Telomer Acids: Monocarboxylic Acids with Long-Chain Branching; Their Derivatives, Properties and Potential Uses in Lubricants

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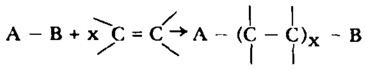
ABSTRACT

Telomer acids are synthesized by addition of acetic anhydride to α-olefins using manganese (III) acetate as a free radical initiator. The telomerization mechanism comprises initiation, propagation and termination steps. The reaction product consists of a mixture of acids having [xn + 2] carbon atoms (n: number of carbon atoms of α-olefin: x:1, 2, 3, 4, ...). The "first telomer" (x=1) is a linear fatty acid. Under appropriate conditions, mainly telomer acid (x:2, 3, 4, ...) are obtained, being α- and γ-branched monocarboxylic acids, characterized by long-chain branches. Telomer acids derived from α-olefins up to n=14 are liquids at room temperature, despite the high molecular weight. Esters of telomer acids show interesting properties in lubricant applications: low pour point, high viscosity index, low viscosity as a function of molecular weight, good thermo-oxidative stability and a remarkably low elastomer swell. In amino amide derivatives, the telomer acid structure gives low viscosity properties, as is, for instance, found in significant viscosity reductions by using telomer acid as coreactant in polyisobutenyl succinic anhydride - tetraethylene pentamine condensation products. Dispersancy properties of these products are retained. Telomer acid metal salts exhibit quite different solubility characteristics and rheological properties than do fatty acid salts. Calcium salts of telomer acids are readily soluble in mineral oil: the rheology of these low viscosity solutions exhibits Newtonian behavior. Solvent-free magnesium salts which are liquid can be obtained. Neutral and overbased calcium salts show pour point depressing activity in paraffinic oils. For overbased calcium salts, decrease of coefficient of friction with increasing temperature has been observed.

INTRODUCTION

The addition of a molecule A − B to a vinyl monomer to yield a series of low molecular weight products is termed telomerization:



$$A - B + x\,{>}C = C{<} \rightarrow A - (\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}})_x - B$$

$$x = 1, 2, 3, \ldots\ldots$$

The reaction products are referred to as telomers. The first example of such reactions was described by Hanford and Joyce (1), viz. the telomerization of ethylene and carbon tetrachloride:

$$CCl_4 + x\,H_2C = CH_2 \rightarrow Cl_3C - (CH_2 - CH_2)_x - Cl$$

Instead of carbon tetrachloride, the so-called telogen, carboxylic acids such as acetic acid and propionic acid have been found to add to olefins, especially ethylene, in telomerizations initiated by peroxides (2,3).

Manganese (III) acetate can be used as the radical initiator. Reactions of ethylene or higher α-olefins with acetic acid or its anhydride in the presence of manganese (III) acetate reportedly yield various types of products: linear saturated carboxylic acids (4,5), linear unsaturated carboxylic acids (6), γ-lactones (6-9), γ-acyloxy carboxylic acids (6,7), as well as higher molecular weight – telomer – products (5). The reaction conditions control the type of product which is mainly formed.

This paper deals with telomer acids selectively prepared by a manganese (III) acetate initiated addition of acetic anhydride to α-olefins.

EXPERIMENTAL PROCEDURES

Preparation of Telomer Acids from 1-Decene (Typical Example)

A slurry of 17.4 g of manganese (III) acetate in 100 mL of acetic anhydride and 84 g of 1-decene is slowly added to a stirred mixture of 900 mL of acetic anhydride and 42 g of 1-decene in a nitrogen atmosphere. Reaction temperature is controlled at 125 C, while the addition is made at such a rate that the reaction mixture remains colorless. On completion of the reaction, the mixture is allowed to cool to room temperature, and is filtered to remove the precipitated manganese (II) acetate. Subsequently, acetic anhydride, acetic acid and unconverted 1-decene are distilled off. The resulting mixed anhydride is hydrolyzed by adding 200 mL of acetic acid and 25 mL of water and by heating to 100 C for 1 hr. The acetic acid-water mixture is then distilled off. When required, lauric acid (the "first telomer") can be removed by distillation in vacuo.

Determination of Telomer Distribution

The telomer distribution is determined by gel permeation chromatography (GPC) and by gas chromatography (GC).

GPC conditions. A glass column, 140 × 1.5 cm, containing Merckogel OP-PVA 2000 (Merck) as the stationary phase was used. Methyl ethyl ketone was used as the mobil phase. Speed of elution was 1 mL/min. Sample concentration was 25 mg/ml. Detection was by differential refractometer.

GC conditions. A 0.45-m glass column of 2.3 mm id, containing 5% Dexsil 300 GC on Chromosorb WHP 100-120 mesh, was used. Temperature was programmed from 80 C to 360 C at 16 C/min. Nitrogen was used as carrier gas, 30 mL/min. Detection was by flame ionization at 350 C. The sample was injected as methyl esters after esterification by diazomethane.

