrated H_2SO_4 were added while stirring and the reaction continued for 4–5 h. At the end of the reaction sodium acetate trihydrate was added to quench further reaction. Excess vinyl acetate was removed under vacuum at 30–35°C. The crude vinyl ester was taken in hexane and washed two to three times with water to remove the catalyst and the inorganic impurities. This compound was dissolved in hot hexane and filtered to obtain crude oxovinyl ester (yield 85–90%).

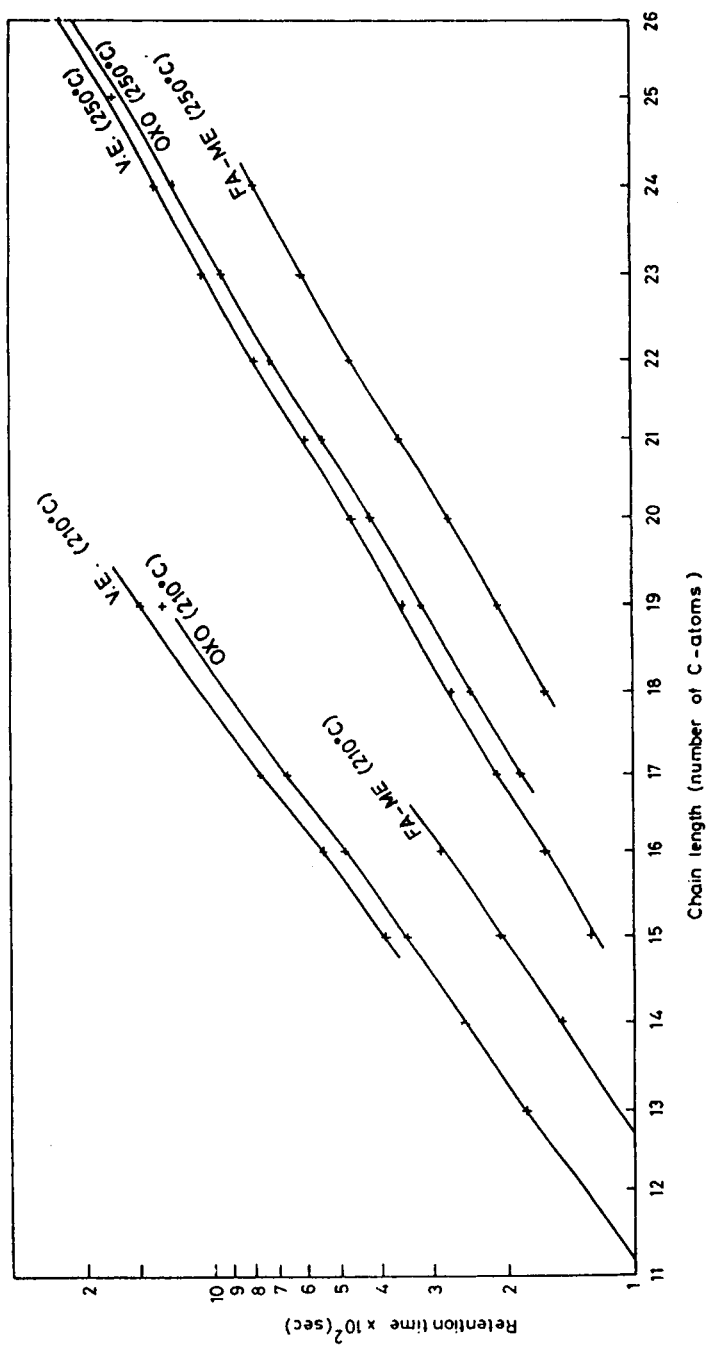


Fig. 1. Retention time (GLC) of oxo vinyl esters (VE), oxomethyl esters and fatty methyl esters (FA-ME).

