Oligomeric Plasticizers from Crambe Oil-Derived Dicarboxylic Acids for Poly(vinyl chloride)[1]

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ABSTRACT

Seventeen oligomeric plasticizers were prepared by polyesterification of long chain dicarboxylic acids with propylene glycol and terminator acid or alcohol. All, except one terminated by dodecyl alcohol, were compatible with poly(vinyl chloride). Films plasticizied with these polyesters were similar in transparency and flexibility to films plasticized with bis(2-ethylhexyl) phthalate. Poly(vinyl chloride) sheets containing brassylic acid polyesters with $\bar{M}_n$ of 2200-2300 or a crambe mixed dicarboxylic acids polyester with $\bar{M}_n$ of 2100 exhibited superior permanence with overall performance comparable to sheets plasticized with bis(2-ethylhexyl) phthalate commercial polymeric plasticizer.

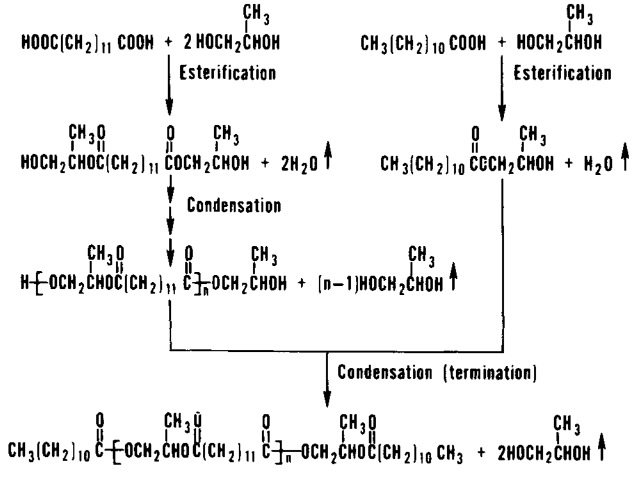
INTRODUCTION

Polyesters from long chain dicarboxylic acids are especially attractive now as attention is being given to replacing traditional plasticizers in auto upholstery (1), food packaging materials (2), and blood storage bags (3,4). Concern over biological effects of phthalate ester plasticizers (5) clouds prospects for their continued high volume use. Aliphatic polyesters, which are more susceptible to biological degradation (6) than are aromatic esters, offer possibilities for developing structural variations that impart low volatility, better permanence, and good performance. To this end, our laboratories have examined some 60 different materials made from brassylic acid (C_{13}) or a mixture of straight chain dicarboxylic acids (mainly C_{13} and C_9) that is readily available from crambe oil (7).

Certain monomeric diesters of brassylic acid (8) and of the mixed crambe dicarboxylic acids (9) are efficient low temperature plasticizers with excellent light stability but relatively high migration and volatility losses. Permanent plasticization is achievable with 2-methylpentyl vinyl brassylate which copolymerizes with vinyl chloride to give internally plasticized polymers (10) that make good films, but this alkyl vinyl ester is apparently less effective than diesters used externally (11).

Intermediate performance, plasticization with good residence characteristics, can be realized with oligomeric esters described in this paper, which extends accumulated knowledge (12,13) of chain length effects in terminated polymeric dicarboxylic acid-propylene glycol plasticizers.

Polyesterification



Scheme 1

EXPERIMENTAL PROCEDURES

Materials

Brassylic acid (95.2% C_{13} by gas liquid chromatography [GLC]) was obtained from ozonolysis of erucic acid by the Welsbach Corp., Philadelphia, Pa.; crambe mixed dicarboxylic acids (31.3% C_9, 46.6% C_{13}, and 15.4% others) from Emery Industries, Cincinnati, Ohio; propylene glycol from Fisher Scientific Co., Chicago, Ill.; lauric acid from Aldrich Chemical Co., Milwaukee, Wis.; Geons 101 and 102 (poly[vinyl chloride] [PVD]) from B.F. Goodrich Co., Cleveland, Ohio; and polystyrene standards from ArRo Laboratories, Joliet, Ill.