Determination of Properties

–Kinematic viscosity: ASTM-D–445.
–Dynamic viscosity (cold cranking simulator): ASTM-D-2602.
–Viscosity index (VI_E): ASTM-D-2270.
–Pour point: ASTM-D-97.
–Elastomer swell : DIN 53521-78E.
–Total base number (TBN): ASTM-D-2896.
–Mineral oil used as solvent of derivatives: paraffinic mineral oil, 150 neutral; kinematic viscosity at 25 C, 60 mm^2/sec; kinematic viscosity at 40 C, 30 mm^2/sec; kinematic viscosity at 100 C 5.2 mm^2/sec;

Symbols and abbreviations: n, number of carbon atoms in starting α-olefin: x, degree of telomerization (number of α-olefin molecules built into telomer acid molecule): T10 (e.g.), telomer acids derived from 1-decene (n=10): TMP, trimethylolpropane: diPE, dipentaerythritol: TEPA, tetraethylene pentamine: PIBSA, polyisobutenyl succinic anhydride.

pour point, -9C.

- Volatility and thermooxidative stability by thermogravimetry: apparatus – DuPont Thermogravimetric Analyzer 951; conditions – runs in nitrogen (100 mL/min) and in air (100 mL/min); heating rate 10 C/min, sample size 30 mg; results – $T_{10\%}$, being the temperature at which 10% loss of weight is observed (run in nitrogen); T_{OX}, being the temperature at which onset of oxidation is observed, viz. by comparing the run in air with the run in nitrogen.
- Dispersancy test (carbon black): 25 mg of carbon black is added to 5 mL of white spirit, containing the dispersant to be tested in a concentration of 5% active. The carbon is dispersed ultrasonically for 10 min, and subsequently sedimented by centrifuging for 20 min. Light absorbance of the supernatant is measured at 620 nm using a 1-cm cell. Absorbance is a measure of the amount of carbon dispersed, and is expressed as relative dispersancy by dividing by the absorbance induced by the reference compound, polyisobutenyl succinimide.
- Coefficient of friction: determination by pin and ring precision tribometer (10,11) which is operated under conditions of boundary lubrication. Pin and ring are made of hardened ball bearing steel AISI 52100, overall hardness 8,000 N/mm^2. Rotational speed of ring applied is 0.0075 m/sec. The load is 100 N, resulting in a pressure of 0.1-0.3 GPa. Measurements are done over a temperature range of 30-110 C.

FORMATION OF TELOMER ACIDS

When manganese (III) acetate is added to a solution of α-olefin ($R-CH=CH_2$, n carbon atoms) in acetic anhydride at 125 C under nitrogen, the telomer products depicted in Figure 1 are formed. On hydrolysis of these anhydrides, the corresponding telomer acids are obtained. The first telomer is a linear fatty acid, which has (n+2) carbon atoms. The higher telomer acids have (xn + 2) carbon atoms. Their structures are characterized by α- and γ-branching. The chain length of the α-branch is equivalent to that of the starting α-olefin (n).

Reaction Mechanism

Initiation step. Manganese (III) acetate in acetic anhydride produces manganese (II) acetate and a carboxymethyl radical (Fig. 2). This reduction of manganese (III) acetate is faster in acetic anhydride than in acetic acid (12,13), and is zero-order in Mn (III) in the case of the anhydride (13). Enolization of acetic anhydride is assumed to be the rate-determining step (Fig. 3). Carboxymethyl radicals thus formed react with α-olefin to produce the first intermediate adduct radical (Fig. 2).

Propagation steps. The first adduct radical can abstract a H radical from acetic anhydride in a chain transfer reaction, so as to form the first telomer and a new carboxymethyl radical (Fig. 4). More important when aiming at higher telomers is the chain growth reaction of the first adduct radical with α-olefin in excess (Fig. 5). The γ-substituted dimer radical may yield the γ-branched second telomer (x = 2) by a chain transfer reaction. Figure 5 also shows intramolecular rearrangement of the first adduct radical to the α-radical. Chain growth and subsequent chain transfer lead to the α-branched second telomer. The ratio α-branched/ γ-branched in the second telomer decreases with increasing α-olefin concentration. Still, under the conditions applied in this work, α-branching is predominant, as is shown in the structure of the higher telomer acids (Fig. 1), which are formed by further chain growth.

Termination steps. Usually it is assumed that free radical chain reactions terminate in a bimolecular process by coupling or disproportionation. The main termination mechanism observed in the chemistry presented here is oxidation of intermediate radicals by manganese (III) acetate. Oxidation of the first intermediate adduct radical is supposed to lead to the corresponding carbenium ion (9). Figure 6 shows three types of termination products which are

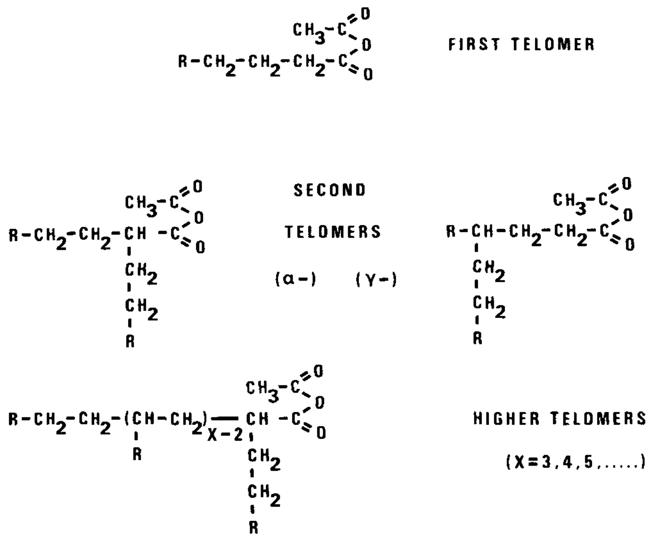


FIG. 1. Telomer reaction products.

