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## **Production of Polymers from the Seed Oil of Crambe Abyssinica. III. Polyurethane Elastomers Based on Tridecanedioic (Brassylic) Acid**

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### ABSTRACT

A series of predominately hydroxyl-ended polyesters were made from tridecanedioic acid derived from crambe oil. Comparison materials with sebacic and adipic acids were also prepared. Suitable polyesters were converted into polyurethane elastomers by chain extension and cross-linking with a diisocyanate and further diol. Polyesters based on ethandiol were unsuitable for the production of flexible urethanes as a slow crystallization occurred on standing; this did not happen when mixed ethane- and propan-diols were employed in polyesterification. Polyurethanes based on diphenylmethane diisocyanate are stronger than those made with the mixed isomers of toluene diisocyanate. Polyurethane networks based on brassylic acid have a lower

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polymer-solvent interaction parameter against tetrahydrofuran than those from sebacic acid.

## INTRODUCTION

The preparation of elastomers by the reaction of diisocyanates with preformed hydroxyl-ended, polymers has developed into an important industrial synthesis. For the present work, it was decided to use brassylic acid, itself obtained from crambe oil as described earlier [1], as a component of linear polyesters which were then evaluated as precursors for polyurethane elastomers. Polyesterification by reaction of a dibasic acid with excess diol starts as a direct esterification but polymer growth is continued by elimination of the excess glycol by alcoholysis. Careful control over the polyesterification is necessary to obtain a product with terminal hydroxyl as is required for polyurethane formation. An excess of diisocyanate is added to the hydroxyl-terminated polyester to yield an isocyanate-ended extended chain polymer; this is then reacted with a diol (or diamine) for further chain extension but under circumstances such that some isocyanates are left unreacted. These, under the influence of heat in the final stage of reaction, form the network by their attack on chain urethane links to give trifunctional allophanate groups.

## EXPERIMENTAL RESULTS

Ethylene glycol was treated with sodium metal, refluxed under a stream of nitrogen, and then distilled. Toluene diisocyanate (mixed esters) was distilled under nitrogen, while diphenylmethane diisocyanate was recrystallized from dry hexane. Brassylic acid was obtained from crambe oil [1], and other materials were purified as before [2].

Polyesters were prepared by the general procedure given previously [2], but with an initial molar ratio of total diol to diacid of 2.5. This excess was chosen so as to ensure that the resulting polyesters were largely hydroxyl-ended; the recommended [3] minimum hydroxyl-to-carboxyl ratio for successful chain extension with diisocyanates is 12:1. The following polyesters were synthesized: poly(ethan brassylate) (PEB), poly(ethan-co-propan brassylate) (PEPB), poly(ethan-co-propan sebacate) (PEPS), poly(ethan-co-propan adipate) (PEPA), and poly(ethan adipate) (PEA). When mixed

diols were used, the ethandiol: propan-1,2-diol molar ratio was 3:2; the polyesters had number-average molecular weights in the range 1000-5000.

Unlike the terminated polyesters studied previously [2], these preparations were more difficult to control in respect of the molecular weight of the product. The first stage of reaction was made at 140° C for 16 hr with p-toluenesulfonic acid (0.1-0.2% on total reaction mass) as esterification catalyst. The ester interchange stage was conducted at 170° C/0.1-0.2 Torr with tetra-n-butyl orthotitanate as catalyst; this stage was concluded after the reaction time judged, on the basis of preliminary experiments, to give the required product molecular weight. The hydroxyl content of the polymer was found by refluxing a known mass in a 5% solution of acetic anhydride in dry pyridine for 3 hr, after which the contents were titrated against alcoholic potassium hydroxide to a phenolphthalein endpoint. The acid end-group content was found by dissolving a sample of polymer in ethanol-benzene (1:3) and titrating with alcoholic potassium hydroxide; corrections are made for the acid catalyst. The polyesters made are listed in Table 1.

Although the time of alcoholysis gives a rough measure of the extent of polymerization, there are numerous exceptions; furthermore, a considerable proportion of the samples are relatively high in acid endgroups and do not meet the specification that  $[OH]/[COOH] > 12$ .

Polyurethanes were made from those polyesters which passed the above specification. The procedure was to dehydrate a known quantity of polyester under a stream of dry nitrogen at 130° C for 1-2 hr. A quantity of diisocyanate such as to give a  $[NCO]/[OH]$  ratio of 3:2 was added with mechanical stirring over a period of 30-60 min; the catalyst (a mixture of equal amounts of dibutyltin dilaurate and triethylenediamine, each 0.25% of the final polymer) was added immediately before the diisocyanate. To this prepolymer was then added butan-1,4-diol as chain extender so that the overall molar formulation was polyester 1.0/diisocyanate 3.2/diol 2.0. Polymerization was now very rapid, as judged by the increase in viscosity of the mixture, and solid polymer was soon formed as a mass of crumbs. This product was press-cured at 155° C at approximately 100 kg/cm<sup>2</sup> for 20 min in a PTFE-coated mold to give a sheet 1.6 mm thick, and the molding was postcured overnight in an oven at 100° C. This procedure ought to produce networks of identical molar crosslink content if reaction is complete and takes place without loss of functional groups by side reactions. The formulation does not, of course, represent the optimum balance of reactants for the best physical properties of a particular polyester diisocyanate combination.

