

Synthesis of Some New Polymers by the Polycondensation of 1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane with Bisphenols and Phase-Transfer Catalysts*

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ABSTRACT: Two new polymers were synthesized by the polymerization of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane with 4,4-isopropylidenediphenol (bisphenol A) and 4,4-sulfonyl diphenol in a two-phase system of water and dichloromethane in the presence of dibenzo-24-crown-8. The polymers were characterized by IR and NMR spectroscopy.

Thermogravimetric analysis of the aromatic bisphenol A polymer showed a 10% weight loss in air at 225°C. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 651–654, 2004

Key words: infrared spectroscopy; phase transfer catalysis; poly(ether sulfones); synthesis

INTRODUCTION

Interfacial polycondensation with various phase-transfer catalysts (PTCs), such as crown ethers and quaternary ammonium and phosphonium salts, for the synthesis of a variety of condensation polymers has been studied intensively.^{1–3}

My coworkers and I reported on an aromatic nucleophilic substitution polymerization with PTCs, which led to the formation of aromatic polyethers.^{4–6}

As a continuation of this study, we synthesized some new polymers by PTC polymerization between various bisphenolate anions and 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT). Further work is underway on the polymerization of DDT with other diphenols and their biological and industrial applications. The polymerization of DDT with bisphenol A is promising for the growth of new markets for aromatic plastics.

EXPERIMENTAL

Materials

All of the reagents and monomers were obtained from commercial sources or were prepared by procedures

in the literature and were subjected to standard purification procedures before use.

Polymerization method

The polymers were synthesized by the reaction of DDT with bisphenols. In a typical synthesis, recrystallized DDT (1.0 mmol) in dichloromethane (25 mL) was added to a magnetically stirred solution of recrystallized bisphenol A (1.0 mmol) in deionized distilled water (25 mL) containing sodium hydroxide (2.2 mmol) and dibenzo-24-crown-8 at 50°C in a 100-mL flask equipped with a nitrogen inlet, a water-cooled condenser, and a thermometer. After the solution was stirred for 24 h under nitrogen, it was cooled and slowly poured into 150 mL of methanol. The polymer was then filtered off. This solid was worked up by boiling three times for 1 h with 150 mL of methanol and then by boiling three times for 1 h with 150 mL of water.

The product was dried overnight at 100°C to render the polymer.

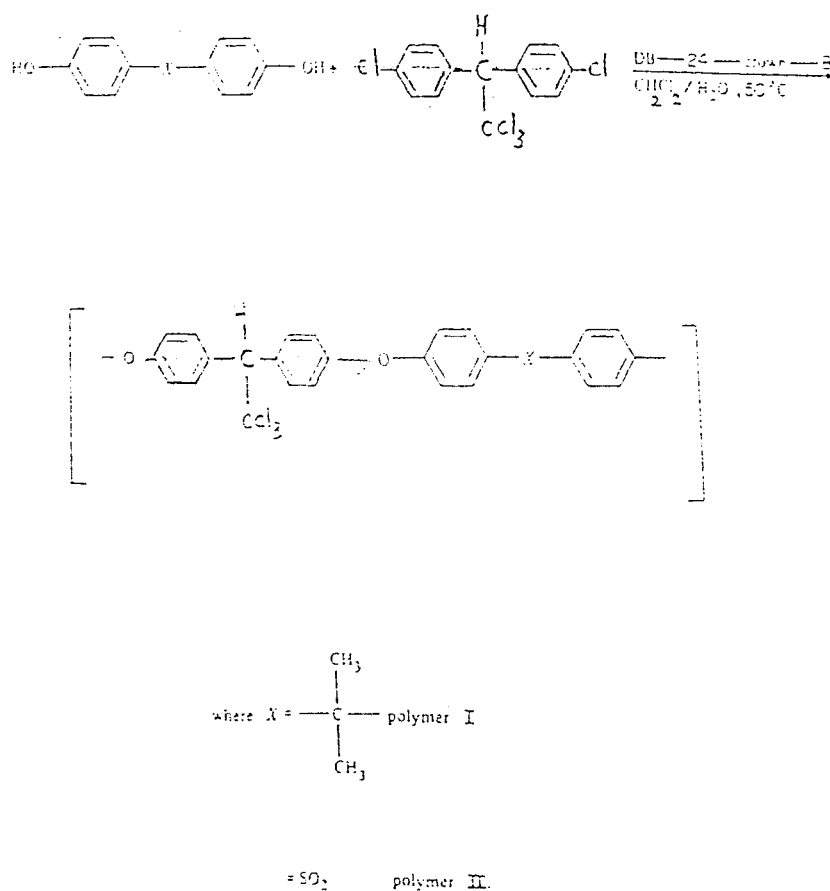
Measurements

IR spectra of the polymer samples were scanned in KBr pellets on a PYe-Unicam SP-1000 IR spectrophotometer (Harlow, Essex, UK).

