Polymerization of furandicarbonyl chloride with bisphenol A poly(2,5-furandiylcarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenyleneoxycarbonyl)

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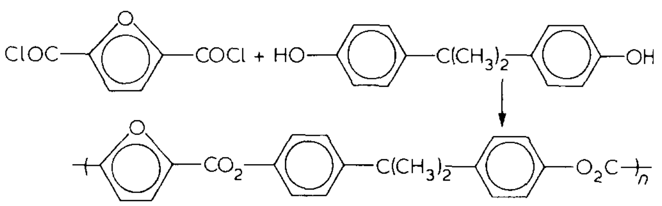
Polymerization of 2,5-furandicarbonyl chloride with bisphenol A in four systems was studied. Catalysed polymerizations in tetrachloroethane solution at 155°C using $AlCl_3$ or Zn dust yielded coloured polymer with intrinsic viscosities of 0.24 and 0.23, respectively in about 80% yield. Uncatalysed solution polymerization in chloroform at ambient temperature using triethylamine as an acid acceptor gave a 90% yield of a white, film-forming polymer with an intrinsic viscosity of 0.5. Interfacial polymerization in benzene yielded a polymer of the same viscosity but in reduced yield (16%). Thermal analysis by differential scanning calorimetry revealed that thermal decomposition begins at about 225°C and is superimposed on an apparent crystallization exotherm at ~250°C and an apparent melting endotherm at ~320°C.

INTRODUCTION

In the course of a program to synthesize and study the properties of polymers containing heterocyclic units[1] a brief study of the relative merits of several synthetic procedures for the preparation of a polyester from 2,5-furan dicarbonyl chloride and bisphenol A were conducted and the results obtained are described here.



It has been reported[2] that the polymer could be prepared by interfacial polymerization using benzene as the organic solvent and sodium hydroxide as the acid acceptor in the aqueous phase. A film-forming polyester was reportedly obtained in 90% yield. An attempt was made to reproduce the reported results. Although a film-forming polyester was obtained, the yield of polymer after precipitation, washing and drying was low. This polymerization has been studied[3] as a function of organic solvent and stirring rate and it was found that polymer yields, as well as molecular weights were dependent on both variables. Thus differences in stirring rates may account for the discrepancy in yields between the reported value and that obtained in this work.

It has been reported[4] that high molecular weight polyesters could be prepared by employing a solution polymerization using refluxing tetrachloroethane, diacid chlorides, bisphenols and aluminium chloride as the catalyst. This method was tried as was polymerization using freshly-opened zinc dust as catalyst. In both instances, high yields of discoloured polymer with relatively low inherent viscosities were obtained.

Polymerizations in homogeneous solution have been accomplished using diacid chlorides, bisphenols and an amine as acid acceptor[5]. We have found that this approach is also useful for preparing the polymer described here. The reaction was conducted in chloroform using triethylamine as the base. The molecular weight of the polymer was the same as that formed by interfacial polymerization, but the yield was much higher. The results of the polymerizations are collected in *Table 1*. Judging from the experimental results it appears that, for the furan system, the chloroform–triethylamine system not only gives reasonably high molecular weight polymers, but also high yields of polymer. The catalysed reactions may be less successful because of the

Table 1 Polymerization of 2,5-furandicarbonyl chloride with 2,2′-bis(4-hydroxyphenyl) propane

Method	Catalyst	$[\eta]^{25°C}$ [e]	Polymer colour	Yield (%)
Solution catalysed	$AlCl_3$ [a,b]	0.24	Brown	80
Solution catalysed	Zn [a,b]	0.23	Brown	75
Interfacial [c,d]	–	0.51	White	16
Solution uncatalysed [d,e]	–	0.50	White	90

[a] Solvent was 1,1′, 2,2′-tetrachloroethane. [b] Reaction temperature was 155°C. [c] Solvent was benzene. [d] Reaction was performed at ambient temperature. [e] Solvent was chloroform

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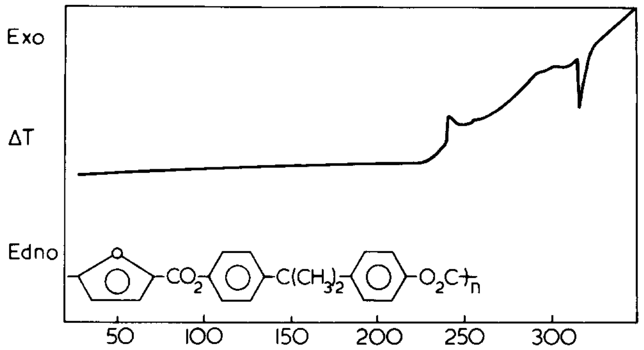

Figure 1 Differential scanning calorimetry of poly(2,5-furandiylcarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenyleneoxycarbonyl)

known sensitivity of the furan system to acid-catalysed decomposition.

The material as prepared either by the interfacial or solution method was a white, film-forming material which had good thermal properties (*Figure 1*). No thermal transitions are noted until about 225°C. At this point exothermic decomposition begins and is superimposed on what may be a crystallization exotherm (~250°) and a melting endotherm (~320°C).

