Polyketoetheresters from 4,4'-Dichloroacetyldiphenyl Ether and their Characterization

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NOTE
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INTRODUCTION

Benzyl chloride and phenacyl chloride are reported to condense with sodium acetate or sodium benzoate, affording the corresponding esters [1-4]. This suggested that a dichloride monomer can polycondense with a sodium dioate, affording a polyester. Akhmedzade and Yasnopolskii reported one such polyester synthesis based on polycondensation of p-xylylene dihalide with sodium terephthalate [5]. As phenacyl chloride is more reactive than benzyl chloride is more reactive than benzyl chloride [4], 4,4'-dichloroacetyldiphenyl ether (DADE) should prove even more reactive than a dichloride of the $Ar(CH_2Cl)_2$ type. The work presented here comprises a study of the polycondensation of DADE with sodium adipate (ADP), sebacate (SEB), or terephthalate (TER).

Huand and coworkers [6] synthesized polyketoetheresters by polycondensing DADE with adipic, sebacic, or terephthalic acid in the presence of triethylamine in DMF and also in N-methylpyrrolidone, but did not report any properties of their polyketoetheresters other than solution viscosity and number-average molecular weight [6].

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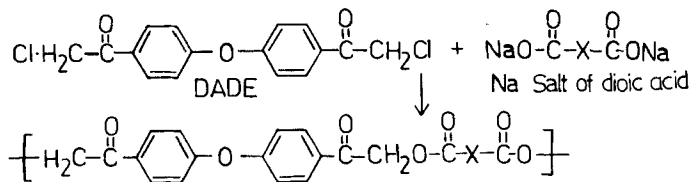
EXPERIMENTAL

Materials

Chemically pure reagents were used. DADE was prepared by the literature method [6]. It was crystallized from isopropanol by yield colorless needles, mp 114°C [7]. The sodium salts of the acids were prepared in methanol.

Polymerization

A solution of DADE (3.22 g, 0.01 mol) and sodium adipate (1.90 g, 0.01 mol) in DMF (20 mL) was refluxed at 152°C for 8 h and poured in a thin stream into a well-stirred ice-water mixture (200 g). The solid which separated out was filtered, washed with water, dried, and then washed with boiling methanol to remove the dihalide monomer. The polyketoetherester was a light yellow solid. The yield was 50%. This sample fused in the range 208-215°C. It was partly soluble in dioxane and completely soluble in DMF and DMSO.

Analysis. Calculated for $C_{22}H_{20}O_7$: C, 66.6; H, 5.0%. Found: C, 65.0; H, 5.0%.

The polycondensation was also carried out as described above with nitrobenzene (20 mL) as solvent, removing it by steam distillation. The yield of the dark brown solid was 56%. This sample fused in the range 210-225°C and was insoluble in dioxane and DMF but partly soluble in DMSO.

The conditions of the other polycondensations are shown in Table 1.

Measurements

The C and H contents of all the polyketoetheresters agreed well with the values calculated on the basis of the structure of the repeat unit of the concerned polyketoetherester sample.

IR measurements of all the polyketoetherester samples were performed on a Perkin-Elmer 983 infrared spectrophotometer in KBr. Endgroup analysis (EGA) of swelled polyketoetherester samples in methanol was done by titration with 0.01 M aqueous sodium hydroxide solution [8]. The number-average molecular weights of DMF-soluble polymer samples were measured on a Hewlett-Packard vapor pressure osmometer at 70°C, with DMF as solvent and benzil as a calibrant. The values of $\overline{M}_n$ estimated by EGA and VPO methods agree and lie in the range 1000-3000. Viscosity measurements were performed with an Ubbelohde viscometer in concentrated H_2SO_4 at 35°C.

TGA of selected polyketoetherester samples was carried out on a Du Pont 951 thermogravimetric analyzer in air at a heating rate of 10°C/min.

