Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Gidanian, K. and Howard, G. J.(1976) 'Production of Polymers from the Seed Oil of *Crambe Abyssinica*. II. PVC Plasticizers Based on Tridecanedioic (Brassylic) Acid', Journal of Macromolecular Science, Part A, 10: 7, 1399 — 1414

To link to this Article: DOI: 10.1080/00222337608060760

URL: http://dx.doi.org/10.1080/00222337608060760

J. MACROMOL. SCI.–CHEM., A10(7), pp. 1399-1414 (1976)

Production of Polymers from the Seed Oil of *Crambe Abyssinica*. II. PVC Plasticizers Based on Tridecanedioic (Brassylic) Acid

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ABSTRACT

Brassylic acid obtained from crambe oil has been used to make linear polyesters by condensation with 1,3-butandiol; other polyesters were synthesized for comparison purposes. Number-average molecular weights were determined from the saponification equivalent and by vapor-phase osmometry; viscosity measurements are also reported. These polymers, together with comparison materials, have been evaluated as plasticizers for poly(vinyl chloride). The poly(butan brassylates) give plasticized PVC having good mechanical properties at room temperature and, except for extraction with hydrocarbon, with low migration of plasticizer and which are particularly good in retaining flexibility at low temperatures.

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INTRODUCTION

The utilization of tridecanedioic (brassylic) acid, derived from the seed oil of Crambe abyssinica, as the basis of PVC plasticizers has been reported by previous workers. Thus, a series of brassylic diesters were prepared and evaluated [1, 2] as plasticizers for vinyl chloride resins. Esters from the mixed dibasic acids from crambe oil, that is, of a mixture of brassylic and azeleic acids, have also been so evalutated [3] as have some N,N-disubstituted amides [4]. However, in certain applications, monomeric plasticizers are not fully suitable because of the tendency to migrate from the poly(vinyl chloride). Polyesters of low molecular weight have therefore been developed for more permanently plasticized resins [5]. In this report we describe the preparation and performance of some linear aliphatic polyesters based on brassylic acid.

EXPERIMENTAL RESULTS

Preparation of Polyesters

A series of polyesters was synthesized by condensation of 1,3-butandiol with brassylic acid; the latter was obtained from crambe oil as described previously [6]. For the purposes of comparison, poly(1,2-propan brassylate), poly(1,3-butan adipate), and poly(1,3-butan sebacate) were also made. Dodecanoic (lauric) acid was used as chain terminator in all the preparations. Diols were purified by refluxing over sodium prior to fractional distallation; other reagents were used as received. A two-stage polycondensation technique was used; stage one is a direct esterification of the acids by excess diol, while in the second stage the stoichiometric excess of the glycol is removed by alcoholysis. First, the calculated amounts of monofunctional and difunctional acids together with approximately 2.2 times the theoretical content of the diol were placed in a reaction tube heated in a vapor bath. A slow stream of oxygen-free nitrogen was passed through the mixture and as the temperature approached 140° C, tetrabutyl orthotitanate, 0.2% on the weight of the carboxylic acids, was added as catalyst. After 16 hr at 140° C the reaction tube was transferred to a second vapor bath, operating at 170° C, and a vacuum of approximately 0.1 Torr applied. The progress of this alcoholysis was followed by monitoring the glycol distillate. The progress of one reaction which was followed in detail by taking samples at intervals and measuring their acid numbers and viscosities (25° C) is shown in Fig. 1.