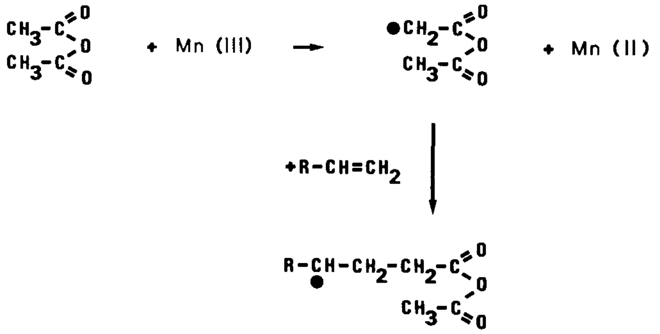


FIG. 2. Initiation step.

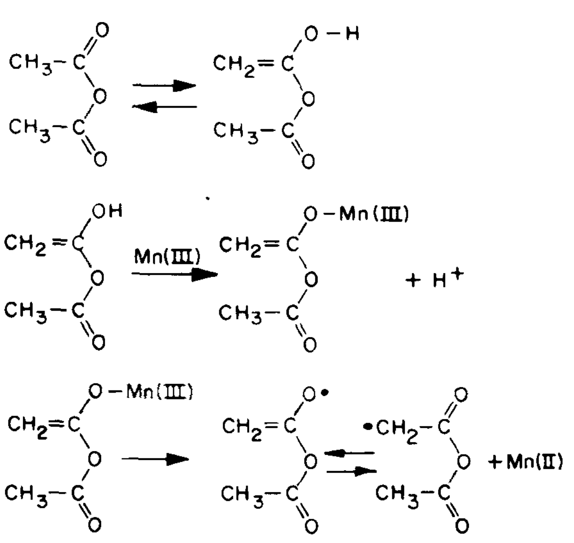


FIG. 3. Formation of carboxymethyl radicals.

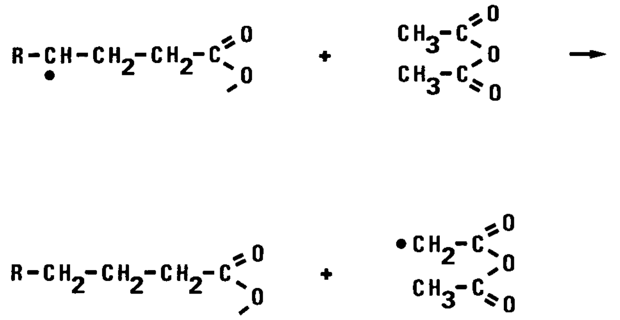


FIG. 4. Chain transfer.

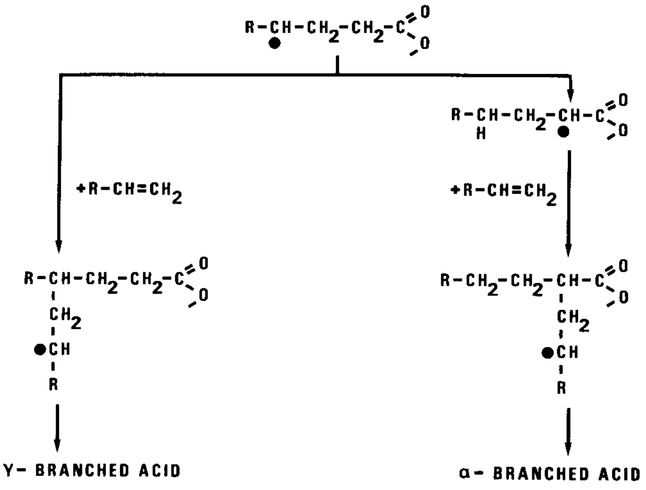


FIG. 5. Chain growth.

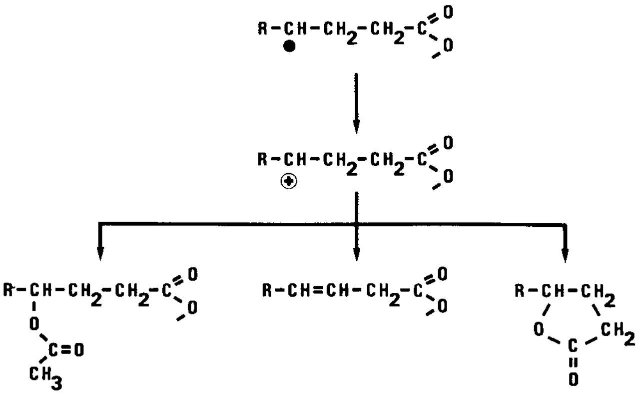


FIG. 6. Termination steps.

formed from this carbenium ion, viz. a γ-acyloxy derivative by reaction with acetic acid (or anhydride), unsaturated acids by loss of a proton, and a γ-lactone by intramolecular cyclization.

Reaction of manganese (III) acetate and olefins may yield these oxidation products (6-9) as main products by applying high concentrations of manganese (III) acetate. At low manganese (III) acetate and increased α-olefin concentrations, telomer acids can be obtained as main products instead.

PROPERTIES OF TELOMER ACIDS

Chemical Properties

The telomer acid product as it is prepared under the reaction conditions indicated (cf. experimental procedures) consists of a mixture of acids; a range in degree of telomerization (x) is found. As an example, Table I gives typical compositions of telomer acid products derived from 1-decene, viz. the product as it is obtained (total product), and products from which the first telomer, lauric acid, has been removed by distillation, partly (type A) and almost completely (type B).