TABLE I
Physicochemical Characteristics of Vinyl Esters of Long Chain Acids

Vinyl ester no. of carbons in the acyl radical of oxo acids	Yield (%)	Iodine value		Retention factor on TLC $R_f \times 100$	Melting point (°C)	Purity (%)	
		Found	Theory				
C ₁₆	7-Oxo	80	85.7	85.8	77.0	51.2	98
C ₁₇	6-Oxo	80	81.5	81.9	77.5	50.1	98
C ₁₇ (W - Δ)	7-Oxo	80	164.2	165.0	77.5	—	99
C ₁₈	7-Oxo	82	77.8	78.4	78.0	53.0	98
C ₁₉	6-Oxo	80	75.0	75.1	78.5	66.2	97
C ₂₀	7-Oxo	79	72.0	72.2	78.9	60.5	97
C ₂₁	6-Oxo	77	68.9	69.4	79.3	64.8	98
C ₂₂	7-Oxo	78	66.9	66.8	79.7	68.2	98
C ₂₃	6-Oxo	75	64.3	64.5	80.0	71.0	99
C ₂₄	7-Oxo	75	62.1	62.3	80.5	72.0	98

All the oxovinylesters were purified by column chromatography. Conditions were established to find out the percentage purity by gas liquid chromatography. Retention times of methyl esters of long chain oxo acids and methyl esters of fatty acids were recorded under the same conditions for comparison. The results are presented graphically (Fig. 1).

Structural characterization of oxovinyl esters was done by IR, PMR, and MS. Physicochemical characteristics are tabulated in Table I.

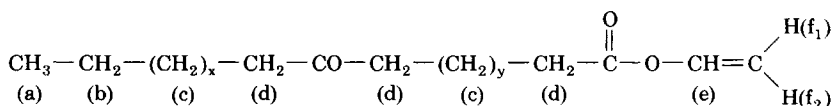
Characterization of Oxovinyl Ester

Infrared Spectroscopy

IR spectra of all the ten vinyl ester monomers were taken in carbon tetrachloride. A typical IR spectrum of 7-oxotricosanoic vinyl ester is shown in Figure 2. The correlation between the absorption maxima related to functional groups and frequencies are shown in Table II.

Proton Magnetic Resonance Spectroscopy

PMR spectra of the pure monomers in carbon tetrachloride solution were recorded using a Varian 60 MHz NMR spectrophotometer and the chemical shifts were recorded in δ values (ppm) with TMS as the internal standard. A generalized structural formula of vinyl esters of oxoacids is represented as follows:



Characteristic absorption positions of various protons in δ values (ppm) of vinyl oxo esters are shown in Table III. A typical PMR spectrum of vinyl oxo ester is shown in Figure 3.

