

Synthesis and Investigation of Some Polyesterurethanes Based on Hydroxy Terminated Polyesters

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ABSTRACT. Hydroxy terminated polyesters were synthesized by the reaction of tetrabromophthalic, phthalic, and maleic anhydrides with polyethylene glycol via melt condensation technique. They were characterized by hydroxyl number and intrinsic viscosity measurements. Also, the fire retardancy of polyesters was reacted with excess toluene-2, 4-diisocyanate to yield isocyanate terminated prepolymers which were subsequently reacted with 5,5-dihydroxymethyl-2-trichloromethyl-1,3-dioxane or ethylene diamine. These polymers were characterized by IR and ^1H NMR spectra, viscosity measurements, and thermogravimetric analysis. A change of the electrical conductance of the compounds with increasing temperature is observed for the solid samples.

KEYWORDS: Synthesis polyesterurethanes, IR, ^1H NMR, Viscosity, TGA, DTA and Electrical conductance.

Introduction

Polyurethanes form a class of industrially useful materials because of their excellent properties. The polyurethanes are used in a wide variety of applications but relatively few isocyanates are employed commercially in their manufacture. The most important are the toluene diisocyanates (TDI), although other types are now being developed and adopted industrially. The initial studies on polyurethane synthesis were based on simple diisocyanates and diols but the main importance of the reaction is now concerned with the use of intermediates which are often themselves polymeric in character (polyesters, polyethers) and carry terminal groups (usually $-\text{OH}$ or NCO) capable of further reaction and thus of increasing the molecular size, often during the actual fabrication processing, by either chain extension, branching, or crosslinking.

One such method of preparing a polyurethane derivatives is first to prepare an isocyanate terminated prepolymer which is often reacted with diols^[1]; diamines^[2], and water^[3]. Hydroxy terminated polyesters^[4] are starting material for many of the urethane polymers. The polyesters were prepared by the melt condensation of glycols and dibasic acids of both aliphatic and aromatic type, or a mixture of both^[5].

The electrical conductivity of solid organic compounds is a property which is covered by a very wide range of studies^[6]. The enthusiasm for discovery and research of organic compounds which conduct the electric current owes to Mahmoud-El-Haty^[7] who speculated about the conducting properties of proteins. This plays an important role in the life process. Recently, polyesters were shown to have semiconducting properties in an attempt for their use in solar energy storage^[8]. In the present work some polyesterurethanes and polyesterurethaneureas were prepared by the reaction of isocyanate terminated prepolymers with 5,5-dihydroxymethyl-2-trichloro-methyl-1,3-dioxane and ethylene diamine respectively. In addition, the electrical conductance properties of the relevant compounds have been studied.

Experimental

Materials

Tetrabromophthalic anhydride (TBPA), phthalic anhydride (PA) maleic anhydride (MA) and polyethylene glycol (PEG) (Mwt., 400) were products of Aldrich Chemical Company. Toluene-2,4-diisocyanate (TDI) were used as supplied by British Drug Houses Chemicals, Ltd, England (BDH). 5,5-dihydroxymethyl-2-trichloromethyl-1,3-dioxane (HMCMD) was prepared according to the previous method^[9]. All solvents used were of A.R. equivalent grade.

Preparation of Hydroxy Terminated Polyesters

A mixture of TBPA (0.04: 0.10 mol), PA (0.00: 0.10 mol), MA (0.00: 0.10 mol) and PEG (0.25 mol) was heated in the presence of oxygen-free nitrogen for 2h at 180°C, for 2h at 200°C, then for a further 3h at 220°C to give a syrupy mass with an acid number less than one. The polyesters were purified twice by dissolving in chloroform and precipitating with light petroleum and then dried under reduced pressure.

Preparation of Polyesterurethanes and Polyesterurethane-Ureas

To a solution containing 0.1 equivalents of polyester in 40 ml dimethylformamide (DMF) and five drops of triethylamine as catalyst, 0.3 equivalents of TDI in 20 ml DMF were added at room temperature in N₂ atmosphere.

The reaction mixture was heated to 80°C with stirring for 1hr, followed by addition of 0.2 equivalents of 5,5-dihydroxymethyl-2-trichloromethyl-1,3-dioxane or ethylene diamine in the cases of polyesterurethanes and polyesterurethane-ureas respectively. Reaction was done at 120°C for 3h. The same reaction conditions were adopted for all polymerization to ensure the same amount of chain extension. The viscous solution was precipitated with water, filtered, washed with water, methanol and dried in a vacuum desiccator. The yield of polymers was 63-87 %.