These telomer distributions, which can be determined by gel permeation chromatography and by gas chromatography, are typical distributions also found for telomer acids from other α-olefins (n = 8, 12, 14, 16, 18), when prepared under similar process conditions.

Some chemical characteristics of telomer acids derived from various α-olefins are shown in Table II. The ester value (saponification value minus acid value) is an indication of the presence of lactones and acetoxy esters. Infrared measurements on fractionated products show that these termination structures are predominantly present in the higher telomer fractions. The iodine value is rationalized by the presence of unsaturated acids and some unsaturated hydrocarbon. Since formation of unsaturated acids is inherent with the termination mechanism, low iodine values can only be obtained by subsequent hydrogenation.

The data in Table II refer to products of type A (cf. Table I, i.e., containing 5-10% linear acid), as is the case for other data presented in this paper, unless mentioned otherwise.

Physical Properties

The long-chain branches in the structure of telomer acids give rise to unusual properties when compared with normally available monocarboxylic acids. This is particularly reflected in solubility characteristics and liquidity in relation to the molecular weight. Telomer acids are very soluble in *n*-heptane, toluene and carbon tetrachloride at 25 C, and in 2-propanol and acetone at 70 C. They are insoluble in water. The liquidity of telomer acids is exemplified by pour point determinations. Figure 7 shows the pour point of telomer acids as a function of the α-olefin feedstock used (n, being equivalent to the chain length of the α-branch) and as a function of the average number of carbon atoms. As a reference, the melting point curve for *n*-fatty acids is included in Figure 7. The curve for telomer acids shows an increase in pour point with increasing chain length of the α-branch, viz. from − 47 C for T8 to 20 C for T18.

TABLE I

Telomer Acid T10: Telomer Distribution

Distribution x	Total product	Type A	Type B
x = 1 (lauric acid)	24%	8%	<1%
x = 2	21%	23%	20%
x = 3	23%	29%	33%
x = 4	15%	19%	22%
x = 5 + higher	17%	21%	24%

TABLE II

Chemical Characteristics of Telomer Acids

Typical examples	T10	T14	T18
Acid value (mg KOH/g)	99	82	67
Saponification value (mg KOH/g)	118	93	80
Iodine value (g I_2 /100 g)	21	15	12
Average molecular weight	475	605	700

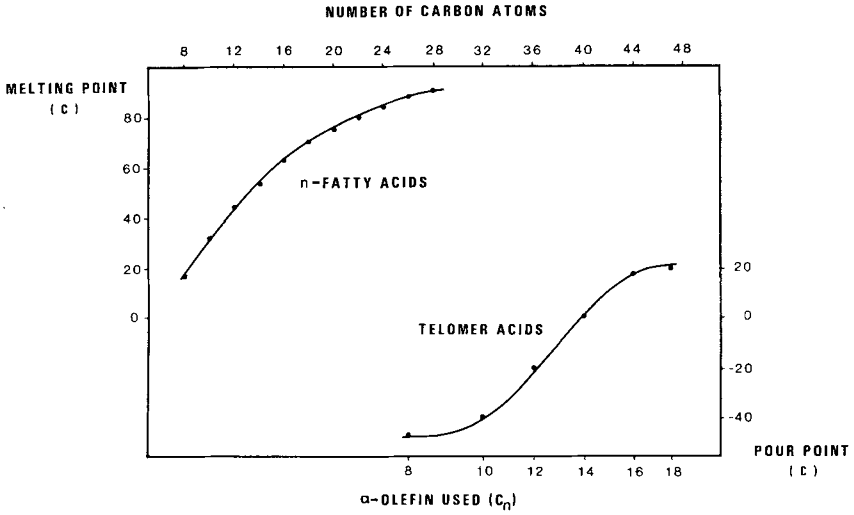


FIG. 7. Pour points of telomer acids.

TELOMER ACID ESTERS

Taking into account the low pour points of telomer acids with respect to their high molecular weight, the effect of the telomer structure on the properties of esters was investigated. Particularly esters prepared from telomer acids and neopentyl polyols were studied. Fatty acid esters of neopentyl glycol, trimethylolpropane and pentaerythritol are well known for their good thermooxidative stability, and consequently find application as base fluids in lubricants. Viscosity of such esters is a function of both molecular weight and molecular shape (14). This is illustrated in Figure 8, showing the viscosity at 40 C of neopentyl polyol esters as a function of molecular weight. For *n*-fatty acids a straight line is found, irrespective of the polyol (neopentyl glycol, trimethylolpropane, pentaerythritol) (14). However, for fatty acids containing short-chain (methyl, ethyl) branched structures, viscosities are at a significantly higher level (15,16). This illustrates the effect of molecular shape: short-chain branching induces an increase in viscosity and a corresponding decrease in viscosity index.

The long-chain branches in the telomer structure lead to an intermediate viscosity level at a given molecular weight, as appears from the viscosity of trimethylolpropane esters of telomer acids combined with *n*-fatty acids. To arrive at a broad range of molecular weights, the type of telomer acid as well as the telomer acid/fatty acid ratio have been varied. In the molecular weight range 650-1100, the viscosity of these esters shows a practically linear relationship.