Networks made from poly(ethan brassylate) with both toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) were hard and became brittle after standing for a few weeks at room

TABLE 1. Polyesters

Polymer code	Reaction time (min) <sup>a</sup>	$\bar{M}_n^b$	Hydroxyl number (mg KOH/g polymer)	Acid number (mg KOH/g polymer)	[OH]	
					[COOH]	
PEPB-1	120	1960	52.0	4.8	10.8	
PEPB-2	90	1820	54.5	7.3	7.5	
PEPB-3	60	1550	70.5	2.1	33.6	
PEPB-4	45	1310	83.0	2.7	30.7	
PEPB-5	120	1250	87.0	2.7	32.2	
PEPB-6	90 <sup>c</sup>	1540	73.0	0.1	730	
PEB-1	150	2930	38	0.4	95	
PEB-2	150	3310	31	2.9	10.7	
PEB-3	105	5820	17	2.3	7.4	
PEB-4	60	1210	82	11.0	7.5	
PEB-5	420 <sup>d</sup>	2890	34	4.8	7.1	
PEPS-1	150	5000	20	0.4	50	
PEPS-2	105	2360	46	1.6	29	
PEPS-3	90	1620	68	1.2	57	
PEPS-4	60 <sup>c</sup>	1830	61	0.4	153	
PEPA-1	90	1910	51	7.1	7.2	

PEPA-2	60 <sup>e</sup>	2980	36.5	1.1	3.3
PEA-1	120 <sup>f</sup>	1460	74	5.9	12.5

<sup>a</sup> Alcoholysis stage: at 170° C except where specified otherwise.

<sup>b</sup> End groups.

<sup>c</sup> Zinc chloride catalyst, 200° C.

<sup>d</sup> Antimony oxide/calcium acetate catalyst.

<sup>e</sup> 200° C.

<sup>f</sup> *p*-Toluenesulfonic acid only, 200° C.

TABLE 2. Polyester-Based Polyurethane Networks

Code	Density $\rho$ (g/cm <sup>3</sup> of dry network)	Volume fraction polymer $v_2^a$	Sol fraction
PEPB-4-TDI	1.140	0.278	0.024
PEPS-3-TDI	1.159	0.189	0.031
PEPB-3-TDI	—	0.175	0.070
PEB-4-MDI	—	0.156	0.110
PEB-4-TDI	1.173	0.116	0.310
PEPB-3-MDI	1.152	0.081	0.360
PEPS-3-MDI	1.173	—	—

<sup>a</sup>Volume fraction polymer in THF-swollen network.

temperature; this was attributed to a slow crystallization which was confirmed by inspection of the x-ray diffraction pattern. Of the elastomeric networks, two were selected on the basis of their mechanical properties (see later) for further study. These were PEPB-4-TDI and PEPS-3-TDI; both were based on polyesters with a very low acid end-group content and both gave x-ray diffractographs showing only an amorphous halo. The equilibrium swelling in tetrahydrofuran, and the sol fraction, of these and some other networks were measured; densities of dry networks were found by use of a density gradient column. These results are given as Table 2.

For the determination of mechanical properties, dumbbell test pieces (dimensions as previously reported [2]) were die cut from the molded sheets and tested at 20°C on an Instron Tensile testing machine at a crosshead speed of 5 mm/min. The distance between the bench marks was noted during extension in order to measure the strain. The extension remaining 10 min after rupture was found and is recorded as the percent set relative to the initial length. To measure the tear resistance of the elastomers rectangular test pieces 60 × 20 mm were punched from the sheet and were cut along the longitudinal axis for 25 mm from one end. These were then tested in the "trousers-leg" mode at a separation rate of 10 mm/min; the average load per unit initial thickness is taken as the measure of tear resistance.

The Flory-Huggins polymer-solvent interaction parameter may be found by combining the swelling data with the modulus in extension; for this, however, it is necessary to have some criterion to establish that the stress-strain data represent equilibrium behavior. Several methods have been discussed [4], and we have adapted the procedure of finding the exponent  $n$  in the equation

$$\alpha S = E\gamma^n \quad (1)$$

Here  $E$  is the modulus,  $S$  the stress referred to the initial cross-section,  $\alpha$  the extension ratio ( $l/l_0$ ), and  $\gamma$  the nominal strain [ $(l - l_0)/l_0$ ]. A value of  $n$  close to unity is taken as the criterion for equilibrium elastic behavior; the stress-strain data were analyzed by plotting  $\log \alpha S$  against  $\log \gamma$ .