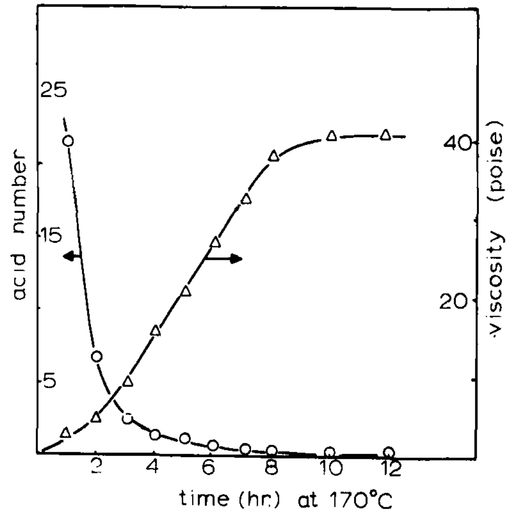

FIG. 1. Alcoholysis stage in formation of laurate-terminated poly(butan brassylate): (o) acid number; (△) viscosity.

The final average molecular weight of the polyester is largely determined by the charge of monofunctional acid and at high extents of reaction the polyester may be represented as

$$L - G - [A - G]_m - L$$

where A represents the difunctional acid moiety, G the diol, and L, lauric acid. In the limit of complete reaction

$$m = 2N^\circ_A/N^\circ_L \tag{1}$$

where N°_A and N°_L are the initial molar contents of difunctional and monofunctional acids, respectively [5]. Koroly and Beavers [5] studied the formation of linear polyesters in detail and showed that under conditions such as used here the content of free hydroxyl groups is extremely small but that there remained a small, but finite, content of acid end groups; that is, that the chain given above is an idealized one. Assuming that the extent of reaction of hydroxyl groups is unity, the number-average degree of polymerization $\bar{x}_n$ as conventionally defined [7] is given by

$$\bar{x}_n = 2[N^\circ_A(1 + P_A) + N^\circ_L]/[N^\circ_A(1 - P_A) + N^\circ_L] \qquad (2)$$

where P_A is the extent of reaction of acid groups. Equation (1) is adequate for the purpose of calculating the quantities of monomers to be used in polyester preparation. Koroly and Beavers [5] also showed that the number-average molecular weights of terminated polyesters could be estimated by determination of the alkali consumed in complete hydrolysis of the polymer and they defined the saponification equivalent S as the mass of polyester that requires one mole of alkali for hydrolysis. In terms of the idealized polyester structure given above

$$m = (M_{LGL} - 2S)/(2S - M_{AG}) \qquad (3)$$

where M_{LGL} is the molecular weight of the diester formed between the glycol and the monofunctional acid and M_{AG} is the molecular weight of the AG repeat unit. Although in a typical example the amount of alkali consumed in ester hydrolysis is some 200 times that required to neutralize the small number of acid end groups, it has to be appreciated that the number-average molecular weights calculated from Eq. (3) are very sensitive to errors in the value of the saponification equivalent; thus in the mid-range of the series of poly(butan brassylates) an error of ±1% in the saponification equivalent leads to ±9% uncertainty in $\bar{M}_n$. Molecular weights were also found by vapor-phase osmometry (Mechrolab 301A) in toluene at 65°C. Details of the polyesters are given in Table 1; all are lauric acid-terminated, and the formulation $\bar{M}_n$ is that calculated from Eq. (1).

Considering the errors in determination of number-average molecular weights, the two experimental methods are in reasonable accord. All the PBB samples were liquids at room temperature and their viscosities were measured in a cone-and-plate viscometer (Shirley-Ferranti) and were found to be Newtonian. The PBB data fit the empirical equation:

$$\log \eta = A + B\bar{M}_w^{1/2} \qquad (4)$$

first proposed by Flory [8]; the weight-average molecular weight is taken to be twice the number-average value (most probable distribution),

TABLE 1. Laurate-Terminated Polyesters

Polymer code[a]	$\overline{M}_n$ (formulation)	$\overline{M}_n$ (saponification)	$\overline{M}_n$(VPO)[b]	Acid number[c]	Viscosity (poise)[d]
PBB-1	2240	2210	1570	1.9	–
PBB-2	1650	1570	1370	1.9	11.5
PBB-3	3430	2910	2820	1.2	95.5
PBB-4	1050	1070	1040	0.8	4.5
PBB-5	–	1790	1510	0.8	20.0
PBB-6	2420	2430	2420	0.7	78.5
PBB-7	2240	2340	2160	0.4	52.0
PBB-8	1280	–	1030	1.2	–
PPB	1860	–	1900	–	e
PBA	2050	2020	2410	1.5	40.0
PBS	2250	2270	1750	1.2	65.0

[a] Polymer code: PBB, poly(1,3-butan brassylate); PPB, poly(1,2-propan brassylate); PBA, poly(1,3-butan adipate); PBS poly(1,3-butan sebacate).