Preparation

Seventeen oligomeric esters were prepared via polyesterification (12) of the various dicarboxylic acids with propylene glycol in the presence of a terminator acid or alcohol. A single example illustrates conditions. Brassylic acid (0.4 mole), propylene glycol (0.8 mole), lauric acid (0.4 mole), zinc chloride (0.15 g), and toluene (50 ml) were charged into a 500 ml reaction vessel and heated under positive nitrogen pressure. All reactants dissolved at ca. 100 C, and reflux began at ca. 140 C. The reaction temperature was raised slowly to 220 C by withdrawing azeotropes through a Barrett trap connected to a glass helix-packed column with steam cooling to separate toluene-water (bp 85 C) from toluene-propylene glycol (bp 110 C), which was removed after esterification. Reaction times were measured from first reflux to 1 hr after no further condensate collected. After completion of reaction, the mixture was heated slowly to 230 C under 1-2 mm Hg and held at that temperature to remove all volatiles. The resulting viscous liquid was cooled to 80 C, mixed with 15 g filter aid, and filtered. Suspended material that appeared in the product after several months' storage at room temperature was separated with a Spinco ultracentrifuge (Beckman Instruments, Palo Alto, Calif.), model L, rotor no. 30, at 30,000 rpm for 30 min with samples at room temperature; recovery, ca. 90%.

Characterization

Acid value (14), hydroxyl value (14), and saponification equivalent (15) were determined according to reported methods. Number-average mol wt ($\bar{M}n$) were determined osmometrically, using a Mechrolab model 301A vapor pressure osmometer and three solute concentrations in benzene; the data were extrapolated to infinite dilution. Monodisperse ($\bar{M}w/\bar{M}n$ <1.1) polystyrenes, ArRo 500-2

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TABLE I

Preparation and Physicochemical Properties of Oligomeric Esters

	Polyesterification				Purified products					
	Charge									
No.	Reactants[a]	Mole ratio	N[b]	Time (hr)	Acid value	Hydroxyl value	Saponification equivalent (calculated)	$\bar{M}_n$ (calculated)	Viscosity (cp)	Gardner color
1	B/G/L	1/2/1	2	4.5	5	16	170(168)	1900(1008)	246	2
2	B/G/L	2.5/5/1	5	6.0	2	11	156(155)	2100(1860)	NN[d]	1-2
3	B/G/L	2.5/5/1[c]	5	11.0	1	19	153(155)	1800(1860)	4670	5
4	B/G/V	2.5/3.75/1	5	30.0	4	8	155(151)	2100(1816)	2570	5
5	B/G/L	5/7.5/1	10	---	2	20	152(149)	2200(3280)	3845	2-3
6	B/G/P	5/6.2/1	10	---	28	24	145(145)	2100(3196)	2370	5
7	B/G/L	7.5/15/1	15	8.0	8	28	150(147)	2300(4700)	10000	5
8	C/G/L	1/2/1	2	8.0	23	6	163(165)	1200(990)	170	9
9	C/G/P	1/2/1	2	6.5	5	3	150(151)	1800(906)	207	6
10	C/G/L	2.5/5/1	5	6.0	8	6	149(151)	1900(1815)	555	10
11	C/G/L	5/10/1	10	7.0	4	9	144(145)	2100(3190)	1830	10
12	S/G/L	2.5/5/1	5	12.0	29	10	140(137)	2000(1650)	2040	10
13	Z/G/L	1/2/1	2	11.5	1	7	151(149)	1700(896)	160	1-2
14	Z/G/L	2.5/5/1	5	9.8	4	5	134(132)	2100(1580)	769	1-2
15	Z/G/L	5/10/1	10	10.0	3	15	126(124)	2200(1720)	2920	1-2
16	A/G/L	2.5/5/1	5	7.8	3	11	116(114)	1800(1370)	634	1
17	B/G/D	3/2.5/1	5	16.0	5	95	170(167)	---	---	6

[a] B = brassylic acid, C = crambe mixed dicarboxylic acids, S = sebacic acid, Z = azelaic acid, A = adipic acid, G = propylene glycol, L= lauric acid, V = 5-phenyl valeric acid, P = pelargonic acid, and D = dodecyl alcohol.

[b] The degree of polymerization. Calculated by 2[dicarboxylic acid charged]/[terminator charged].

[c] p-Toluenesulfonic acid monohydrate as catalyst.

[d] Non-Newtonian. At 6, 12, and 30 rpm the observed viscosities were 4280, 3600, and 2900 cp, respectively, indicative of pseudo-plastic behavior.

and ArRo 500-6 with $\bar{M}n$ of 555 and 2115, respectively, served as standards. Viscosity was measured with a Brookfield Synchro-Lectric viscometer, model LVT, at 25 C. Measurements were made with the same spindle at three speeds to detect non-Newtonian behavior.