The data in Table III show the viscosity/molecular weight relationships for trimethylolpropane esters of different acids. Replacing linear C_{10} acid by methyl-branched C_{10} acid leads to an increase in viscosity, a decrease in viscosity index, and a decrease in pour point. Partial replacement of linear C_{10} acid by telomer acid T8 increases the molecular weight and thereby gives an interesting balance of properties. Despite its higher molecular weight, this telomer acid containing ester has an equal 100 C viscosity (but lower 40 C viscosity) compared with the trimethylolpropane ester of methyl-branched C_{13} acid. Its viscosity index is higher and its pour point is lower.

This combination of relatively low viscosity as a function of molecular weight, high viscosity index and low pour point is generally found for telomer acid containing esters.

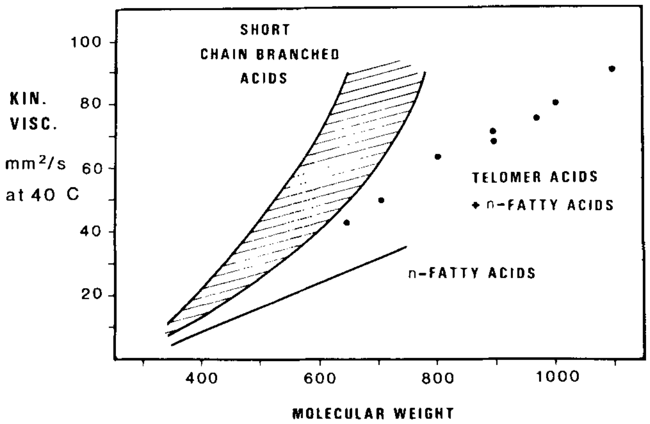


FIG. 8. Neopentyl polyol esters of *n*-fatty acids, fatty acids with methyl- or ethyl-branching, and telomer acids.

TABLE III

Esters from Trimethylolpropane

Acid in TMP ester	Ester MW	Kinematic viscosity (mm^2/sec) 40 C	100 C	Viscosity index	Pour point (C)	Reference
3 mol n-C_{10}	600	24	5.2	153	+ 8[a]	
3 mol br-C_{10}	600	46	6.6	95	-51	15
3 mol br-C_{13}	730	105	10.6	82	-37	15
1.35 mol telomer acid T8 1.65 mol n-C_{10}	920 (average)	72	10.5	132	-57	

[a]Crystallization temperature.

TABLE IV

Properties of Telomer Acid Esters

Alcohol	Acid 1	Acid 2	Kinematic viscosity (mm^2/sec at 100 C)	Viscosity index	Pour point (C)	Thermogravimetry $T_{10\%}$ (C)	Thermogravimetry T_{ox} (C)
2-Ethylhexanol	T10	–	5.0	143	-39	267	215
1,2-Propanediol	T8	n-C_{10}	5.7	134	-51	284	210
TMP	T8	n-C_{10}	10.5	132	-57	333	209
diPE	T8	n-C_7	29.0	136	-34	327	214
TMP	n-C_8	n-C_{10}	4.6	142	-30	283	213

Table IV shows a few examples, covering a viscosity range of 5-29 mm^2/sec at 100 C. The trimethylolpropane ester of C_8/C_{10} fatty acids is included as a reference.

Thermooxidative stability determined by thermogravimetry and expressed in T_{OX} (onset of oxidation) is at the same level for the telomer acid esters and the reference ester. The hydrolytic stability has also been found to be comparable.

Elastomer swell is an important property in lubricant applications. A lubricating liquid can affect the dimensional and mechanical properties of elastomers used in seals, gaskets, etc. In immersion tests, standard nitrile, acrylic and fluoro elastomers appear to be hardly affected by telomer acid esters, i.e., only slight changes of volume and of hardness are found. Compared with other base fluids, telomer acid esters induce less swell of silicone elastomers. As an example, Figure 9 shows the changes of volume and hardness of nitrile elastomer after immersion in various test fluids (all in the viscosity range 4.5-10.5 mm^2/sec at 100 C). High swell is observed for the trimethylolpropane ester of C_8/C_{10} fatty acids, whereas poly-α-olefin gives shrinkage due to extraction of soluble constituents. In comparison, the trimethylolpropane ester derived from telomer acid shows hardly any volume change and only slight hardness increase, as do mineral oil and formulated engine oil.

This effect can be rationalized if one considers the structure of the telomer ester as a combination of the structure of the poly-α-olefin and that of the trimethylolpropane-fatty acid ester, i.e., in terms of molecular shape and of polarity.

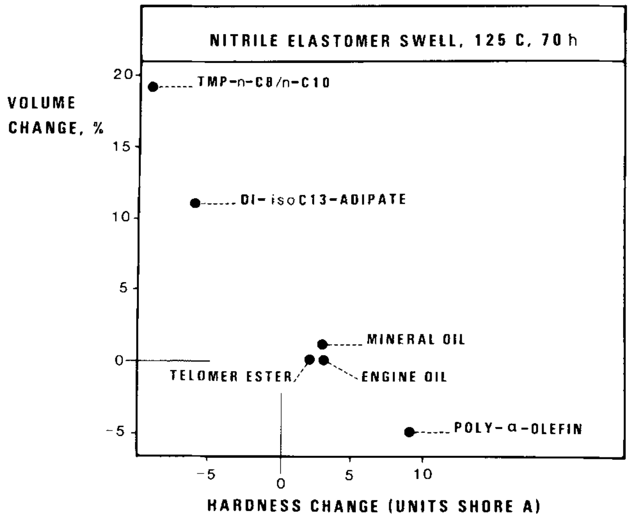


FIG. 9. Nitrile elastomer swell in various test fluids.