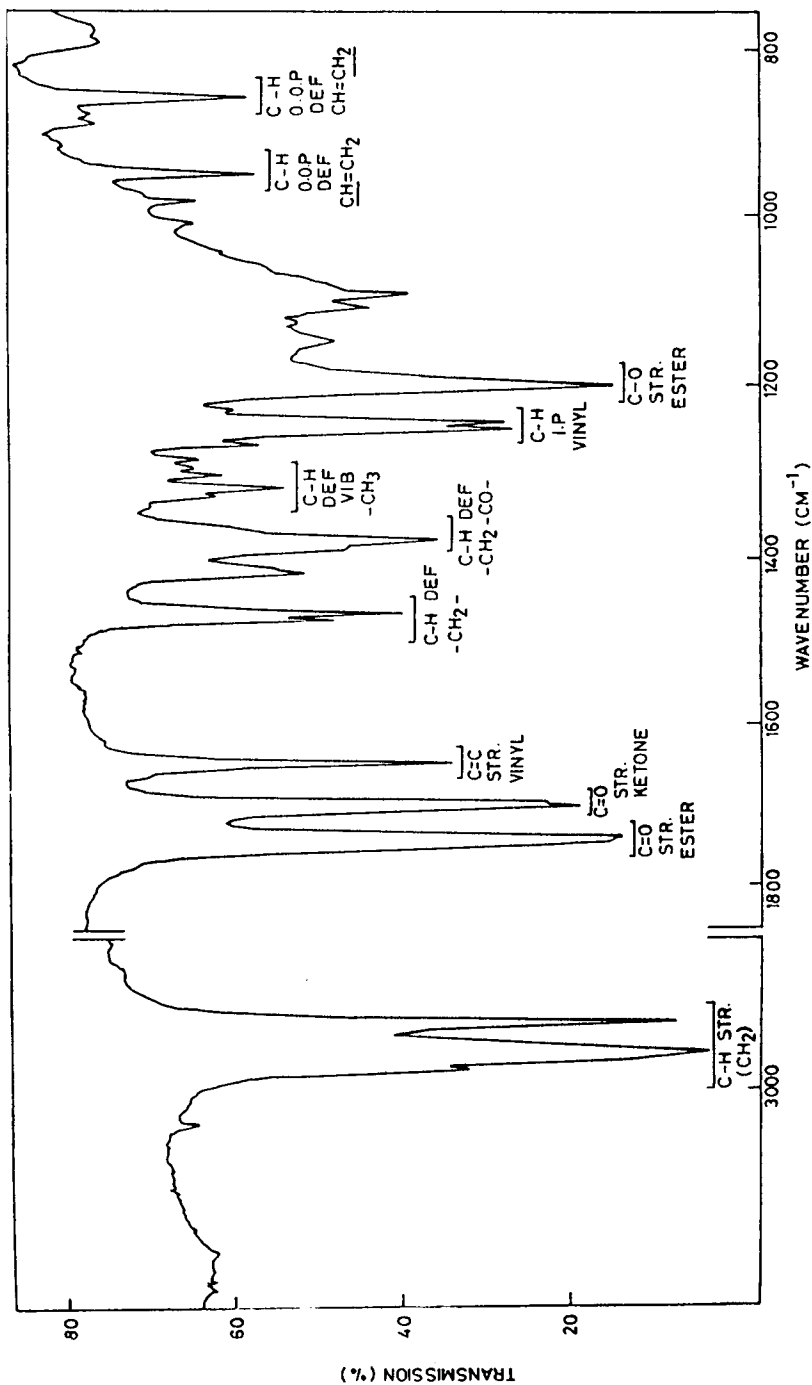


Fig. 2. IR spectrum of 6-oxo tricosanoic vinyl ester.

TABLE II
 Comparative Absorption Frequencies in the Infrared Spectra^a

Nature of the vibrations and functional groups in brackets	Wavelength positions of maxima (cm ⁻¹)	
	Vinyl ester of oxo acids	Oxo-acid
C—H str. vib. (—CH=CH ₂)	3080	—
C—H str. vib. (—CH ₂ —)	2925	2925
	2855	2855
C=O str. vib. (ester)	1750	—
C=O str. vib.	1700	1700
C=C str. vib. (alkene)	1640	—
C—H def. vib. (—CH ₂)	1460	1460
	1470	—
C—O—H in-plane def.	—	1410
C—H def. vib. (C—CH ₃)	1320	1320
CH ₂ —C=O str. vib.	1380	1380
C—H I.P. def. vib. (—CH=CH ₂)	1245	—
	1250	—
C=O str. vib. ester	1200	—
C—H O.O.P def. vib. (—CH=CH ₂)	950	—
C—H O.O.P def. vib. (CH—CH ₂)	860	—
C—H str. vib. (=CH ₂)	720	—
	730	—

^astr. = stretching; I.P. = in plane; def. = deformation; O.O.P. = out of plane; vib. = vibrations.