Physical Testing

Plasticized PVC films for visual evaluation were cast in 10 cm petri dishes from tetrahydrofuran solution. Each contained 15 g Geon 102 (10% by wt) and polyester plasticizer at 20% and 50% levels. Comparison films were prepared in the same manner with bis(2-ethylhexyl) phthalate (DOP) at 10%, 20%, 30%, 40%, and 50% levels.

Test PVC sheets containing 65 parts Geon 101, 1 part epoxidized oil (G-62), 2 parts Ba-Cd complex (Mark M), and 32 parts plasticizer were prepared according to reported procedures (9). Torsional stiffness (American Society for Testing and Materials [ASTM] D1043-69), migration and volatility losses (ASTM D1203-67), tensile properties (ASTM D412-68), and heat stability were determined by the given standard tests or as previously described (8). When changes in sample surface upon heating prevented spectrophotometric measurement of heat stability, the test films were evaluated visually and compared by color with films whose heat stabilities could be measured directly. Compatibility numbers were calculated in keeping with the empirical relationship noted by Riser and Palm (16).

RESULTS AND DISCUSSION

Thermodynamic calculations that consider plasticizers as solvents for resin molecules (17) and observations correlating plasticizer structure with solvating powder (18) suggest that polyesters from short chain dicarboxylic acids should be more compatible with PVC and impart better low temperature flexibility than should like polyesters containing longer chain homologous acids. In reality, according to Brice, et al., (13), who studied polyesters made from propylene glycol and homologous dicarboxylic acids from C_4-C_{10}, the flex temperature decreased with increasing chain length. They also observed opposing trends in soapy water and white gas extractabilities; the former decreased, and the latter increased as the intracarbonyl chain lengthened. Extrapolations from their data, though promising outstanding plasticizer characteristics at dicarboxylic acid chain length longer than 10, must be tempered by the realization that theoretical considerations lead to contrary conclusions. Our studies extend experimental information pertinent to this issue.

The polyesterification comprises two stages, esterification and condensation, which are exemplified by the preparation of lauric acid-terminated poly(propylene brassylate) (correct nomenclature should be α-lauroyl-ω-[(propylenedioxy)lauroyl] poly[(propylenedioxy) brassyloyl] [19]) in Scheme 1. Reaction times and descriptive properties of the products are given in Table I.

We tried to predetermine the degree of polymerization (n) at 2, 5, 10, and 15 by charging reactants according to n = 2 [dicarboxylic acid]/[terminator]. Agreement between calculated and found saponification equivalents (Table I) and different viscosities of the products indicate that some structural variation was achieved, but the number average mol wt suggest that this variation was not so great as originally intended. Similar difficulty was experienced by Koroly and Beavers (12), who attributed their problem to the formation of cyclic structures (20), especially during preparation of high mol wt polyesters. Cyclic esters are possible, as are other unwanted products, such as unterminated polyesters and simple monomeric esters, which could also contribute to the disparity between saponification equivalent data and the number average mol wt.

An NMR spectrum (100 MHz; CCl_4) of one brassylate polyester (Table I, no. 1) showed a triplet at δ 0.87 for the terminal methyl group, which established the presence of noncyclic molecules. Other chemical shifts were as expected. Acid and hydroxyl protons were apparently below detection limits and were not observed. The degree of polymerization calculated from signal strengths (n = 2.8) compares favorably with the predetermined value (n =2) but is subject to the same errors that affect other methods of end-group analysis. Values of n determined from saponification equivalent and number average mol wt were 3.6 and 5.1, respectively. Most likely, n for polyester no. 1 falls between these two figures.

