



New Comb-like Polyamides and Polyesters

Sergei M. Fomin, Svetlana A. Makarova, Irina A. Volegova, Elena V. Pastyshenko, Alla N. Flerova and Eduard N. Teleshov

L. Ya. Karpov Physico-Chemical Research Institute, 103064 Moscow, Russian Federation. Fax: +7 095 975 2450

The synthesis of new *para*-structured aromatic polyamides and polyesters, containing a rigid-rod backbone and rigid-rod side chains, is described.

Dowell proposed^{1,2} that *p*-linked polymers containing regularly repeated mesogenic side chains could form three dimensional ordered structures, in which both the main and the side chains would be ordered. As a result, these polymers should possess better mechanical properties than those of ordinary liquid crystalline (LC) polymers. Only one report on the synthesis of polymers according to Dowell's idea has been published to date.³ In this paper the synthesis of poly(*p*-phenyleneterephthalamide) (PPTA), containing long heterocyclic substituents

attached to the terephthalic acid moiety, was described. Substituted terephthalic acid dimethyl ester was reacted with *p*-phenylenediamine at 300 °C, but only oligomers were obtained by this method ($\eta_{inh} = 10 \text{ cm}^3 \text{ g}^{-1}$).

We attempted to prepare high molecular weight polymers according to Dowell's proposal in order to investigate their structure and mechanical properties. This communication describes the synthesis of these polymers, which consist of an aromatic *p*-linked backbone with long aromatic side chains.

The polymers were obtained *via* polycondensation of new substituted terephthalic acid dichlorides and *p*-phenylenediamine or hydroquinone, respectively. The syntheses of both monomers and polymers are shown in Schemes 1 and 2, respectively.†

The IR spectra of polyesters **9a,b** showed an absorption band at 1735 cm^{-1} ($\text{C}=\text{O}$ ester) and no absorption band corresponding to the carboxylic carbonyl group (1690 cm^{-1}) was observed. The IR spectrum of polyester **9b** showed an absorption band at $2800\text{--}3000\text{ cm}^{-1}$ which was attributed to C—H vibration of the *n*-butoxy group. In the IR spectrum of polyamides **11a,b** absorption bands at 1670 and 1735 cm^{-1} were observed, corresponding to amide and ester carbonyl groups, respectively. In addition, the spectrum of **11b** showed an absorption band in the region of $2800\text{--}3000\text{ cm}^{-1}$, corresponding to C—H vibration of the *n*-butoxy group. There was no absorption band at 1690 cm^{-1} in the spectra of polyamides **11a,b** corresponding to a carboxylic carbonyl group.

Polyamides **11a,b** are soluble in NMP apart from PPTA which was soluble only in conc. sulphuric acid. This observation confirms Dowell's conclusions^{1,2} that rigid rod polymers, containing long rigid side groups are more soluble than unsubstituted ones. The incorporation of a butoxy group into the

† *Experimental procedure:* 4-(Benzoyloxy)benzoic acid **3a** and 4-(benzoyloxy)benzoyl chloride **4a** were prepared according to ref. 4. T_m 216–217 and 129–130 °C, respectively.

4-(4-*n*-Butoxybenzoyloxy)benzoic acid **3b**: to 4-hydroxybenzoic acid (4.77 g, 34.5 mmol) in 40 ml of pyridine, 4-*n*-butoxybenzoyl chloride (7.35 g, 34.5 mmol) was added with stirring at 5 °C. After 15 h the reaction mixture was poured into cold diluted HCl, filtered and the product was recrystallized from acetic acid. Yield 80%, T_m 140–143 °C; IR ν/cm^{-1} : 2900 (C—H aliphatic), 1735 ($\text{C}=\text{O}$ ester), 1690 ($\text{C}=\text{O}$ carboxylic).

4-(4-*n*-Butoxybenzoyloxy)benzoyl chloride **4b**: acid **3b** (5.3 g, 16.9 mmol) was refluxed with a mixture of SOCl_2 (20 ml), CCl_4 (40 ml) and *N,N*-dimethylformamide (DMF) (two drops). After refluxing for 6 h, the solvent was removed under vacuum and the residue was recrystallized from a mixture of heptane (20 ml) and 1,1,2,2-tetrachloroethane (TCE) (10 ml). Yield 50%, T_m 120–122 °C; IR ν/cm^{-1} : 2900 (C—H aliphatic), 1780 ($\text{C}=\text{O}$ acid chloride), 1735 ($\text{C}=\text{O}$ ester).