Characterization of Polymers

The hydroxy and acid numbers of polyesters were determined by standard methods^[10].

Densities were measured by means of a pycnometer using hexane at 30°C. Viscosity measurements were carried out with an Ostwald viscometer using a 1% solution in dioxane and DMF for polyester resins and polyesterurethanes or polyesterurethane-ureas respectively.

Thermal Analysis

DTA was performed at a heating rate of 10°/min using a Shimadzu X-D-30 Thermal analyzer. TG Thermograms were obtained at a heating rate of 10°/min using a DT-30B. Thermal infrared spectra were recorded on a Shimadzu IR. 470 spectrophotometer in the range 4000-600 cm⁻¹.

The proton magnetic resonance spectra (in d6-dimethyl-sulfoxide as solvent and using TMS as zero reference) were obtained at room temperature with a Marian Gemini spectrometer operating at 200 MHz.

Preparation of Varnish Films

Plywood of dimensions 5" × 0.5" × 0.05" were varnished by dipping. The weight of the dried varnish film is equal to the weight of plywood strip. The strips are prepared for flammability test (ASTM D 635-56T, 1956).

Electrical Conductivity Measurements

These were carried out on some of the investigated polyesterurethane using a Super Megometer Electrometer Model RM 170. The samples had the form of discs of a diameter of 13 mm and a thickness 1 mm produced under a pressure of ~ 300 kg.cm². The cross section area of the pellets was covered with silver paste to eliminate as much as possible the contact resistance between the electrodes and the discs. The temperature was measured in air using a Ca-CuNi

thermocouple placed close to the sample. Measurements were carried out from room temperature up to 460 K and then on cooling down to room temperature. The electrical conductivity control was accurate to $\pm 0.3 \Omega^{-1} \cdot \text{cm}^{-1}$.

Results and Discussion

In the present work hydroxy terminated polyesters (I-VII) were prepared from the reaction of TBPA, PA and MA with PEG (Mwt: 400) at different molar ratios as illustrated in Table 1.

TABLE 1. Moles of components.

Polyester	TBPA	PA	MA	PEG
I	0.06	–	0.08	0.21
II	0.07	0.01	0.07	0.22
III	0.04	0.03	0.08	0.20
IV	0.06	0.08	–	0.21
V	0.07	0.06	0.01	0.20
VI	0.04	0.07	0.03	0.21
VII	0.02	0.08	0.04	0.20

The prepared hydroxy terminated polyesters (I-VII) shown in Figure (1a) were brown or amber yellow, viscous materials soluble in various organic solvents except alcohol, n-hexane, and light petroleum. These linear polyesters showed greater resistance to gelation and remained soluble after long storage periods. The yield, hydroxyl number and intrinsic viscosity of the prepared polyesters are summarized in Table 2.

TABLE 2. Physical characteristics of the hydroxy terminated polyesters (I-VII).

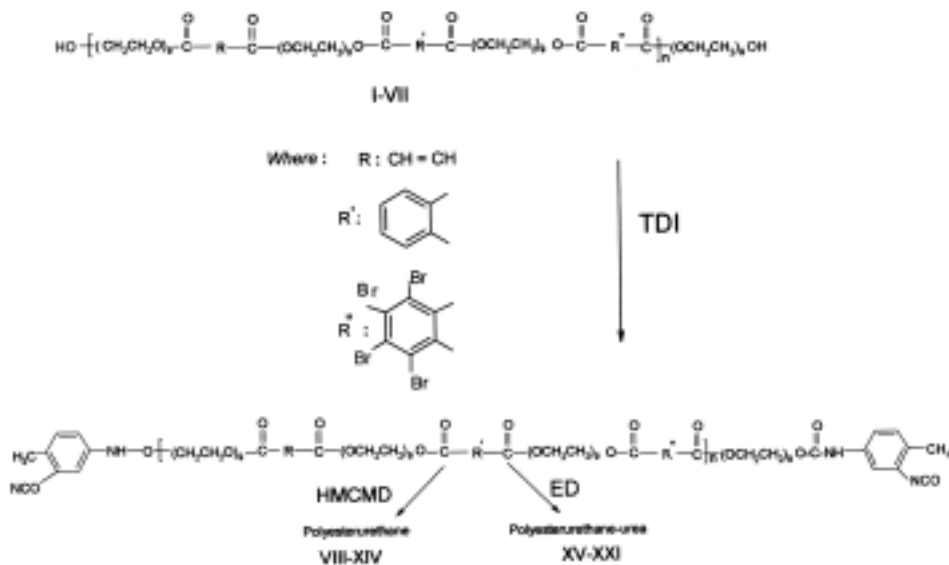
Polyester	Nature of polyester	Yield percentage	Hydroxyl value	η (dl/g)
I	Brown resin	93	67.28	0.019
II	Brown resin	81	57.97	0.003
III	Yellow resin	88	88.50	0.022
IV	Yellow resin	85	84.00	0.034
V	Yellow resin	90	74.21	0.029
VI	Yellow resin	87	80.00	0.048
VII	Yellow resin	88	68.00	0.013