TABLE II

Mechanical Properties of Poly (vinyl chloride) Sheets Containing 32% Plasticizer

		Torsional stiffness		Compatibility number	Permanence		Performance			
No.	Plasticizer[a] (idealized structure)	T_F C	T_4 C	T_4-T_F	Migration loss (%)	Volatility loss (%)	Tensile strength psi	Ultimate elongation (%)	100% Modulus psi	Heat stability (hr)
1	L-$(G\text{-}B)_2$-G-L	-27	13	40	7.7	1.2	2715	290	1470	7.0
2	L-$(G\text{-}B)_5$-G-L	-21	13	34	3.3	0.9	2795	215	1650	5.5
3	L-$(G\text{-}B)_5$-G-L	-21	20	41[b]	6.2	4.2	2350	230	1570	8.0
4	V-$(G\text{-}B)_5$-G-V	-15	14	29	1.3	0.8	2520	230	1425	4.0
5	L-$(G\text{-}B)_{10}$-G-L	-16	15	31	1.9	0.5	2945	275	1715	8.0
6	P-$(G\text{-}B)_{10}$-G-P	-16	18	34	1.8	0.7	2540	240	1720	4.0
7	L-$(G\text{-}B)_{15}$-G-L	-17	18	35	1.1	0.5	2265	175	1610	2.5
8	L-$(G\text{-}C)_2$-G-L	-30	14	44	9.7	2.5	2395	235	1460	5.0
9	P-$(G\text{-}C)_2$-G-P	-27	4	31	6.4	2.2	2970	255	1460	6.0
10	L-$(G\text{-}C)_5$-G-L	-23	10	33	3.8	0.7	2890	300	1550	5.5
11	L-$(G\text{-}C)_{10}$-G-L	-19	13	32	2.1	0.6	2950	260	1595	3.0
12	L-$(G\text{-}S)_5$-G-L	-21	12	33	3.7	1.1	2950	180	1525	4.0
13	L-$(G\text{-}Z)_2$-G-L	-30	6	36	6.3	1.0	2240	195	1205	7.0
14	L-$(G\text{-}Z)_5$-G-L	-19	9	28	2.9	0.8	3175	255	1635	2.5
15	L-$(G\text{-}Z)_{10}$-G-L	-13	13	26	0.9	0.3	2640	245	1500	4.0
16	L-$(G\text{-}A)_5$-G-L	-15	10	25	2.2	0.8	3235	270	1675	6.5
Control	Plastolein 9720	-21	8	29	3.5	1.4	2705	270	1315	5.0
Control	DOP	-26	0	26	4.3	1.6	2890	270	1260	6.4

[a] B = brassyloyl, C = acyls of crambe mixed dicarboxylic acids, S = sebacoyl, Z = azelaoyl, A = adipoyl, G = propylenedioxy, L = lauroyl, V = 5-phenyl valeryl, P = perlargonoyl, D = Dodecoxy, plastolein 9720 = polymeric plasticizer from Emery, and DOP = bis(2-ethylexyl) phthalate.

[b] After 1 month moderate exudation occurred from polyester prepared using p-toluenesulfonic acid monohydrate as catalyst.

Evaluation of Films

When examined visually, PVC films containing 20% polyesters showed excellent transparency and flexibility equivalent to those plasticized with 20% DOP; films containing 50% polyesters exhibited transparency and flexibility like those having 40% DOP. The only exceptions were films containing dodecyl alcohol-terminated polyester, which appeared milky to opaque at plasticizer levels above 20%.

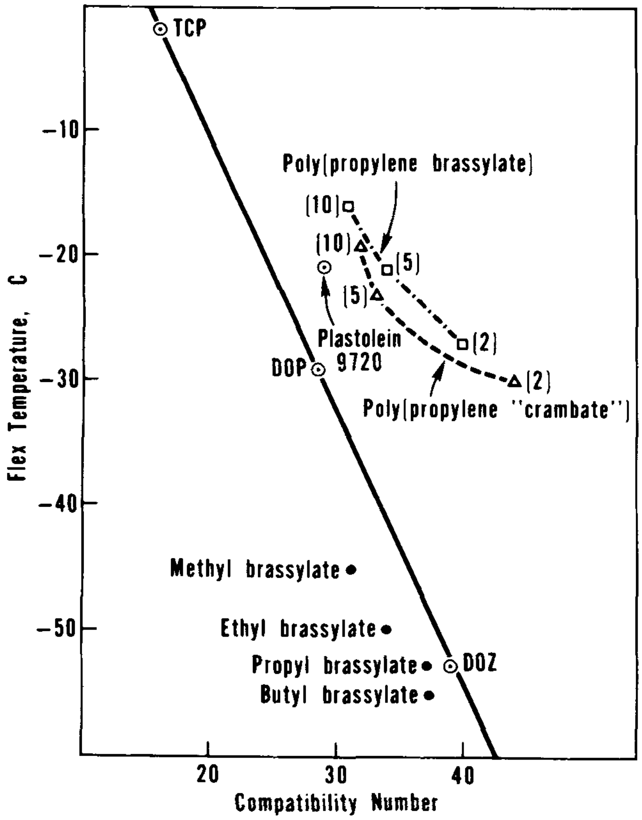

FIG. 1. Compatibilities of oligomeric esters prepared from brassylic and crambe mixed dicarboxylic acids [poly(propylene "crambate")]. Numbers in parentheses are predetermined degrees of polymerization. Data on tricresyl phosphate (TCP), bis(2-ethylhexyl) phthalate (DOP), bis(2-ethylhexyl) azelate (DOZ), and monomeric brassylates are from ref. 16.