2-(4-*n*-Benzoyloxybenzoyloxy)terephthalic acid **6a**: to hydroxyterephthalic acid (1.38 g, 7.6 mmol) in *N*-methylpyrrolidone (NMP) (20 ml) pyridine (10 ml) was added, followed by acid chloride **4a** (2.0 g, 7.67 mmol) at 0 °C with stirring. After 15 h the reaction mixture was poured into dilute H_2SO_4 , the precipitate was filtered, washed with cold water, dried under vacuum and recrystallized from acetic acid. Yield 60%, T_m 251 °C.

2-[4-(Butoxybenzoyloxy)benzoyloxy]terephthalic acid **6b** was synthesized in a similar way to **6a** from **4b** (1.88 g, 5.65 mmol) and hydroxyterephthalic acid (1.03 g, 5.65 mmol). Yield 62%, T_m 253 °C.

4-(Benzoyloxybenzoyloxy)terephthaloyl dichloride **7a**: diacid **6a** (7.2 g, 17.7 mmol), CCl_4 (100 ml), SOCl_2 (10 ml) and five drops of DMF were refluxed for 7 h, the solvent was removed under vacuum and residue recrystallized from CCl_4 . Yield 93%, T_m 127–129 °C.

2-[4-(4-Butoxybenzoyloxy)benzoyloxy]terephthaloyl dichloride **7b** was synthesized in a similar way to **7a** from **6b** (5.56 g, 11.6 mmol). Yield 64%, T_m 125–127 °C.

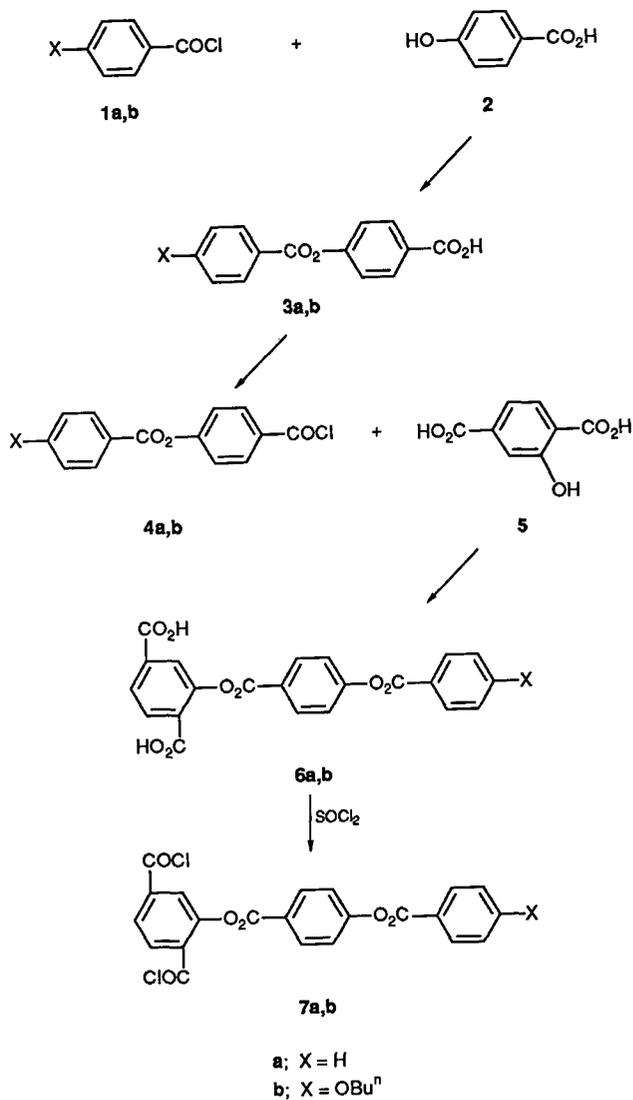
Polymer **9a**: to hydroquinone (1 mmol, 0.1101 g) in 5 ml of freshly distilled TCE was added triethylamine (2 mmol, 0.28 ml) followed by **7a** (1 mmol, 0.4432 g) at 0 °C with stirring under argon. The reaction mixture was kept at 25 °C for 3 h, and diluted with acetone (100 ml). The polymer was filtered off, washed with water and acetone and dried under vacuum at 100 °C. Yield 95%, η_{inh} $241\text{ cm}^3\text{ g}^{-1}$ (0.5% solution in TCE–phenol (40:60 by wt.) at 25 °C).

Polymer **9b** was prepared in a similar way to **9a**, yield 94%, η_{inh} $64\text{ cm}^3\text{ g}^{-1}$ under the above-mentioned conditions.

Polymer **11a**: to a solution of *p*-phenylenediamine (1 mmol, 0.1081 g) in 5 ml of freshly distilled NMP, **7a** (1 mmol, 0.4432 g) was added with stirring under argon at 0 °C. After 20 min stirring the very viscous solution was poured into water and the polymer was filtered, washed with distilled water and dried under vacuum at 100 °C. Yield 98%, η_{inh} $287\text{ cm}^3\text{ g}^{-1}$ (0.5% solution in NMP at 25 °C).