 TABLE III
 Characteristic Position of Various Protons of Vinyl Oxo Esters^a

Group	(protons)	Chemical shift values
CH ₃	(a)	0.9–1.0 (t)
CH ₃ —CH ₂ —CH ₂	(b)	1.2–1.4 (m)
CH ₂ —CH ₂ —CO	(d)	2.2–2.3 (t)
—O—CH=CH ₂	(f)	4.5–5.1 (m)
—O—CH=CH ₂	(e)	7.1–7.5 (m)

^at = triplet; m = multiplet.

Mass Spectroscopy

Mass spectra of vinyl esters were recorded using a "Micromass VG"-7070H mass spectrometer at an electron-beam (EB) energy of 70 eV. A general fragmentation pattern of vinyl esters of oxoacids may be represented as in Figure 4.

A typical mass spectrum of oxovinyl ester is shown in Figure 5. The diagnostic peaks of 6- and 7-oxo vinyl esters are given in Table IV.

Polymerization of Vinyl Monomers

In view of the slow and low degree of rate of polymerization of these long chain oxovinyl esters, the bulk polymerization of vinyl esters was preferred over other methods of polymerization.

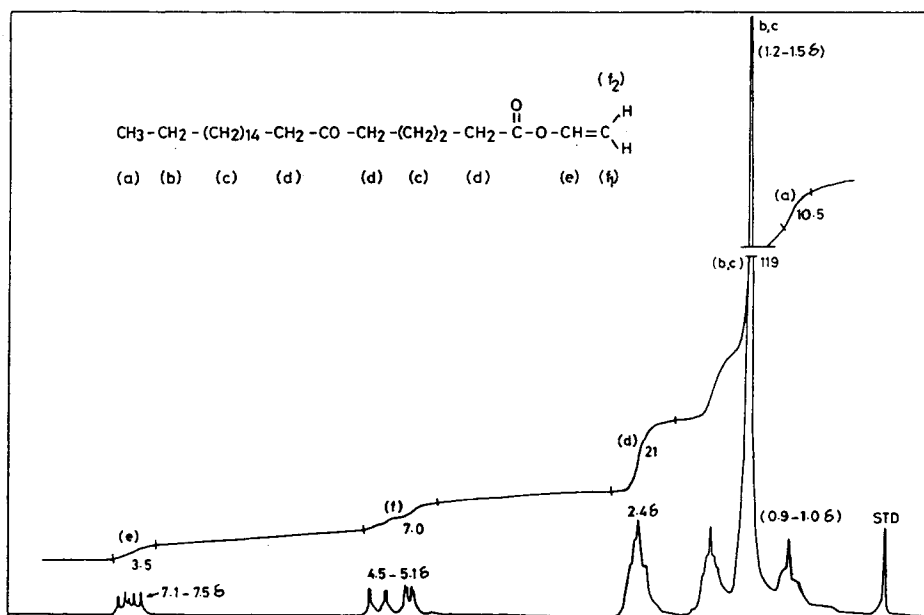
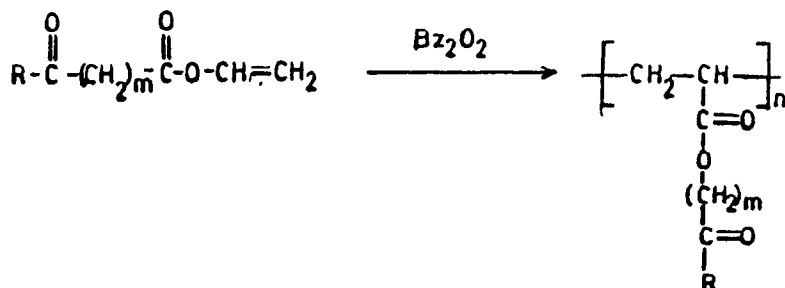


Fig. 3. $^1\text{H-NMR}$ of vinyl ester of 6-oxo tricosanoic acid.