TABLE 1. Polycondensation of 4,4'-Dichloroacetyldiphenyl Ether (DADE) with Sodium Carboxylate

| Sample | Monomers[a] | Solvent | Reaction | | Reagent | Yield, % | Softening interval, °C | $\bar{M}_n$ ± 100 by EGA (VPO) |
			Temperature, °C	Time, h	Catalyst			
1	DADE-ADP	DMF	152	8		50	208-215	1000 (1050)
2	DADE-ADP	DMF	152	8	Cu	58	230-250	1500
3	DADE-ADP	DMF	152	8	NaAc	52	210-217	1200
4	DADE-ADP	DMF	152	8	NaAc [1:1:2]	55	210-225	1300
5	DADE-ADP	φNO₂	208	8		56	210-225	1500
6	DADE-ADP	φNO₂	208	8	Cu	60	280-300	2100
7	DADE-ADP		230	12		65	>300	2400
8	DADE-ADP		230	12	Cu	79	>300	2800
9	DADE-ADP		230	12	NaAc	75	>300	2700
10	DADE-SEB	DMF	152	8		79	195-208	1100 (1200)
11	DADE-SEB	DMF	152	8	NaAc	79	220-235	1500
12	DADE-SEB		230	12	Cu	80	>300	2800
13	DADE-SEB		230	12	NaAc	79	>300	2600
14	DADE-TER	DMF	140	8	NaAc	76	295-300	1500 (1540)
15	DADE-TER	DMF	140	8	Cu	76	298-300	1600
16	DADE-TER		230	12	Cu	81	>300	3000
17	DADE-TER		230	12	NaAc	79	>300	2800

[a]DADE:Na salt = 1:1 mol/mol.

RESULTS AND DISCUSSION

Table 1 shows that increasing the vigor of the reaction conditions increases the yield of the polyketoetherester, slightly raises $\bar{M}_n$, and yields a product with a tendency to be insoluble and infusible. The yields of the esters are higher from adipic and sebacic acid than from terephthalic acid. Only three samples in Table 1, 1, 10, and 14, were soluble in DMF and DMSO. Adipate and sebacate polymers made in DMF at 152°C were soluble in DMF and DMSO, but the equivalent terephthalate sample was insoluble in both solvents. The conditions of Huang and coworkers [6] were somewhat more vigorous than our uncatalyzed DMF solvent conditions and less vigorous than the other conditions in Table 1.

The IR spectra of all the polyketoetherester samples from the same pair of monomers are similar, suggesting that the solubility differences are due to difference in $\bar{M}_n$. The IR spectra of these polymers exhibit all the expected characteristics. The bonded-OH band from 3550 to 3000 cm^{-1} and the out-of-plane deformation band of carboxylic OH groups at 940 cm^{-1}. The ester carbonyl band appears at 1740 cm^{-1} for DADE-ADP and DADE-SEB and around 1725 cm^{-1} for DADE-TER. A strong band due to keto carbonyl is observed at 1695 cm^{-1} for all the samples. The bands characteristic of $4,4'\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}$ are observed at the expected positions [9]. A band at 770 cm^{-1}, observed in the spectra of all the polyketoetherester samples, is attributed to C—Cl end groups [10].

The intrinsic viscosities of the concentrated H_2SO_4-soluble polyketoetheresters, estimated by both the Huggins and the Kramer relation [11, 12], agree with each other. They are very low, 0.09-0.12 dL/g.

Examination of the TGA data of the polyketoetherester samples presented in Table 2 reveals that the degradation commences somewhere between 250 and 300°C. Application of the Broido method [13] to the TG data indicated that the degradation of all the polyesters proceeds in a single step and that the degradation reaction is almost first order with energies of activation of 8.4-12.5 kcal/mol. The temperature characteristics calculated by the method of Doyle [14] (Table 2) show the same order of thermal stability for initial decomposition temperature (IDT), maximum rate of decomposition temperature (T_{max}), half-volatization point temperature (T_s), and integral procedural decomposition temperature (IPDT). The order of thermal stability suggests that samples prepared under more vigorous conditions are more stable.

The present study has revealed that a dichloride monomer like DADE can afford polyesters on reaction with sodium dioate monomers. The infusibility and insolubility which appears at the lower stage of $\bar{M}_n$, even when an ali-

TABLE 2. Thermogravimetric Analysis of Polyketoetheresters from DADE

Sample[a]	IDT, $°K$	T_{max}, $°K$	T_s, $°K$	IPDT, $°K$	$E_a \pm 0.5$, kcal/mol	Reaction order, $n \pm 0.2$
1	473	600	680	676	8.4	1.1
6	483	654	681	689	11.5	1.2
7	472	650	700	680	10.0	1.1
8	485	699	735	750	12.5	1.3
10	485	720	723	731	8.5	1.1
12	490	734	730	771	11.0	1.3
14	470	670	665	685	10.7	1.1
16	481	688	673	742	11.2	1.3

[a]See Table 1.

phatic dioic acid is employed as monomer, seem to suggest strong intermolecular interaction between the vicinal flat and planer biphenylene moieties of the repeat units of polymer chains since simple intermolecular attractive dipolar interaction cannot account for these properties.

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