[b] In toluene, 65° C.

[c] As mg KOH to neutralize 1 g polymer.

[d] At 25° C.

[e] Not determined as in solid.

and the best fit is with A = -1.386 and B = 0.044, if the saponification values are used.

Evaluation as Plasticizers

The following procedure was adopted to evaluate the polyesters as plasticizers for poly(vinyl chloride). A single batch of high molecular weight poly(vinyl chloride) in powder form (Breon 121) was used after drying in a vacuum oven at 50° C. A 100-g portion was added to 50 g polyester and 4 g of proprietary stabilizer (Lankro Mark KCB), and the whole mixed for 30 min at ambient temperature in a Brabender

Plastograph fitted with a Z-blade mixing head. The paste was heated in an oven at 180°C for 10 min and then press-molded in a three-plate mold (160 × 100 × 1.6 mm) for a further 5 min at 180°C and approximately 100 kg/cm^2. The platens were cooled to approximately 40°C before the pressure was released and the mold opened. All measurements reported are on sheets so prepared. These conditions were selected after the following preliminary tests. First, the so-called gel temperature was found by a standard method [9]: a 5% suspension of resin particles in plasticizer was made, and a drop placed on the stage of a hot-stage microscope (Kofler). The temperature at which the turbidity disappears is taken as the gel temperature, and the mean value of several determinations is reported (Table 2).

Gelation conditions must satisfy the requirements of the PBB plasticizers and thus be in excess of 160°C. Two further sets of measurements were therefore undertaken. In the first the PPB plastisol paste was pressed at 100 kg/cm^2 for 25 min at various temperatures and the (room temperature) tensile strength of test pieces then determined; the data indicate 180°C as an adequate processing temperature with minimum danger of thermal breakdown (Fig. 2). A second set of experiments was made in which the plasticsol was heated at 180°C for 10 min before being pressed at 180°C and 100 kg/cm^2 for various times; the tensile strengths and elongations to break of pre-cut test pieces were measured and are shown in Fig. 3. Hence, the standard process time of 5 min was judged to be adequate.

TABLE 2. Gel Temperatures of PVC/Polyesters

Polymer code	Gel temperature (°C)
PBB	158-160
PBS	146-148
PBA	136
PPB	153
Hexaplas LMV[a]	149-151
Hexaplas PLA[a]	143-144
Hexaplas PPL[a]	140

[a] Commercial materials (ICI) described as modified poly(propan adipates) (PPA).

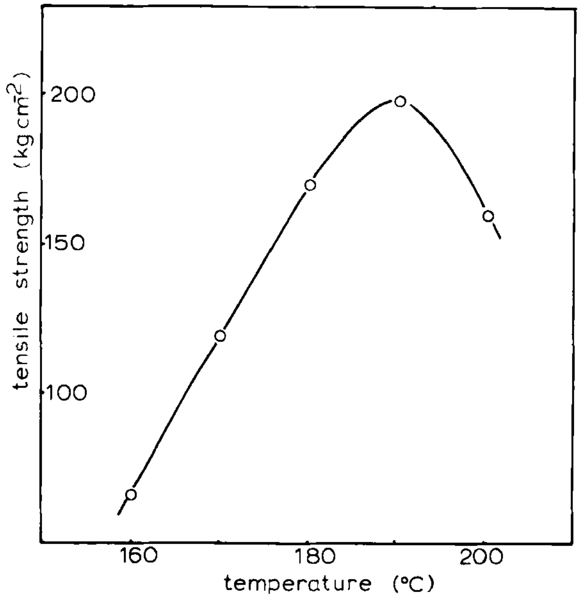

FIG. 2. Effect of fusion temperature on tensile strength of PBB-plasticized PVC.