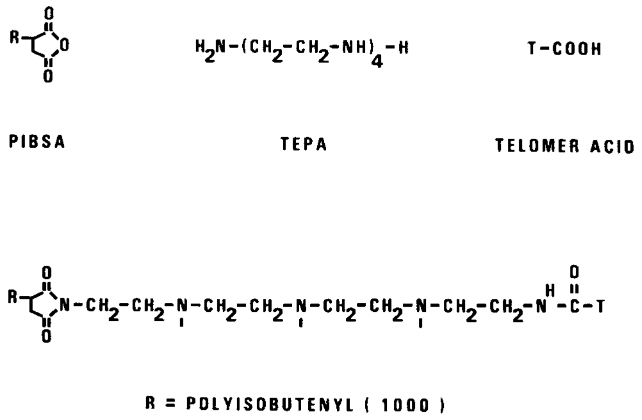


FIG. 10. Simplified structure of TEPA-PIBSA-telomer acid condensation products.

TELOMER AMINO AMIDES

Condensation products of telomer acids with polyamines such as tetraethylene pentamine (TEPA) were synthesized and their properties determined. Such product types are used in the lubricant industry as "ashless dispersants", oil additives which disperse oil sludge thus preventing deposition of the sludge on internal engine parts. Polyisobutenyl succinimide, the condensation product of polyisobutenyl succinic anhydride (PIBSA) and polyamine (e.g., TEPA) is a commonly used type of ashless dispersant (17).

Characteristic properties of the telomer acid condensation products with TEPA are in line with those of telomer acid containing esters: low viscosity with respect to molecular weight, and low pour point. The efficacy to keep carbon black in dispersion was found to be moderate. Hence, structure/property relationships were examined of TEPA condensation products with mixtures of PIBSA and telomer acids (Fig. 10). The resulting products were dissolved in mineral oil (50% concentration). Rheological data are given in Table V. At equivalent molar intakes, viscosity decreases with increasing chain length of the α-branch (T8 through T18), despite the increase in calculated average molecular weight, as shown in the upper series of 5 products in Table V. In this series, a minimum is found in the pour point of the mineral oil solution as a function of the α-branch chain length, viz. for the 1-tetradecene based telomer acid. T14 coreacted amino amides showing a good combination of low viscosity and low pour point were chosen for further structure/property relationship studies.

Viscosity and pour point reductions at several mole ratios are shown in the lower series of 4 products in Table V. When 1.8 moles of PIBSA, reacted with 1 mole of TEPA, are replaced half by T14 acid, viscosity and pour point decrease considerably. Even when 0.9 moles of T14 acid are used in addition to 1.8 moles of PIBSA, the decrease in viscosity and pour point is significant. This remarkable effect is not observed with stearic acid. Figure 11

TABLE V

Condensation Products with Tetraethylene Pentamine, Effect of Type of Telomer Acid

PIBSA (moles/mole)	Telomer acid (moles/mole)	Telomer acid Type	Product MW (calcd)	50% Solution in mineral oil: Viscosity (mm²/sec) 25 C	Viscosity (mm²/sec) 100 C	Pour point (C)
0.6	1.0	T8	1200	1440	35.0	-15
0.6	1.0	T12	1300	960	30.0	-21
0.6	1.0	T14	1400	850	28.8	-24
0.6	1.0	T16	1500	510	21.3	0
0.6	1.0	T18	1550	420	18.3	+13
1.8	0	–	2150	5730	83.6	-9
0.9	0.9	T14	1700	660	23.6	-25
1.8	0.9	T14	2700	1315	36.7	-23
1.8	0.9	Stearic	2400	4630	77.2	-4

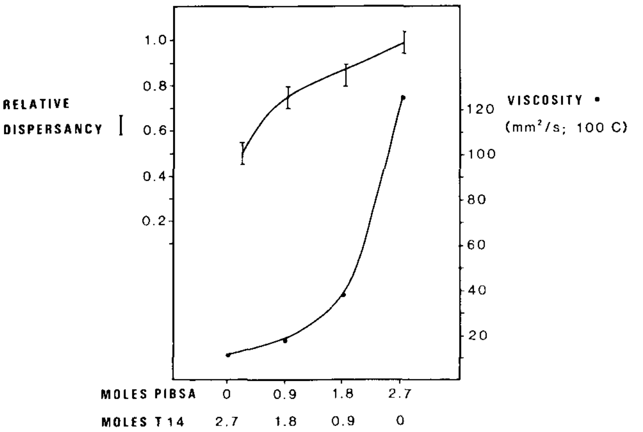


FIG. 11. TEPA-PIBSA-telomer acid condensation products: dispersancy and viscosity as a function of mole ratio.

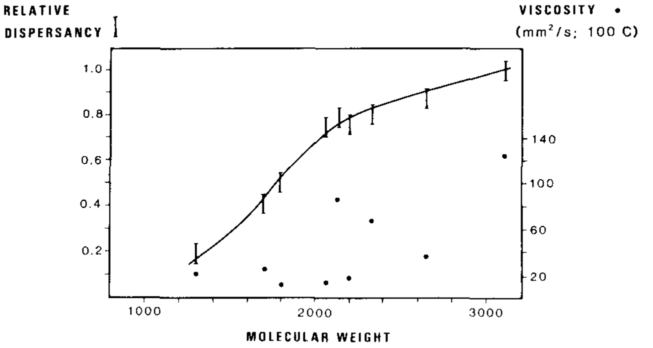


FIG. 12. TEPA-PIBSA-telomer acid condensation products: dispersancy and viscosity as a function of molecular weight.