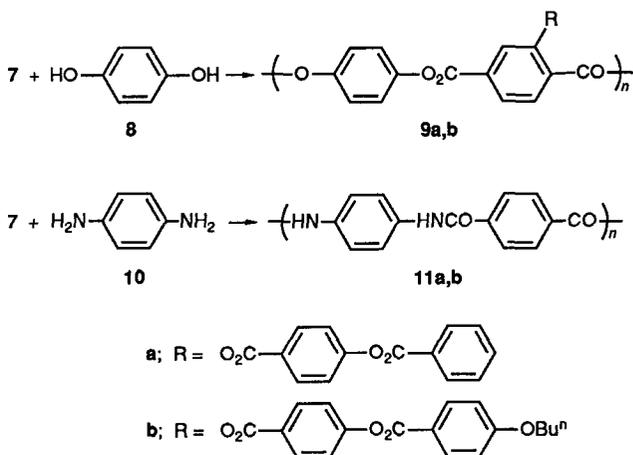
Polymer **11b** was prepared in a similar way to **11a**. Yield 96%, η_{inh} $191\text{ cm}^3\text{ g}^{-1}$ under the above-mentioned conditions.

Satisfactory elemental analyses were obtained for compounds **6a,b**, **7a,b**, **9a,b** and **11a,b**.



Scheme 1

substituent increases the solubility. Thus, polymer **11a** ($\eta_{inh} = 287\text{ cm}^3\text{ g}^{-1}$) is soluble in NMP only up to 5%, while polymer **11b** easily forms a 20% solution. Similar property changes have been observed for PPTA on alkoxy or phenyl substitution.^{5,6} Poly(*p*-phenyleneterephthalate) (PPTP) is infusible and is insoluble in any solvent without decomposition.⁷ Polymers **9a,b** are substituted PPTP and these polymers are



Scheme 2

both fusible and soluble. As in the case of PPTA, PPTP substitution improved the processibility of the polymers. Differential scanning calorimetry for polymers **9a,b** the T_m was 290 and 275 °C, respectively (endotherm maximum). Polymers **11a,b** are infusible. Fusion endotherms were registered only on the initial heating cycle for 'as made' samples. It is probable that the melting and subsequent cooling of fresh samples leads to glass formation. We prepared samples of polymer **9a** with η_{inh} in the range 50 to 241 cm³ g⁻¹. Increase in η_{inh} does not affect T_m in this viscosity range, but it does affect the enthalpy of fusion: the greater the viscosity, the lower the enthalpy of fusion. High molecular weight samples possess a smaller degree of crystallinity than samples of low molecular weight. This leads to a decrease in the enthalpy of fusion for high molecular weight polymers.

Solutions of **11a,b** in NMP were cast to form tough films. High quality films were obtained from solutions of **9a** in CH₂Cl₂-CF₃CO₂H (1:1 by volume). Polymer **9b** gave brittle films because of its low viscosity. It is noteworthy that polyesters **9a,b** degrade in solution. For instance, in CH₂Cl₂-CF₃CO₂H, η_{inh} of polyester **9a** changed from 190 to 91 cm³ g⁻¹ after 3 h at room temperature. Almost the same degradation took place in phenol-TCE, but other solvents did not dissolve

these polymers. The IR of the spectra polymers exhibit neither of the absorption bands corresponding to the end groups. This suggests a fairly high molecular weight for our polymers. This conclusion is confirmed by the preparation of tough, flexible films from polymers **9a** and **11a,b**.

Preliminary dynamic mechanical loss data give a value for moduli unoriented films of polymers **9a** and **11a,b** of 2.0, 5.5 and 4.9 GPa, respectively at 20 °C.

Received: Moscow, 20th May 1991

Cambridge, 17th July 1991; Com. 1/03360K

References

- 1 F. Dowell, *J. Chem. Phys.*, 1989, **91**, 1313.
- 2 F. Dowell, *J. Chem. Phys.*, 1989, **91**, 1326.
- 3 R. Brian and C. Benicewicz, *Polym. Bull.*, 1990, **23**, 477.
- 4 G. Stacy, R. Mikulec, C. Bresson and L. Starr, *J. Org. Chem.*, 1959, **9**, 1099.
- 5 M. Ballauff, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 93.
- 6 J. Jadhov, J. Preston and W. Krigbaum, *J. Polym. Sci., Polym. Chem. Ed.*, 1989, **27**, 1175.
- 7 W. Jacson, *Br. Polym. J.*, 1980, **12**, 154.