Inspection of Tables 2 and 3 shows that only the samples of low sol fraction have an acceptably elastic behavior in tension and are thus suitable for study of network parameters; it will be seen that the two selected samples are also of low permanent set. Other samples, although having similar mechanical properties, show considerable nonreversible deformation. As this is associated with high sol contents, we conclude that the crosslinking was inefficient and did not permit the full development of network properties. Further, these samples which contain considerable amounts of non-network polymer exhibit a degree of viscous response on elongation that is exemplified by the low values of the exponent  $n$  of Eq. (1).

To combine the stress-strain data with equilibrium swelling the modulus was determined both by plotting  $\alpha S$  against  $\gamma$  and by plotting  $S$  against  $(\alpha - \alpha^{-2})$  as required by the statistical theory of rubber elasticity [6]; concordant results are found for  $\gamma < 1.0$  in accord with expectation [4]. The polymer-solvent interaction parameter  $\chi$  is found from the expression

$$\chi v_2^2 = \frac{EV_1}{3gRT} \left( \frac{2}{3} v_2 - g^{2/3} v_2^{1/3} \right) - v_2 - \ln(1 - v_2) \quad (2)$$

where  $g$  is the gel fraction of the network,  $V_1$  is the molar volume of the swelling liquid, and the other symbols are as defined before. Also given in Table 4 are the values of  $M_c$ , the effective molecular weight between trifunctional network junctions and the equivalent parameter  $\nu_e$  the number of effective chains (mole) per unit volume ( $\text{cm}^3$ ) of



TABLE 3. Mechanical Properties of Polyurethane Networks

Code	Tensile strength at break (kg/cm <sup>2</sup> ) <sup>a</sup>	Elongation at break (%) <sup>a</sup>	100% Modulus (kg/cm <sup>2</sup> ) <sup>2</sup>	Set (%)	Tear strength (kg/cm)	n [in Eq. (1)]
PEPB-4-TDI	167	236	28.5	2	9.3	0.98
PEPS-3-TDI	160	523	12.8	10	5.9	1.06
PEPB-3-TDI	163	298	39.5	22	30.3	0.41
PEB-4-MDI	242 <sup>b</sup>	222	108.6	55	—	—
PEB-4-TDI	172 <sup>b</sup>	300	45.5	33	—	—
PEPB-3-MDI	207	334	81.7	44	60	0.35
PEPS-3-MDI	293	231	61.2	48	23.2	—

<sup>a</sup>Mean of four determinations.<sup>b</sup>Measurements made before crystallization on storage had occurred.

TABLE 4. Network Parameters

Code	E (kg/ cm <sup>2</sup> )	Volume fraction v <sub>2</sub> <sup>a</sup>	χ	v <sub>e</sub>	M <sub>c</sub>	[U] (mole/ kg) <sup>b</sup>
PEPB-4-TDI	55.7	0.278	0.296	6.3 × 10 <sup>-4</sup>	1800	3.17
PEPS-3-TDI	25.3	0.189	0.200	3.4 × 10 <sup>-4</sup>	3400	2.84

<sup>a</sup>Volume fraction of polymer in network swollen to equilibrium in THF.

<sup>b</sup>Urethane group content (mole/kg) assuming full reaction of isocyanate groups.

network. These are obtained from the initial equilibrium modulus E by

$$E = 3\nu_e RT = 3\rho RT/M_c \quad (3)$$

## DISCUSSION

The polymer-solvent interaction parameters of Table 4 are in qualitative agreement with solubility parameter data. Thus the calculated solubility parameters of PEPB and PEPS are 8.87 and 9.06, respectively, whereas the value for tetrahydrofuran is 9.1 [7]. The greater swelling of the sebacate-derived elastomer is to be expected. Smith and Magnuson [4] have shown that, for polyether-based polyurethane networks,  $\chi_1$  is independent of crosslink density per se but increases with [U]. The contribution of the urethane group content is not known in the present case but the solubility parameters calculated for the full networks is very little different to those of the parent polyesters. A knowledge of  $\chi_1$  permits an approximate estimation of initial modulus to be made from equilibrium swelling data.

The general mechanical properties of polyurethane elastomers will be determined, not only by the crosslink density, but also by the extent of hydrogen bonding which may lead to some chain orientation and pseudocrystallization and may affect the extent of chain entanglement. The diisocyanate structure may play a major part in governing the orientation of network chains; polyurethanes based on MDI are generally stronger than those based upon TDI (see Table 3), and this fact

may be attributed to the greater interchain interactions permitted by the structurally symmetrical diisocyanate. Piggott [8] and co-workers have shown that the mechanical properties of polyurethanes are controlled by crosslink density in a different manner to those of hydrocarbon rubbers. With polyurethanes, an increased degree of chemical crosslinking may lead to weakening of the network, probably because of a reduction in the extent of interchain attraction. The limited series of elastomers prepared do not permit the comparison of polybrassylicates with polysebacates under equivalent network properties and it is not possible to tell whether the greater softness and flexibility anticipated for the former could be realized. However, the elastomers are, on the whole, of lower tensile strength and modulus than the polyurethane networks studied by Piggott et al. [8], which were of similar general composition except that the polyesters were based on either succinic or adipic acids. The changed solubility parameter of the elastomers based on brassylic acid might be advantageous in certain service environments.

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