Mechanical properties of the standard sheets of plasticized poly(vinyl chloride) were determined after equilibration at 20° C and 50% R H for one day. Dumbbell test pieces (the dimensions of which are given in Fig. 4) were die-cut and their tensile strength, ultimate elongation, and 100% modulus found on an Instron tensile tester operating at a jaw separation of 20 mm/min following the procedure of ASTM D412-68. Four specimens were taken and the results quoted (Table 3) are of the mean and 95% confidence limits.

Low-temperature behavior was assessed by the rigidity modulus at a range of temperatures (-60 to +15° C) by the method of Clash and Berg [10]. These results are shown in Fig. 5 and are summarized by the T_f value, at which the apparent shear modulus is 3160 kg/cm^2, and by T_g, the temperature of maximum slope. All the mechanical property results are given in Table 3, which also includes data from a sheet plasticized with a monomeric ester (di-2-ethylhexyl phthalate).

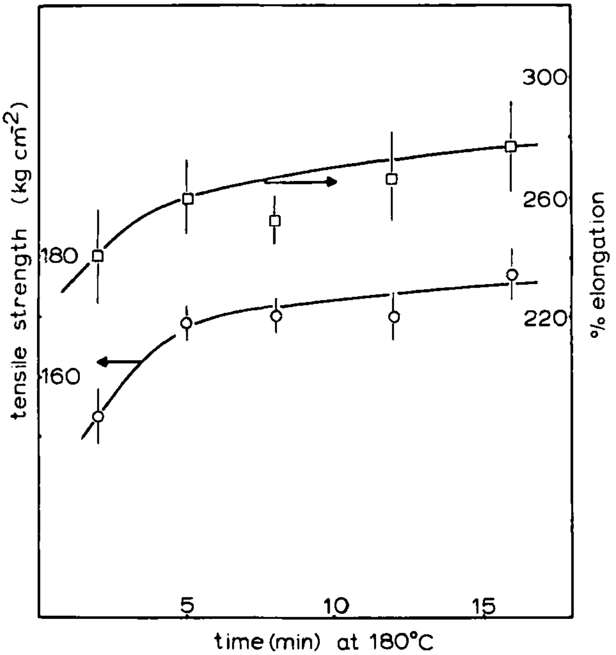

FIG. 3. Effect of time in press (180° C, 100 kg/cm^2) on (○) tensile strength and (□) elongation to break of PBB-plasticized PVC.

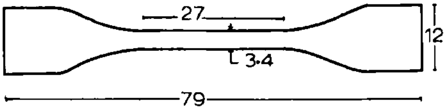

FIG. 4. Tensile test piece. Dimensions in mm.

Migration studies were made by bringing portions of the molded sheet (ca. 50 × 20 × 1.6 mm) into contact with a series of liquids and noting the percent weight loss after the conditions detailed: 75/25 (v/v) mixture of isooctane and toluene, 7 days at room temperature; water, 7 days at 70° C; 1% detergent (Tide) solution, 24 hr at 60° C.

TABLE 3. Properties of Plasticized Poly(vinyl Chloride)