The monomer was weighed into a three-necked flask fitted with a thermometer, nitrogen inlet, and a stirrer. The flask was mounted on an oil bath, maintained at $80 \pm 1^\circ\text{C}$. The polymerization initiator, 0.50% benzoyl peroxide on the weight of the monomer, was then introduced. The course of polymerization was followed by taking out samples at regular intervals and observing the refractive index on the Atago digital refractometer at 50°C . During the course of reaction, the refractive index increased and at the end of the reaction, it became constant. The polymer was dissolved in toluene and precipitated with *n*-hexane. The polymer was filtered to remove the unreacted monomer, if any, and the polymer dried in a vacuum oven at 50°C .

Molecular weights were determined using a vapor phase osmometer and are reported in Table V.



Scheme 3.

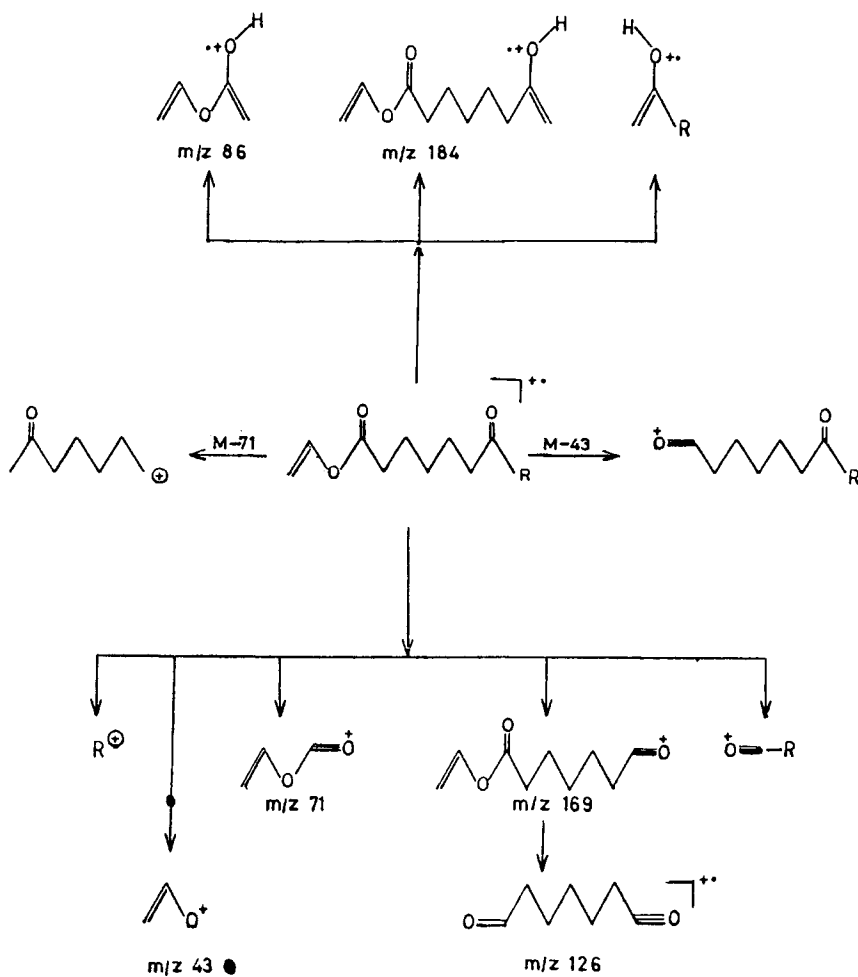


Fig. 4. Mass spectral fragmentation pattern of oxo vinyl esters.