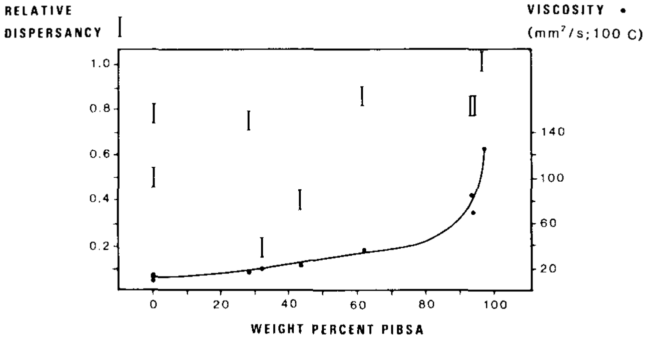


FIG. 13. TEPA-PIBSA-telomer acid condensation products: dispersancy and viscosity as a function of weight percent PIBSA.

shows the viscosity reduction by decrease of the mole ratio PIBSA/T14 at an equal total molar intake of 2.7 moles per mole of TEPA. Dispersancy, relative to the polyisobutenyl succinimide (value 1.0), is lowered when T14 is substituted for PIBSA, but is retained at a fairly high level for lower degrees of substitution. Figures 12 and 13 show that viscosity (50% mineral oil solution) and relative dispersancy do not correlate with the same structure parameter. Dispersancy appears to correlate with the molecular weight of the condensation product. This is in agreement with literature data on polyisobutenyl succinimides (17). Viscosity is not found to correlate with molecular weight, but with the weight percentage of PIBSA incorporated in the molecule. For relative dispersancy, no such correlation is found.

TELOMER ACID METAL SALTS

Rheological properties observed in the telomer acids and other derivatives are retained in the telomer acid metal salts. Depending on the metal ion and the telomer acid composition, a number of liquid metal salts can be made, contrary to fatty acid metal salts which are solids at room temperature. For example, the calcium salt of telomer acid T14 is liquid at room temperature when the linear acid content is low (type B, cf. Table I). When the content of linear acid is 5-10% (type A), the calcium salt is of a jelly nature. Magnesium salts of telomer acids T10 and T14 of both type A and type B are liquid at room temperature. The magnesium salt of telomer acid T14 (type A) has a viscosity of 2100 mm^2/sec at 25 C and a pour point of 8 C. The calcium and magnesium salts of telomer acids are very soluble in chloroform, carbon tetrachloride, toluene and paraffinic mineral oil, but insoluble in 2-propanol, acetone and water. In all those solvents, the calcium and magnesium salts of stearic acid are practically insoluble.

Table VI shows viscosity properties of calcium and magnesium salts of various telomer acids as 50% solutions in mineral oil. Comparable viscosities are found for the magnesium salts, irrespective of the telomer acid used. On the contrary, the calcium salts show a decrease in viscosity when going from T8 to T14. The viscosity of mixtures of magnesium and calcium salts of telomer acid T8 decreases with increasing Mg/Ca mole ratio. Remarkably, a sharp viscosity drop is found between Mg/Ca 1/3 and 1/1.

The solubility and viscosity properties are related to the high molecular weight structure with long-chain branches, and probably also to the fact that the telomer acids consist of a mixture of monocarboxylic acids. Their salts are supposed to associate in oil to micelles. Literature data, describing alkali metal carboxylates of mixed linear and branched structures, confirm that a combination of structures increases the probability of favorable orientation,

TABLE VI

Magnesium and Calcium Salts of Telomer Acids

			Properties of 50% solutions in mineral oil				
					Kinematic viscosity (mm^2/sec)		
Acid	Metal	Mole ratio	wt% Mg	wt% Ca	25 C	40 C	100 C
T8	Mg		1.63	–	220	110	15.0
T10	Mg		1.32	–		100	14.4
T12	Mg		1.09	–		101	14.9
T14	Mg		1.05	–		105	15.3
T8	Ca		–	2.54	1108	495	62.2
T10	Ca		–	2.06		450	37.0
T12	Ca		–	1.74		330	28.0
T14	Ca		–	1.54		305	20.2
T8	Mg/Ca	1/9	0.16	2.35	1033		49.5
T8	Mg/Ca	1/3	0.39	1.95	896		28.6
T8	Mg/Ca	1/2	0.52	1.75	509		18.7
T8	Mg/Ca	1/1	0.79	1.30	304		17.4
T8	Mg/Ca	3/1	1.19	0.65	246		15.5

TABLE VII

Low Temperature Properties of Calcium Telomer Salt (T14) in Mineral Oil

Ca-T14 Salt % wt (active)	Dynamic viscosity at -18 C (CCS) (mPa.sec)	Pour point (C)
0	(1550)	-9
0.1	1550	-20
0.5	1550	-36
1.0	1550	<-46
2.0	1560	-41
4.0	1570	-33
7.0	1700	-26
10.0	1850	-22
20.0	2450	-12

thus giving more stable micelles (18). This improves solubility and affects the viscosity of the solution. The viscosity is dependent on the size and the shape of the micelles, and can be affected by the radius of the cation. Thus, the viscosities of the calcium salt solutions being higher than those of the magnesium salt solutions may be explained by a less complete shielding of the polar core of the micelles by the hydrocarbon chains. Apparently, size and shape of the micelles change rather sharply from one type into another in the case of the mixed magnesium-calcium salts.