Plasticizer	Viscosity (poise)[a]	Ultimate tensile strength (kg/cm^2)	Elongation at break (%)	100% Modulus (kg/cm^2)	T_f (°C)	T_g (°C)
PBB-6	78.5	177 ± 21	271 ± 19	98 ± 16	-26	
PBB-7	52.0	198 ± 10	287 ± 23	107 ± 2	-26	-39
PBB-5	20.0	204 ± 10	302 ± 40	102 ± 5	-25	-40
PBB-2	11.5	171 ± 11	268 ± 6	96 ± 8	-26	
PBB-4	4.5	182 ± 14	280 ± 21	102 ± 5	-26	
PPB	–	164 ± 11	236 ± 20	104 ± 2	-14	-27
PBS	65.0	197 ± 10	326 ± 18	92 ± 4	-22	-33
PBA	40.0	210 ± 20	316 ± 14	91 ± 1	-13	-17
Hexaplas PLA	35.0	245 ± 8	318 ± 13	105 ± 8	-13	-20
Hexaplas LMV	25.0	224 ± 9	319 ± 2	102 ± 6	-12	-25
Hexaplas PPL	8.0	207 ± 30	326 ± 28	93 [illegible] 6	-18	-29
DOP	0.55	187 ± 7	313 ± 5	80 ± 2	-34	-49

[a] At 25° C.

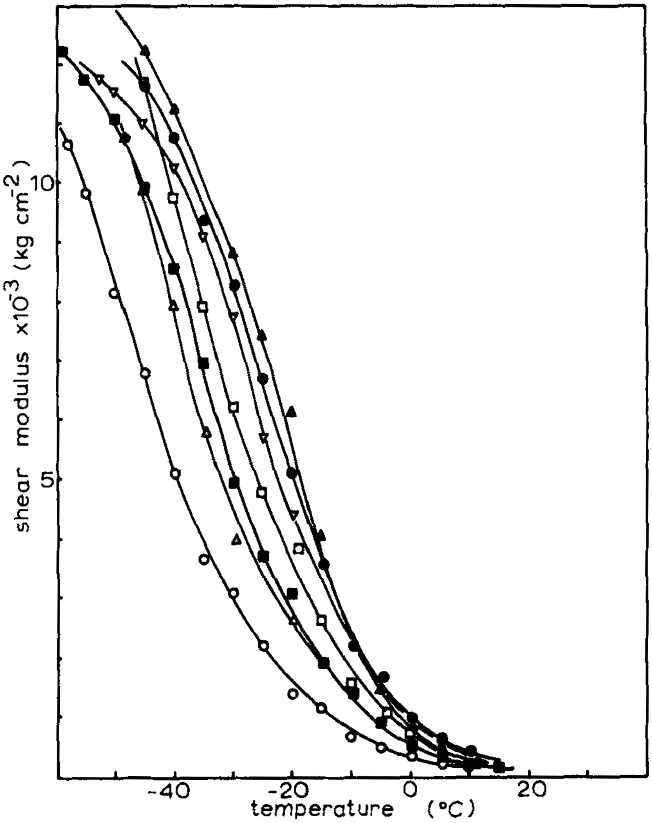

FIG. 5. Low-temperature flexibility of plasticized PVC: (▲) PBA; (●) Hexaplas LMV; (▽) PPB; (□) Hexaplas PPL; (■) PBS; (△) PBB; (○) DOP.

A test portion of 10^{4}mm^2 surface was placed in contact with a similarly sized sheet of neoprene rubber and the pair clamped between aluminum plates. The migration, as percent weight loss, was measured after 7 days at 70° C. The loss on heating the standard sheet after 7 days at 100° C in an oven with a forced air draught is also recorded (Table 4); most of the volatiles loss occurs during the first three days heating (see Fig. 6) except in the case of the DOP plasticizer.

TABLE 4. Migration Studies with Plasticized Poly(vinyl Chloride)

	Weight loss (%)				
Plasticizer	Isooctane/toluene[a]	Water[b]	1% Detergent[c]	Neoprene[d]	Air flow[e]
PBB-6	13.0	–	1.3	–	2.8
PBB-7	13.8	1.4	1.6	4.8	3.0
PBB-5	15.8	1.5	1.9	–	3.0
PBB-2	18.7	–	1.6	–	3.4
PBB-4	18.7	–	2.6	–	3.6
PPB	12.4	–	2.3	–	2.9
PBS	8.6	1.0	1.7	4.4	3.0
PBA	3.0	1.2	1.5	3.0	2.9
Hexaplas PLA	2.7	1.5	1.8	–	3.3
Hexaplas LMV	0.3	2.2	2.0	2.5	3.2
Hexaplas PPL	8.5	2.3	2.7	5.3	3.8
DOP	19.7	1.2	2.5	6.9	5.6
Unplasticized control	–	–	–	–	2.0

[a] For 7 days, room temperature
[b] For 7 days, 70° C.
[c] For 1 day, 60° C.
[d] For 7 days, 70° C.
[e] For 7 days, 100° C.