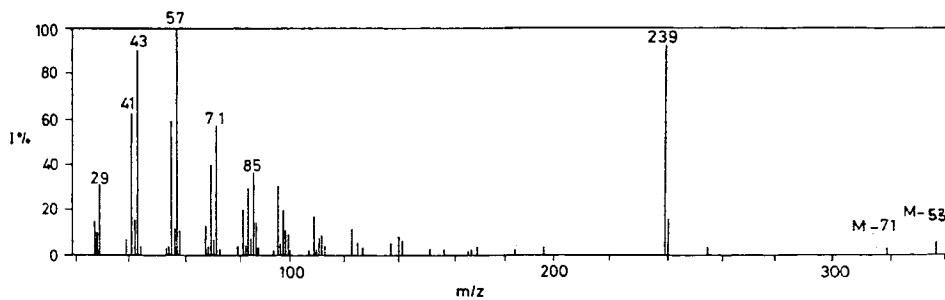


Fig. 5. Mass spectrum of vinyl ester of 7-oxodocosanoic acid.

TABLE IV
Diagnostic Peaks of 6-Oxo and 7-Oxo Long Chain Fatty Vinyl Esters

Vinyl esters of oxo acids (no. of carbons in acyl radical)		Fragmented ions (m/z)							
		M-43	M-71	A	B	C + 1	D + 1	E	H
C ₁₆	7-Oxo	253	225	169	155	184	170	127	113
C ₁₇	6-Oxo	267	239	155	188	170	198	113	141
C ₁₇ (W - Δ)	7-Oxo	265	—	169	167	184	182	127	125
C ₁₈	7-Oxo	281	253	169	183	184	198	127	141
C ₁₉	6-Oxo	295	267	155	211	170	226	113	169
C ₂₀	7-Oxo	309	281	169	211	184	226	127	169
C ₂₁	6-Oxo	323	295	155	239	170	254	113	197
C ₂₂	7-Oxo	337	309	169	239	184	254	127	197
C ₂₃	6-Oxo	351	323	155	267	170	282	127	225
C ₂₄	7-Oxo	365	337	169	267	184	282	127	225

TABLE V
Typical Molecular Weights of Poly(vinyl oxo-ester)s
by Vapor Pressure Osmometry

Sample no.	Poly(vinyl oxo-ester)s (carbon no. in alkyl chain)	Molecular weight
1	16	8,180
2	17	7,120
3	18	8,570
4	19	7,880
5	20	9,960
6	21	8,682
7	22	10,169
8	23	9,469
9	24	12,021

TABLE VI
Pour Point Values of Doped Crude Oil^a

Sample no.	Poly(vinyl oxo-ester)	Pour point (°C)
1	C-24	15 + 3
2	C-23	27 + 3
3	C-22	9 + 3
4	C-21	27 + 3
5	C-20	15 + 3
6	C-19	27 + 3
7	C-18	27 + 3
8	C-17	27 + 3
9	C-16	24 + 3

^aPour-point of undoped crude = 27 + 3°C; doping temperature = 50°C ± 1; dosage = 150 ppm.

TABLE VII
Viscosity at Various Shear Stress^a

Sample no.	Shear rate	Undoped 20°C		Doped (°C)											
		S (Pas)	V (cP)	20°C		25°C		30°C		35°C					
				S	V	S	V	S	V	S	V				
1	43.28	5.5	226.19	2.0	82.25	0.5	20.5	0.5	20.56	0.5	20.56	0.5	20.56		
2	86.56	7.0	143.93	2.5	51.41	0.75	15.42	0.75	15.42	0.75	15.42	0.5	10.26		
3	173.12	10.0	102.81	3.5	35.86	1.25	12.85	1.0	10.28	1.0	10.28	0.75	7.71		
4	346.24	15.5	79.62	5.75	29.56	2.0	10.28	1.5	7.7	1.5	7.7	1.0	5.14		
5	692.48	24.0	61.69	6.5	16.71	3.0	7.7	2.5	6.41	2.5	6.41	1.5	3.85		
6	6384.96	34.0	43.69	12.0	15.42	5.5	7.01	4.0	5.132	4.0	5.132	3.5	3.5		
7	2769.92	40.0	25.70	15.0	9.6	8.0	5.13	6.5	4.178	6.5	4.178	5.0	3.21		

^aS = shear stress; V = viscosity.