¹H-NMR analysis was carried out at New Castel University on a Bruker spectrometer (Bremen, Germany) operating at 200 MHz for proton resonances and on Varian spectrometers (Palo Alto, CA) operating at 90 MHz.

*Due to the political situation in Iraq, the author of this article was unable to submit a copyright agreement form until recently, and therefore, the publication of this article was unavoidably delayed until now.

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Scheme 1

Thermal properties

The material was subjected to thermogravimetric analysis (TGA) with a PL Thermal Sciences simultaneous thermal analyzer. This was carried out at Northern Carbon Research Laboratories (United Kingdom) under the following conditions: room temperature to 700°C temperature range, 10 and 40°C/min heating rates, and an air atmosphere.

RESULTS AND DISCUSSION

Polymerization was carried out with a number of bisphenols with DDT according to the general reaction scheme shown in Scheme 1.

The formation of the solids in the presence of dibenzo-24-crown-8 depended on the nucleophilicity of the phenolate salt, which may be governed by the nature of x according the following order:

TABLE I
Assignment of Characteristic Chemical Shifts from the $^1\text{H-NMR}$ Spectra

Compound	Chemical shifts of the aromatic σ proton (ppm)	Chemical shifts of the aliphatic σ protons (ppm)
I	7.49 (8H doublet, aromatic, $J = 9$ Hz) 7.65 (8H doublet, aromatic, $J = 9$ Hz)	1.6 [6H, (s), 2Me] 5.9 [1H, (s), —CH]
II	7.2 (8H doublet, aromatic, $J = 9$ Hz) 7.35 (8H doublet, aromatic, $J = 9$ Hz)	4.9 [1H(s), —CH]
I ^a	7.4 (8H, two doublet, aromatic, $J = 10$ Hz) 7.2 (8H, two doublet, aromatic, $J = 10$ Hz)	1.59 [6H, (s), 2Me] 5 [1H(s), —CH]

^a The $^1\text{H-NMR}$ spectra run on a Bruker spectrometer operating at 200 MHz is shown in Figure 1.