Flamability test was used to evaluate the fire retardancy of polyesters (I-VII) as varnish films. Table 3 illustrates the time of burning of coated plywood strips. From Table 3, it is clear that the time of burning of coated plywood strips is greater than that of uncoated plywood strip. It is attributed to the presence of tetrabromophthalic moiety in polyester chain which act as fire retardant.

TABLE 3. Time of burning of polyesters (I-VII) as varnish films.

Polyester	Time/min
I	2.02
II	3.88
III	2.96
IV	2.57
V	3.57
VI	2.58
VII	1.89
Uncoated strip	0.57

The structures of polyesters (I-VII) were established by studying their IR and ¹H NMR spectra. The infrared spectra of the polymers showed characteristic absorption bands around 3400 cm⁻¹ (ν_{OH}), 1720 cm⁻¹ (ν_{C=O}), 1630 cm⁻¹ (ν_{C=C}) and intense absorption at 1100 cm⁻¹ (ν_{C-O}). Figure (1a) illustrates the IR spectra of polyester VI as example.



The ¹H NMR spectra of the hydroxy terminated polyesters showed bands at δ 7.2-8.0 due to the proton of phenyl and -CH=CH- groups; at δ 5.42 due to OH group; at δ 4.38 and δ 3.55 due to the protons of -CH₂OCO- and -CH₂OCH₂- groups respectively. Figure (1b) illustrates the ¹H NMR spectrum of polyester VI as example.

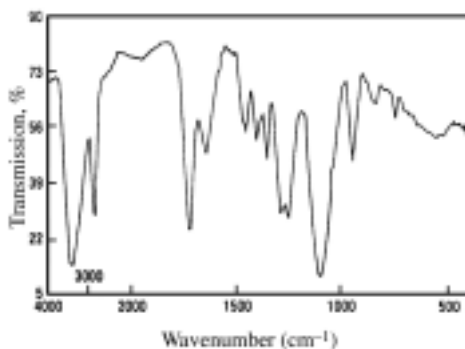
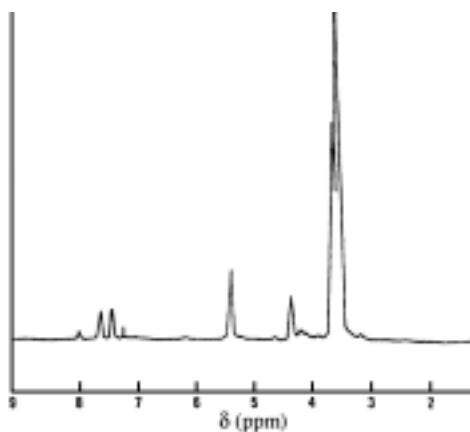


FIG. 1a. IR spectrum of polyester VI.

FIG. 1b. ¹H NMR spectrum of polyester VI.

The hydroxy terminated polyesters (I-VII) were used as starting materials for the preparation of some polyesterurethanes (VIII-XIV) and polyesterurethaneureas (XV-XXI).

The structures of the prepared polyesterurethanes and polyesterurethaneureas were established by studying their IR and ¹H NMR spectra. The infrared spectrum of the polyesterurethane (XIII) (Fig. 2a) showed characteristic absorption bands around 3300 cm⁻¹ (ν_{NH}) and an intense absorption band at 1100 cm⁻¹ ($\nu_{\text{C-O}}$). The carbonyl absorption appeared as three strong bands at 1720, 1600, 1530 cm⁻¹ for ester, amide I and amide II respectively.

The ¹H NMR spectra of the polyesterurethanes displayed bands at δ 6.9-9.2 due to protons of phenyl, CH=CH and NH groups; δ 4.2 due to protons of -CH₂OCO- group; δ 3.5 due to protons of -CH₂OCH₂- group; δ 2.2 due to

(IX) as example.

