

were formed in the samples. Therefore, the results were reproducible.

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Synthesis of poly {2,2 bis[4(*p*-aminophenoxy)phenyl] propane-terephthalic acid}

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INTRODUCTION

One of the greatest limitations of present commercial polymers is their inability to operate at elevated temperatures, due to their relatively low melting points. In recent years, therefore, intensive research programmes aimed at synthesising new thermally stable polymers have been initiated and many new organic polymers have been reported¹⁻⁷. This report describes the synthesis of a new thermally stable aromatic polyamide containing phenylene oxide groups in the main chain. Several aromatic rings are present in the repeating unit, all of which are *para-para* linked. This is desirable, because, only then would the new polyamide be highly symmetric and hence thermally more stable than a non-symmetric structure⁸⁻¹⁰. Low temperature interfacial polycondensation technique was adopted in preference to high temperature melt condensation method because of its well-known advantages¹¹.

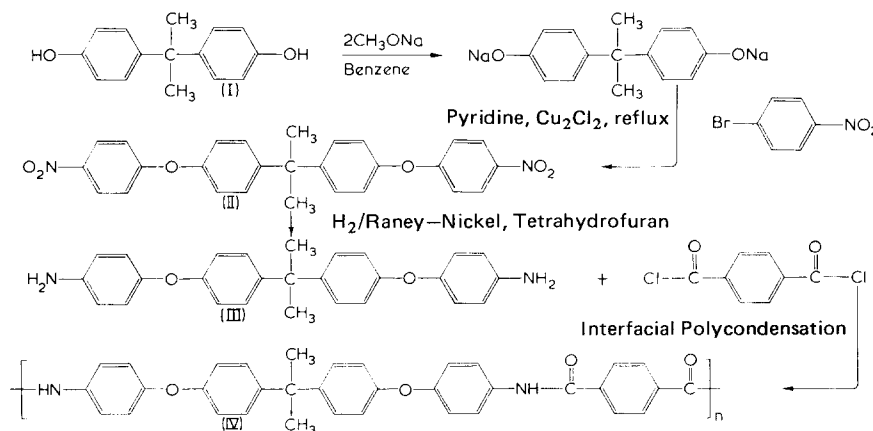
2,2-Bis[4(*p*-nitrophenoxy)phenyl]propane (II) containing the phenylene oxide linkage was first prepared from Bisphenol-A (I) and *p*-bromonitrobenzene. It was then reduced to the diamine (III) which was polycondensed with terephthaloyl chloride to form the polymer, poly {2,2-bis[4(*p*-aminophenoxy)phenyl]propane-terephthalic acid} (IV). As the complimentary compounds reacting are bifunctional, a

condensation polymer (IV) is obtained. The reactions can be represented as follows by equation (1).

EXPERIMENTAL AND RESULTS

Dry sodium methoxide powder was allowed to react with Bisphenol-A in benzene medium and nitrogen atmosphere for 1 h. The methanol formed and benzene were distilled off and the pure dry sodium salt so obtained was then reacted with *p*-bromonitrobenzene in pyridine medium and nitrogen atmosphere. After about 9 h, the products obtained were extracted with ether, washed with alkali, and fractionated using column chromatography. The first fraction suspected to

be the dinitro compound (II), on concentration gave yellow crystals. It was contaminated with *p*-bromonitrobenzene and this was removed using sublimation technique. The dinitro compound so obtained had a melting point of 117°–118°C. The analytical data, i.r. and n.m.r. spectra confirmed the structure (II). The i.r. spectra of the dinitro compound (II) showed peaks at 1018 and 1255 cm⁻¹ corresponding to ether C–O stretching frequency, in addition to all other expected group frequencies. The n.m.r. spectra of II showed a singlet at 1.75δ corresponding to 6 aliphatic protons, a quartet at 6.9–7.5δ corresponding to 12 aromatic protons and a doublet at 8.1–8.45δ showing that the 4-aromatic protons, *ortho* to the two nitro groups, are shifted to a lower field. The dinitro compound (II) was then reduced to give the diamine (III) with hydrogen in presence of Raney Nickel in tetrahydrofuran medium. The pale yellow crystals obtained had a melting point of 121°–122°C. The i.r. spectra of the diamine (III) showed the important



Notes to the Editor

doublet corresponding to a free amine at 3315 and 3395 cm^{-1} and the absorption corresponding to the nitro group disappeared. The n.m.r. spectra of the diamine (III) showed a singlet at 1.6 δ corresponding to 6 aliphatic hydrogens, a singlet at 2.75 δ corresponding to 4 amine hydrogens and a multiplet at 6.8–7.2 δ corresponding to 6 aromatic hydrogens. From the mass spectrum of the diamine (III), the molecular weight was also checked and found to be 410.