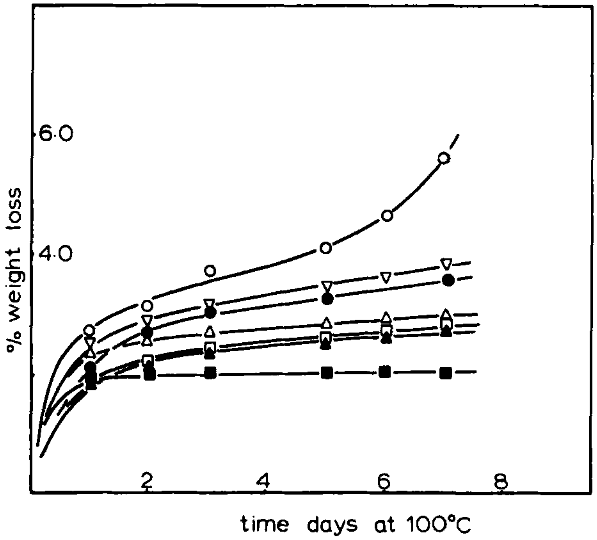

FIG. 6. Volatile loss of plasticized PVC at 100 C: (○) DOP; (▽)Hexaplas PPL; (●) PBB-4; (△) PBB-2; (□) PBB-7; (▲) PBB-6; (■) unplasticized PVC.

DISCUSSION

The mixing of dissimilar polymers is dominated by the enthalpy of mixing since the entropic contribution is small [11]; even in the present case, where the plasticizing polyester is only of low molecular weight, a slightly positive enthalpy of mixing would be sufficient to cause immiscibility. A common method of assessing compatibility in polymer systems is to apply the solubility parameter concept of Hildebrand [12]; in the absence of specific interaction effects the smaller the difference in solubility parameter between polymer and plasticizer, the greater their intrinsic compatibility. The molar attraction constants of both Small [13] and Hoy [4] were calculated for the repeat units of the plasticizers as were their molar volumes, also by a group contribution method [15], to give the mean solubility parameters listed in Table 5; as the experimental values quoted [15] for poly(vinyl chloride) are scattered the calculated value of 9.5_6 was assumed.

TABLE 5. Solubility Parameters δ

Plasticizer	δ ($\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$)	$\Delta\delta$[a]
PBB	8.77	0.78
PPB	8.82	0.73
PBS	8.92	0.63
PBA	9.24	0.31
PPA[b]	9.36	0.19
DOP	7.9[c]	1.65

[a] Difference between solubility parameters of plasticizer and polymer.
[b] Poly(propan adipate).
[c] Experimental [15].

As the exact composition of the commercial polyester plasticizers is not known, the solubility parameter quoted in Table 5 for PPA may be a poor estimate for all or any of the three samples. The four polyesters synthesized in the present work fall into a pattern in which the higher the chain ester content the closer is the solubility parameter to that of poly(vinyl chloride); further, this solubility parameter difference is related to the gelation temperature (Table 2).