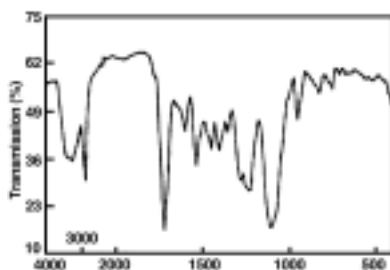


FIG. 2a. IR spectrum of polyesterurethane XIII.

protons of methyl group of TDI. Figure (2b) illustrates the ^1H NMR spectrum of polyesterurethane (IX) as example.

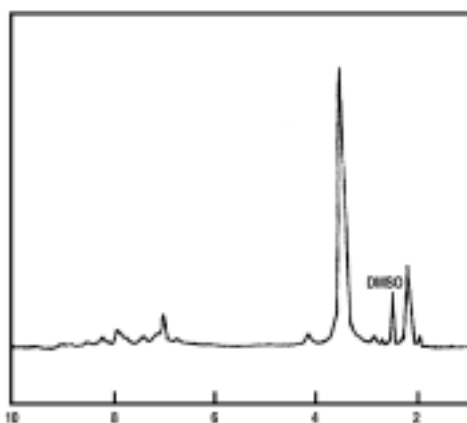


FIG. 2b. ^1H NMR spectrum of polyesterurethane IXI.

The intrinsic viscosities (η) of the polymers ranged from 0.089 to 0.344 dl/g when measured in DMF at 30°C. The densities of the polymers were in the range 0.993-1.20g/cm³. The values of yields, intrinsic viscosities, densities and some decomposition temperatures are given in Table 4.

Thermal analysis of some polyesterurethanes and polyesterurethane-ureas showed that the polymers were stable up to 300-349°C. TG and DTA curves of polymer (XXI) respectively as example. These high thermal stability values obtained for the prepared polyesterurethanes and polyesterurethane-ureas are in agreement with those reported^[11] for polyester based polyurethanes.

TABLE 4. Physical properties of polyesterurethanes and polyesterurethaneureas.

Polyester	Yield percentage	η (dl/g)	Density g/cm ³	Polymer decomposition temperature
VIII	80	0.321	1.150	–
IX	76	0.263	1.174	–
X	70	0.257	1.180	–
XI	61	0.296	1.050	300.25°C
XII	63	0.329	1.080	–
XIII	68	0.344	1.150	315.85°C
XIV	63	0.312	1.120	–
XV	83	0.268	1.172	–
XVI	80	0.287	1.085	–
XVII	85	0.254	0.993	–
XVIII	71	0.089	1.200	320.65°C
XIX	79	0.257	1.200	–
XX	68	0.298	1.159	–
XXI	82	0.288	1.120	348.96°C

Electrical Conductivity Measurements

The electrical conductivity was measured over a relatively moderate temperature range to avoid melting of the materials. Figures (3a,b) represent the variation of the electrical conductivity ($\log \sigma$) as a function of temperature ($1000/TK^{-1}$) for some of the polyester under investigation. The following relation is applicable:

$$\sigma = \sigma_0 \cdot \exp(-\Delta E/KT) \quad (1)$$

The parameters have their usual meanings. The plot of the electrical conductivity as a function of reciprocal absolute temperature. Figs. 3a and 3b show two inflections for compounds I, II, VII and IX. This denotes that the mode of conduction changes during the conductivity measurements. A linear behavior is observed for compounds VIII and V.

The values of the transition temperature and activation energies on heating and cooling rates were calculated according to equation 1 and are listed in Table 5.

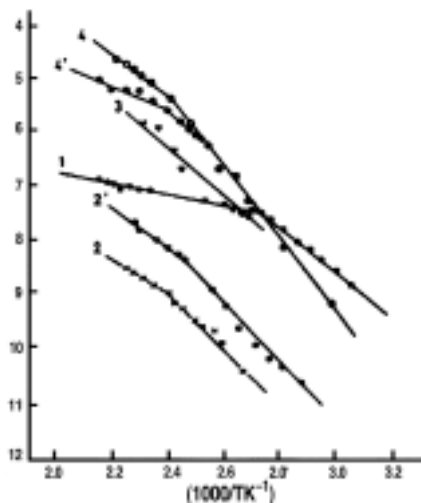


FIG. 3a. Variation of electrical conductivity ($\log \sigma, \Omega^{-1}, \text{cm}^{-1}$) as a function of reciprocal absolute temperature for some solid polyester.