EXPERIMENTAL

Differential scanning calorimetry was performed using a Du Pont Model 900 Thermal Analyzer. Benzene was purified by distillation from sodium hydride. Chloroform was purified by washing it with water, drying it over anhydrous sodium sulphate and then distilling it from calcium hydride. Triethylamine was purified by distillation from phosphorous pentoxide under nitrogen. Tetrachloroethane was purified by washing it sequentially with dilute acid, water, dilute base, water and then by drying it over anhydrous sodium sulphate. Dry benzene (5% by wt) was added and the azeotrope was fractionally distilled. Only benzene-free fractions were used (as determined by n.m.r).

Poly(2,5-furandiylcarbonyloxy-1, 4-phenylenedimethyl methylene-1,4-phenyleneoxycarbonyl)

(a) The following procedure was carried out in a dry box. Purified 2,2′-bis(4-hydroxyphenyl) propane, 1.418 g (0.0062 mol), was placed in a 100 ml round-bottom flask equipped with a magnetic stirrer, 20 ml of purified chloroform and 1.2 g of purified triethylamine. A solution of 2,5-furandicarbonyl chloride, 1.200 g (0.0062 mol), dissolved in 20 ml of chloroform was added dropwise with stirring, with a pressure-equalizing addition funnel over the course of 0.5 h. The system was allowed to stir overnight. The resulting solution was poured into excess light petroleum ether and a white, fibrous solid was isolated by suction filtration. After drying *in vacuo* (0.02 torr) at 40° for 16 h over paraffin wax shavings, the white solid, 1.9 g, 90% yield, had $[\eta]^{25°C}_{CHCl_3} = 0.50$. Clear, cohesive films may be cast from 20% (by wt) chloroform solutions of this polymer; i.r. (KBr) 3500, 3000, 1730 ($-CO_2-$), 1580 (aromatic), 1500, 1290, 1260, 1210, 1190, 1160, 1100, 1060, 1010, 950, 860, 800, 750 cm^{-1}; n.m.r. ($CDCl_3$), $\delta = 1.71$ (s. 6H, $-CH_3$), $\delta = 7.18$ (d, 10H, aromatic), $\lambda^{CHCl_3}_{max} = 267$ nm (ϵ_{max} 2.821); d.s.c., the polymer has an exothermic transition at 240°C and decomposes with weight loss at 315°C, see *Figure 1*.

(b) Following the procedure of Panayotov[2], 2,5-furandicarbonyl chloride, 0.400 g (0.002 mol) (recrystallized in a dry box from purified hexane) was dissolved in 10 ml of purified benzene. This solution was added to a Waring blender (with a capacity of 100 ml) containing 30 ml of distilled water, 0.475 g (0.002 mol) of 2,2′-bis(4-hydroxyphenyl)propane, 0.164 g (0.004 mol) of sodium hydroxide and was stirred for 10 min. The resulting white solid was isolated by suction filtration and washed in a Waring blender with water, 5% aqueous sodium hydroxide solution, water, 10% aqueous hydrochloric acid solution, water and finally dried *in vacuo* (0.02 torr) at 40°C over phosphorous pentoxide for 16 h. The polymer, 0.11 g, 16% yield, was found to have $[\eta]^{25°C}_{CHCl_3} = 0.51$ and was identical by i.r., n.m.r. and u.v. spectroscopy with poly(2,5-furandiylcarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenyleneoxycarbonyl).

(c) The following was carried out in a dry box in accordance with the procedure of Wilson[4]. 2,2′-bis (4-hydroxyphenyl)propane, 0.914 g (0.004 mol), and 15 ml of purified tetrachloroethane were placed in a 100 ml, 3-neck, round-bottom flask equipped with a magnetic stirring bar, reflux condenser and nitrogen inlet and outlet which was connected to a bubbler. 2,5-furandicarbonyl chloride, 0.775 g (0.004 mol), dissolved in 15 ml of purified tetrachloroethane, was poured into the diol suspension, all at once, with stirring while dry nitrogen was passed through the system. Anhydrous aluminium chloride (Fischer), 0.01 g, was added and the solution was refluxed under dry nitrogen for 16 h. The solution was then allowed to cool and the aluminium chloride was destroyed by the addition of 0.5 ml of distilled water. The polymer was isolated by precipitation into light petroleum ether and subsequent suction filtration. After drying *in vacuo* (0.02 torr) at 40°C for 16 h, a brown, granular solid, 1.1 g, 80% yield, was obtained which had $[\eta]^{25°C}_{CHCl_3} = 0.24$ and was identical by i.r., n.m.r. and u.v. spectroscopy with poly(2,5-furandiylcarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenyleneoxycarbonyl).

(d) The following procedure was carried out in a dry box. 2,2′-bis(4-hydroxyphenyl)propane 1.06 g (0.005 mol), and 30 ml of purified tetrachloroethane were reacted following the procedure outlined in section (c), except that 0.01 g of zinc dust (from a freshly opened bottle) was used in place of the anhydrous aluminium chloride. After cooling, the polymer was isolated by precipitation into light petroleum ether and subsequently isolated by suction filtration. After drying *in vacuo* (0.02 torr) at 40°C for 16 h, a brown granular solid, 1.2 g, 75% yield, was obtained which had $[\eta]^{25°C}_{CHCl_3} = 0.23$ and was identical by i.r. n.m.r. and u.v. spectroscopy with poly(2,5-furandiylcarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenyleneoxycarbonyl).

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