Mineral oil solutions of alkaline earth metal salts of telomer acids are Newtonian fluids, as determined with a Weissenberg rheogoniometer (19). This is exemplified in Figure 14 for the calcium salt of telomer acid T8 at two concentrations.

Dynamic viscosity measurements of mineral oil solutions at -18 C, using the cold cranking simulator (CCS), are shown in Table VII. Practically no increase of viscosity is observed at calcium salt concentrations up to 4%. Pour point determinations on these solutions show the distinct pour point depressing effect of calcium-T14 salt at concentrations as low as 0.1%, and a mixmum effect at a level of 1%.

Overbased Calcium Salts

So-called overbased salts are of interest as detergents in lubricating oils, one of their functions being the neutralization of acids formed. Overbased calcium salts of telomer acids, obtained by reaction at elevated temperature with calcium hydroxide and carbon dioxide in mineral oil with methanol as a promoter, are clear and stable dispersions. The degree of overbasing is reflected in the following parameters: percentage calcium; total base number (TBN), expressed as mg KOH/g; and

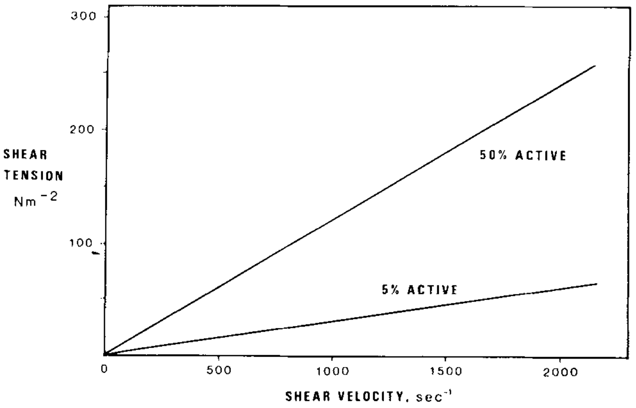


FIG. 14. Newtonian behavior for calcium salt of telomer acid (T8) in mineral oil.

$$X = \frac{\text{equivalents CaCO}_3}{\text{equivalents Ca-soap}} \approx \frac{\text{TBN}_{\text{overbased}} - \text{TBN}_{\text{soap}}}{\text{TBN}_{\text{soap}}}$$

Properties of two overbased calcium salts of telomer acid T14 are given in Tables VIII and IX. X values as high as 7 can be reached. Viscosities of these concentrated dispersions in mineral oil are fairly low. More dilute solutions in mineral oil show properties at low temperature which are comparable to those found for the neutral salts. The dynamic viscosity at -18 C increases only slightly with concentration in the range of 0.1-4% (Table X). Also the pour point depressing effect is similar to that of the neutral salts: pour points of -30 C and lower in the concentration range of 0.5-10%.

Remarkably, overbased calcium salts of telomer acids, at a concentration of 2% in mineral oil, reduce friction lubricated steel contacts and, moreover, bring along an unusual decrease of the coefficient of friction with increasing temperature (Table XI). The coefficient of friction was determined with a pin and ring precision tribometer (10,11), operating under conditions of boundary lubrication, when the bulk flow properties of the lubricant do not affect friction. As a referential measurement, the effect induced

TABLE VIII

Overbasing of Ca-T14 Salt in Mineral Oil

	Ca (%)	TBN (mg KOH/g)	X
Neutral salt	1.4	38	0
Overbased I	7.1	182	3.8
Overbased II	10.3	295	6.8

TABLE IX

Properties of Overbased Ca-T14 Salt at 55-60% Concentration in Mineral Oil

	I TBN 182	II TBN 295
Appearance (room temperature)	Clear	Clear
Kinematic viscosity at 25 C (mm^2/sec)	328	513
Kinematic viscosity at 100 C (mm^2/sec)	23.3	33.2
Pour point (C)	-25	-25

TABLE X

Low Temperature Properties of Overbased Calcium Telomer Salt (T14) in Mineral Oil

Ca-T14 Salt overbased (TBN 182) % wt (active)	Dynamic viscosity at -18 C (CCS) (mPa.sec)	Pour point (C)
0	(1550)	-9
0.1	1570	-17
0.5	1580	-30
1.0	1580	-36
2.0	1600	-40
4.0	1630	-38
7.0	1700	-36
10.0	1850	-34
20.0	2400	-27

TABLE XI

Coefficient of Friction as a Function of Temperature (Pin and Ring Precision Tribometer)

Oil tested	Coefficient of friction at 30 C	70 C	110 C
Mineral oil	0.160	0.170	0.180
+ 2% Neutral Ca-T14	0.155	0.165	0.155
+ 2% Overbased Ca-T14 (TBN 182)	0.140	0.135	0.115
+ 0.25% Oleylamide	0.130	0.150	0.160

by oleylamide, being a known friction reducer of another chemical class, is included in Table XI. The increase of the coefficient of friction with temperature could be explained assuming decrease of adsorption of the amide to the metal surface. The reverse behavior of the overbased calcium salt indicates that a different mechanism is involved with regard to this class of compounds.

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