1,1' (V), 2,2' (IX) and 3,3' (VII) where 1,1': heating and cooling respectively.

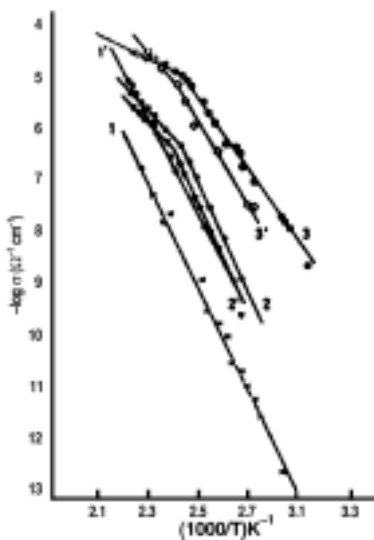


FIG. 3b. Variation of electrical conductivity ($\log \sigma, \Omega^{-1}, \text{cm}^{-1}$) as a function of reciprocal absolute temperature for some solid polyester.

1,1' (V), 2,2' (IX) and 3,3' (VII) where 1,1': heating and cooling respectively.

TABLE 5. Values of activation energy for the conduction (eV) and transition temperature (K) for some of the investigated polyester.

Compd.	Heating activation energy			Cooling activation energy		
	ΔE_1	ΔE_2	Transition temperature	ΔE_1	ΔE_2	Transition temperature
I	0.742	0.260	353.36	–	–	–
II	1.025	0.715	436.68	1.206	0.693	429.18
V	2.121	–	–	2.199	–	–
VII	1.230	0.990	413.22	1.240	0.778	411.52
VIII	1.732	–	–	–	–	–
IX	2.249	1.164	409.84	2.224	1.109	414.94
X	1.320	0.469	399.20	1.237	0.616	402.41

The activation energy of the polyester decreases in the order $I < II < VII < X < VIII$. Consequently, the electrical conductivity increases in a reverse order. This is probably explained on the basis of increased electron density and polarization of the molecule as a function of the substitution inductive effect, facilitating the electron delocalization in the molecule. A justification for the above conclusion stems from the linear relationship observed between the activation energies under and above the transition temperature with σ^+ values of substitution. The electrical conductivity values for compounds of the same type of substituent, at different positions, (e.g. VIII and IV) increase in the order $p > m$ position, due to the mesomeric effect of the substituent^[12].

The difference in the position of the heating and cooling curves has no essential effect on the specific conductivity level and causes only slight changes of the activation energy (Table 5). The activation energies below and above the transition temperature are large. This can be attributed to the following^[13,14]:

1 – As the conjugation is increased through the molecule, the π -electrons are not delocalized over a corresponding greater distance, and the activation energy (ΔE) for generation of the carriers no longer falls linearly with the conjugation chain length;

2– The triazole and the phenyl rings are actually not coplaner. Consequently, the rotation of the two molecules against each other in a twisting motion is considered which breaks the conjugation between them; hence, the atomic p-orbital can no longer overlap.

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تخليق وفحص بعض البوليبوريسان معتمدا على الهيدروكسي بولي استرات

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المستخلص. في هذا البحث تم تخليق وفحص بعض الهيدروكسي بولي استر اليوريسان بتفاعل بين رباعي برومو حمض الفيثاليك والفيثاليك والماليك مع البولي إيثيلين جيليكون بطريقة الاندماج الانصهاري. تتميز هذه المركبات بعدد الهيدروكسي وقياسات اللزوجة وأيضاً مضادات للنار من البولي إسترات. أيضاً تم تفاعلها مع زيادة من الثيوسيانيت والأيزوثيوسيانيت لزيادة خواصها المضادة للنار.

لقد تم فحص ووصف التركيب الجزيئي للبوليمرات باستخدام أجهزة الطيف المختلفة (الأشعة تحت الحمراء)، والرنين المغناطيسي ، وقياسات اللزوجة ، والتحليل الوزني الحراري ، وأيضاً تمت دراسة تغيرات في التوصيل الكهربائي للعينات الصلبة باستخدام معدل زيادة درجة الحرارة .

وتبين أن هذه المركبات - قيد الدراسة - لها توصيلاً كهربياً مميّزاً ، مما يعمم استخدامها كأشياء موصلات ومضادات للاستخدامات النارية .