Evaluation of Sheets

Table II lists properties of test sheets containing polymeric plasticizers, as specified correspondingly in Table I. The 16 polyesters that gave good sample films were all compatible with PVC at the 32% level and, except for the p-toluenesulfonic acid-catalyzed product (Table II, no. 3), showed no exudation after 3 months.

One of the authors (G.R. Riser) earlier suggested that the compatibility number is useful in characterizing monomeric ester plasticizers (16). Figure 1 compares oligomeric esters from brassylic acid and mixed crambe dicarboxylic acids ("crambate") with monomeric and polymeric esters in terms of compatibility number. Data on tricresyl phosphate, DOP, and bis(2-ethylhexyl) azelate as standards and monomeric brassylates for comparison are from previous work by Riser and Palm (16). In this plot, simple esters of brassylic acid fall to the left of the line and are more compatible than standards that impart comparable flex temperatures. The oligomeric esters made for these studies and a commercial polymeric plasticizer fall to the right of the line, but most of them are more permanent than DOP from migration and volatility loss data (Table II). Certain poly(propylene brassylates) (Table II, nos. 1, 2, and 5) and poly(propylene crambates) (Table II, nos. 8, 10, and 11) show a decrease in compatibility number; i.e., compatibility improves with increasing degree of polymerization. Concomitantly, migration and volatility losses for these same materials decrease to values better than those for either DOP or the commercial polymeric plasticizer. Compatibility numbers for the polyesters, however, were equal to or higher than those for the reference materials. Comparison of polyester plasticizers in a series via compatibility numbers appears promising, but properties due to polymeric structures complicate direct comparisons of different structural types.

We are unable to correlate properties of the PVC sheets with acid and hydroxyl values, as have Rushton and Salomons (21), but we suspect that COOH and OH containing polyesters, though small in quantity, contributed to the higher compatibility numbers through their different functionalities and higher mp.

The performance of plasticizers derived from adipic (C_6), azelaic (C_9), sebacic (C_{10}), and brassylic (C_{13}) acids, with a predetermined n of 5 (i.e., in Table II, nos. 16, 14, 12, and 2, respectively) reveals the effect of dicarboxylic acid chain length upon properties. As the dicarboxylic acid chain length increased, so also did the compatibility number (25, 28, 33, and 34), contrary to expectations from calculations according to Fedors (17). Flex temperatures (-15, -19, -21, and -21) decreased but not as much in going from C_{10}-C_{13} as would be projected (-5 C) from data of Brice, et al. (13). Interestingly, the poly(propylene "crambate") (Table II, no. 10), a mixture of C_9 and C_{13} acid polyesters, imparted a lower flex temperature than polyesters based upon either C_9 or C_{13} acids. Such synergism was not predicted from theoretical considerations (17) but might have been expected from general knowledge of freezing point depression. This beneficial effect of the crambe acid mixture was not observed in other properties. Tensile strengths decreased with increasing acid chain length for n = 5. However, at least two properties, 100% modulus (1675, 1635, 1525, and 1650) and, to a lesser extent, migration loss (2.2, 2.9, 3.7, and 3.3), showed trends that reversed unexpectedly in going beyond the C_{10} dicarboxylic acid.

Mechanical properties of sheets plasticized with polyesters terminated by 5-phenyl valeric or pelargonic acids were not substantially different from those of sheets containing lauric acid-terminated ester (Table II, no. 4 vs. no. 3; no. 6 vs. no. 5; no. 9 vs. no. 8). Dodecyl alcohol-terminated poly(propylene brassylate) was not evaluated, because it was semisolid and apparently incompatible with PVC. These characteristics may have been due to residual dodecyl alcohol or the inherent properties of the polyester.

With similar lauric acid-terminated poly(propylene brassylates) (Table II, nos. 1, 2, 5, and 7), migration and volatility losses diminished as mol wt increased, and, in the same series, tensile strength and 100% modulus rose to maxima at n = 10 and then decreased. Polyesters from the crambe mixed dicarboxylic acids behaved similarly.

At least one of the brassylic acid polyesters (Table II, no. 5) imparted excellent properties to plasticized PVC, being more permanent in this evaluation then either comparison material and contributing excellent heat stability. The results indicate that similar polyesters derivable from crambe oil have good potential as plasticizers for PVC.

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