Migration will be determined both by the compatibility between plasticizer and resin, and by that between plasticizer and outside environment, as well as by the mobility of the plasticizer. Thus, the general level of extractibility by the hydrocarbon is determined by the solubility parameter of the plasticizer relative to that of the poly(vinyl chloride) (9.55) and the extracting fluid (approximately 7.9). Among the PBB series, the migration into hydrocarbon is in the inverse order of the average molecular weight of the polyester; preferentially it will be the lower molecular weight species of the polyester that are lost, as found by Rushton and Salmons [17]. The variation within the Hexaplas series suggests that these commercial materials differ in chemical structure as well as in viscosity. Major variation among the plasticizers is not shown for migration into aqueous systems. Brice and co-workers [18] found that, in a series of polyesters extending from the succinate to the sebacate, the water and aqueous detergent extraction decreased as the carbon chain of the diacid moiety was lengthened. The brassylate polyesters are as least as good as the commercial materials in this test. Migration into neoprene, which has a (calculated) solubility parameter of 9.3 $cal^{1/2}/cm^{3/2}$, is relatively high, but the differences between the polyesters do not seem explicable on compatibility arguments. Volatilization of plasticizer species in an oven at 100° C is, among the PBB series, a function of molecular size, but there is little distinction among polyester chain structures. In this test, as in migration to neoprene, the simple diester plasticizer is noticeably poorer.

The mechanical properties (tensile strength, elongation to break, and 100% modulus) of the poly(butan brassylates) are, at the 95% confidence level, independent of the polyester molecular weight. This is in contrast to the tensile behavior of poly(vinyl chloride), sheets which incorporate monomeric plasticizers, where, in some cases at least, there is a relationship with molecular size [19]. The ultimate tensile strength of the PBB-plasticized resin is about the same as that containing dioctyl phthalate, but the latter is rather more extensible and less stiff. Indeed PBB and PPB give less extensible specimens than any of the other plasticizers although, apart from the diester, all give values of the 100% modulus which are not significantly different (at the 95% level) from each other. The largest differences are in the tensile strengths where the PBB and PPB plasticizers impart a lower ultimate strength to the PVC sheets than any of the other polyesters. The three commercial polyesters (Hexaplas), whose tensile strengths are significantly different from each other, are particularly good at providing high strength sheets, especially the higher viscosity samples.

The low-temperature behavior of plasticized PVC is affected by the transition temperature of the plasticizer itself and it is noticeable that the poly(propan brassylate), which is solid at room temperature, is not particularly good in this respect and behaves similarly to the modified poly(propan adipates) (Hexaplas). The transition and flex temperatures (Table 3) of PVC plasticized with polyesters based on 1,3-butandiol depend strongly on the spacing of the chain ester groups; the brassylates have very good low-temperature properties, being the best of all the polyesters studied, although still inferior to dioctyl phthalate. These transition temperatures do not depend on the molecular weight of the PBB which suggests that the plasticizing efficiency relates to chain-segment flexibility and not to molecular motion of the polyester chain as a whole. Riser and Palm [20] relate the shape of the modulus–temperature curve to the resin–plasticizer compatibility, the sharper the fall in modulus through the transition range, the better the interaction between plasticizer and polymer. Our data for T_f and T_g (Table 3) fit in well with this concept if the solubility parameter differences (Table 5) are taken as the measure of compatibility.

CONCLUSIONS

Brassylic acid from crambe oil has been polycondensed with 1,2-propandiol and with 1,3 butandiol. The polyesters so produced have been assessed as plasticizers for poly(vinyl chloride) by comparison against other polyesters, including some commercial samples. The poly(propan brassylate), which is solid at room temperature, is an undistinguished plasticizer but the poly(butan brassylates), especially those of higher viscosity, give plasticized compounds that have very adequate mechanical properties at ambient temperatures, adequate resistance to migration or extraction in most environments, and very good low-temperature flexibility; their major defect is in their poor resistance to a hydrocarbon liquid.

ACKNOWLEDGEMENTS

We are indebted to Dr. M. M. Neenan of the Irish Agricultural Institute for his interest and encouragement. One of us (K. G.) was in receipt of a scholarship awarded by the Iranian Ministry for Higher Education during the period of the work (1970-73). We acknowledge also the gift of representative polyester plasticizers by ICI Ltd.

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Accepted by editor December 4, 1975
Received for publication December 22, 1975