EVALUATION OF LONG CHAIN POLYVINYLOXO ESTERS

Pour Point Determination

Bombay high crude oil (100 mL) was taken in a 20 mL iodine flask fitted with a condenser. This was kept in a water bath mounted on a magnetic stirrer. The temperature of the water bath was kept at $50 \pm 2^\circ\text{C}$ for 15 min. At the end of 15 min, the iodine flask was taken out and 150 ppm of the corresponding poly(vinyl oxo ester) was added to the flask and the heating continued for another 30 min, with stirring. At the end of the period, the contents of the flask were allowed to cool down to 36°C ; then the additive-treated crude oil was loaded into a pour point jar and pour point was determined as per ASTM D-97-66 modified method.

The pour points of treated and untreated crudes are given in Table VI.

Viscosity Determination

Viscosity determinations were carried out on rotational viscometer (Haake) type RV-12 with NV sensor system. It is equipped with PG-142 programmer and x-y-t-recorder for continuous scanning and recording.

Ten milliliters of the sample heated to 50°C was loaded into the viscometer cup, which was preheated to 50°C . The temperature was brought down to the test temperature, 20°C , while shearing the sample at low shear rate (dynamic cooling). Shearing was continued for 10 min, at 20°C , and rheograms were recorded. Results are given in Table VII.

RESULTS AND DISCUSSIONS

Among the series of poly(6-oxo) and 7-oxo vinyl esters synthesized, the most pronounced activity on Bombay high crude is exhibited by both poly (6-oxo) vinyl dodecanate and poly (7-oxo) vinyl dodecanate. Our apprehension that incorporation of an oxo group at the 6 or 7 position might affect their activity was not only unfounded but appeared to increase the activity. This has led to a minor variation of the polarity of these compounds as evidenced by TLC and solubility properties. We assume that this slight increase in polarity led to better dispersion of asphaltenic material of crude oil. Hence, the increased activity as compared to the normal straight chain poly(vinyl aliphatic ester)s. This approach has offered an excellent method for obtaining fatty acids in the range of 20–22, which are otherwise scarcely available from natural sources.

References

1. A. H. Wagenaar and P. H. Vander Meij, Ger. Offen. 1,963,567 (1970); Br. Pat. 1,282,946 (1968); *Chem. Abstr.*, **73**, 89848K (1970).
2. P. Y. Gee and H. J. Andrus (Jr.), U.S. Pat. 3,574,575 (1971); *Chem. Abstr.*, **75**, 8255f (1971).
3. P. G. Pappas, W. C. Edmisters, and H. S. Von Levern, U.S. Pat. 3,846,092 (1974); *Chem. Abstr.*, **82**, 158562n (1975).
4. N. V. Maatschappij, Neth. Pat. 7,202,748 (1972); U.S. Pat. 3,957,659 (1976); *Chem. Abstr.*, **78**, 74539q (1973).

5. G. A. Holder and J. Winkler, *Nature*, **207**, 719 (1965).
6. (a) M. S. R. Nair, H. M. Nair, and S. C. Bhattacharya, *Tetrahedron*, **19**, 905 (1963).
(b) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkowicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).
7. G. Pratap, K. L. Shantha, and V. S. Bhaskar Rao, *Fett Wiss. Technol.*, to appear.
8. K. L. Shantha, G. Pratap, and V. S. Bhaskar Rao, *Fett Wiss. Technol.*, to appear.
9. Prof. Von, Dr. H. Schilokheecht and Dr. G. Runner, *Fette Seifen Anstrichm.*, **66**(3), 176-182 (1964).
10. D. Swern and E. F. Jordan, *Org. Synth*, **30**, 106 (1950).
11. R. L. Adelamn, *J. Org. Chem.*, **14**, 1057 (1949).

Received March 21, 1988

Accepted June 2, 1988