The diamine (III) was dissolved in CHCl_3 , sodium carbonate solution and sodium lauryl sulphate solution added and the content of the flask stirred vigorously for 5 min. All of the terephthaloyl chloride in chloroform was added and stirring was continued for another 5 min. Hexane was then added and the contents were slowly stirred for 2 min, filtered, washed with water, chloroform and hexane. The residue was redissolved in DMF and reprecipitated with methanol and dried at 100°C under reduced pressure. The i.r. spectrum of the polymer (IV) showed the disappearance of the free amine frequency and the appearance of peaks at 1595 and 1645 cm^{-1} cor-

responding to amide $-\text{NH}$ stretching and amide $\text{C}=\text{O}$ stretching respectively and a broad band at 3200 cm^{-1} again corresponding to $\text{N}-\text{H}$ stretching, confirming the structure (IV) for the polymer¹². The polymer was soluble in dimethyl sulphoxide and dimethylformamide. The inherent viscosity was found to be 1.7 in DMF at 30°C at a concentration of 0.025 g/100 ml. Differential thermal analysis showed that the polymer was unaffected up to 380°C. Further work regarding molecular weight, viscosity etc. are in progress.

ACKNOWLEDGEMENTS

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ERRATA

'Some aspects of stereoregulation in the stereospecific polymerization of vinyl monomers' by Piero Pino and Ulrich W. Suter, *Polymer* 1976, 17, 977–995

Page 978, left hand column, line 28: *for* 33, *read* 33 monomeric units
Page 979, Table 1, 2 lines from bottom, under Solvent: *for* pentene, *read* pentane
Page 981, Table 2, line 4, under Dyads (m): *for* 0.8 *read* 0.3; line 19, under Monomers: *for* Menthyl vinyl ketone *read* methyl vinyl ketone
Page 982, left hand column line 4: *for* include *read* induce; right hand column line 23: *for* anylsodium *read* amylsodium
Page 983, Table 4 2 lines from bottom under Stereoregularity: *for* Atactic, (m) = 40, *read* Atactic, (m) = 0.40; bottom line, under Stereoregularity: *for* predicted, *read* predominantly
Page 984, right hand column, line 34 should read: With ethyl-(Z)- β -d₁-methacrylate, Fowells, Schuerch, Bovey and Hood . . .
Page 985, Table 9, footnote: *for* (E)- β -d₁-methyl methacrylate, *read* methyl-(Z)- β -d₁-methacrylate
Page 986, Table 10, caption and left

hand column, line 27: *for* (Z)- α -ethyl- β -d₁-methyl acrylate, *read* ethyl-(Z)- β -d-methacrylate; left hand column, line 32: *for* contact with ion pairs, *read* contact ion pairs; left hand column, line 40 should read: For poly(vinyl ethers), for instance, a ring structure is suggested as shown in Figure 3, the oxygenated chain acting as a specific solvating agent itself⁹⁹; right hand column, line 6: *for* the same *read* some
Page 987, Table 11, bottom line under Monomer: *for* 1-Methyl propyl vinyl, *read* 1-methyl propyl vinyl ether;
left hand column line 3: *for* (Z)- α -ethyl- β -d₁-methacrylate, *read* ethyl-(Z)- β -d₁-methacrylate
Page 988, schemes (3) and (4): *for* Me, *read* [Me]; right hand column, 5 lines from the bottom: *for* (2b), *read* (4b)
Page 989, left hand column, 10 lines from the bottom: *for* (E)-1-deuteropropylene, *read* (E)-1,3,3,3-d₄-propylene
Page 990, left hand column, line 7: *for*

(equation 2), *read* (equation 11); right hand column, scheme (9): *for* $\text{Ti}(\text{Bz})_4/\text{Al}(\text{Br})_3$, *read* $\text{Ti}(\text{Bz})_4/\text{Al}(\text{Bz})_3$
Page 992, Figure 6 caption: *for* $H_M - H_R = 2.2$ kcal/mol; $S_M - S_R = 5.0$ cal/mol K, *read* $H_i - H_s = 2.2$ kcal/mol; $S_i - S_s = 5.0$ cal/mol K; Scheme 12, structure (1), the geminal 'CH₃' and 'H' on the propylene complexed to the catalyst should be interchanged
Page 993, reference 19 should read: White, D. M. *J. Am. Chem. Soc.* 1960, 82, 5678; Brown, Jr J. F. and White, D. M. *J. Am. Chem. Soc.* 1960, 82, 5671
Page 994 reference 46: *for* Kirsch Yu. E., *read* Kirsh, Yu. E.; reference 68: *for* Isio, G. A., *read* Audisio, G.; references 61, 77 and 86 *for* Urgu, T. *read* Uryu, T.
Throughout the text *for* $4(\text{mm})(\text{rr})(\text{mr})^2$ *read* $(\text{mm})(\text{rr})(\text{mr})^2$
We apologise for the omission of these printers and authors errors at the proof stage.