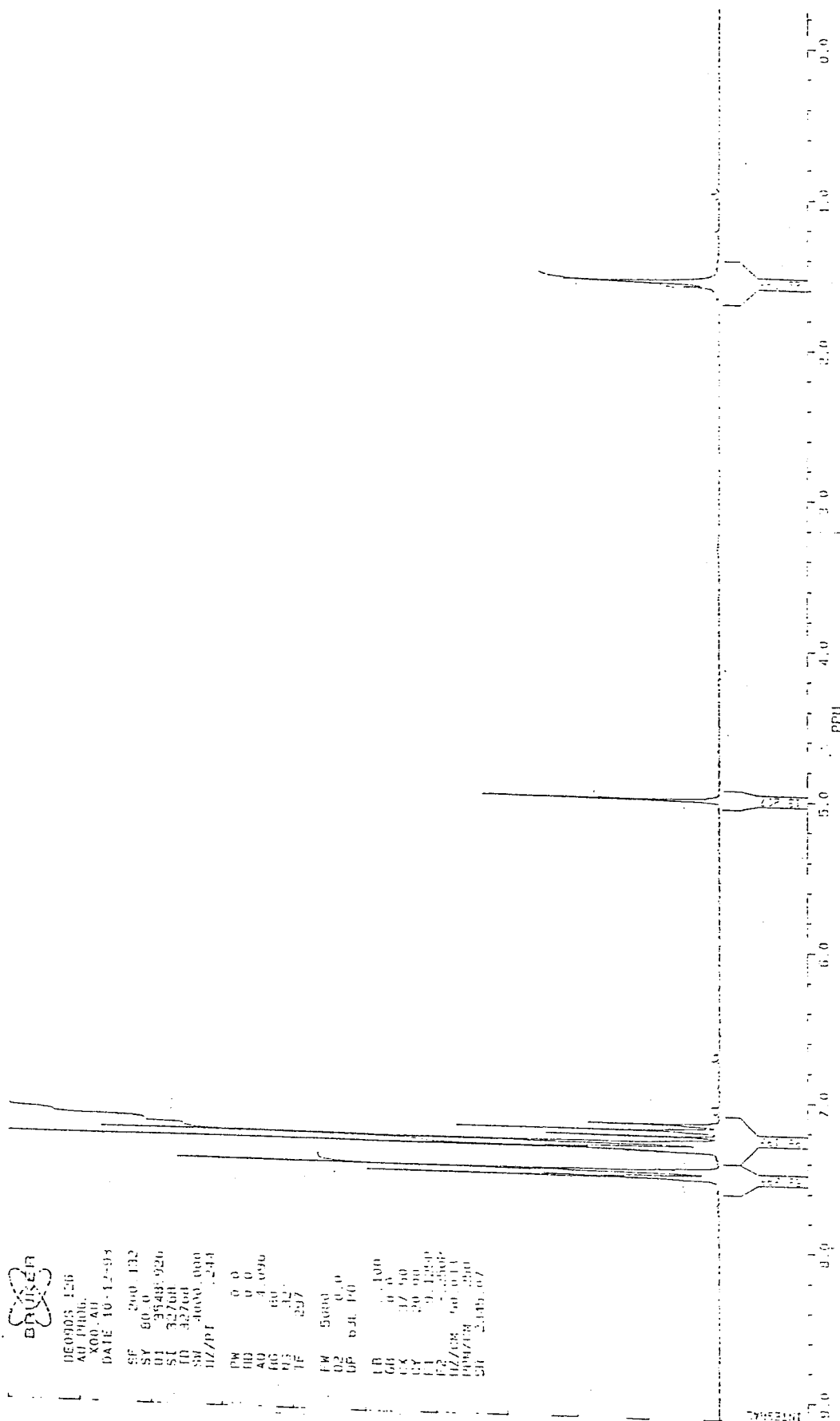


Figure 1 ¹H-NMR spectrum of polymer I.

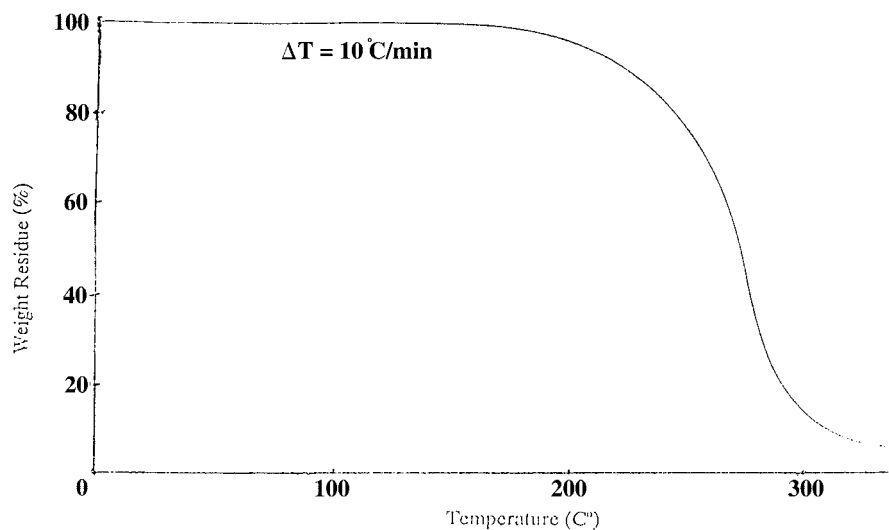
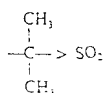


Figure 2 TGA curve of polymer I.



This was in line with the expected nucleophilicity of the anions.

The chemical shifts in the $^1\text{H-NMR}$ spectra of the polymers are shown in Table I. These were in agreement with published results.^{7,8}

These polymers were defined by the comparison of their IR spectra with those of model compounds (Table II). The IR spectra exhibited characteristic absorp-

tions at 1365 and 1385 cm^{-1} due to $\begin{array}{c} \text{CH}_3 \\ | \\ \text{---C---} \\ | \\ \text{CH}_3 \end{array}$ for polymer I

and 1400 cm^{-1} due to $\text{---SO}_2\text{---}$ for polymer II.

The thermal stability of the polymer was evaluated by TGA. A typical trace for polymer I is shown in Figure 2.

The polymer showed a 10% weight loss at 225°C in air at a heating rate of 10°C/min.

The results indicated two decomposition temperatures. The predominant decomposition occurred between 200 and 300°C, and a smaller proportion decomposed between 300 and 500°C.

TABLE II
Assignments of Characteristic Frequencies^a in the IR Spectra

Compound	Wave number (cm^{-1})	Intensity	Assignment
Polymers I and II	1365, 1385	s, sh	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \\ \\ \text{CH}_3 \end{array}$
	1400	s	SO_2
	1260, 1240	vsh	C---O---C
	1600, 1500	vsh	Aromatic ring
	780, 765	vsh	---C---Cl

s = strong; sh = sharp; vsh = very sharp.

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