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Novel Aromatic Rigid-rod Comb-like Polyamides and Polyesters

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The synthesis of novel *para*-structured aromatic polyamides and polyesters containing mesogenic side groups is described.

Recently we reported the synthesis of rigid-rod aromatic comb-like polyesters and polyamides having rigid-rod mesogenic ester side groups.[1] These polymers were found to be soluble in common solvents and fusible (polyesters) unlike unsubstituted ones. Tough, flexible films were obtained from the solutions and from the melts (polyesters). Polymers were prepared by polycondensation of monosubstituted terephthaloyl dichloride and *p*-phenylenediamine or hydroquinone. The goal of the work presented is to synthesize rigid-rod polymers containing symmetrically-disposed rigid-rod substituents and to compare their properties with those of the unsymmetrically substituted ones described in ref. 1. Moreover, we describe the synthesis of rigid-rod polymers having 4-carboxybiphenyl side groups in order to study the effect of side groups other than (4-benzoyloxy)benzoyloxy on the properties of such types of polymer. We attempted to synthesize a series of polyamides and polyesters containing substituted terephthalic acid moieties in the polymer chain, based on substituted terephthaloyl dichloride and *p*-phenylenediamine or hydroquinone. The synthetic procedure is shown in Scheme 1.† All mesogenic side groups were connected to the polymer chain *via* ester groups. The key stage of monomer synthesis was acylation of hydroxyterephthalic **8** or 2,5-dihydroxyterephthalic **1** acids with acid chlorides **7** or **2**, respectively. Reactions were carried out in pyridine–*N*-methylpyrrolidone (*N*-MP) mixtures at 0°C. Acid dichlorides **2** and **7** were prepared according to the methods described in refs. 2 and 3, respectively. Substituted terephthalic diacids **3** and **9** were converted into acid dichlorides **4** and **10** by treatment of the diacids with boiling thionyl chloride in the presence of traces of DMF. Diacid dichloride **4** was very poorly soluble, even in boiling thionyl chloride, and at the end of the reaction it was filtered off from the hot thionyl chloride and recrystallized from xylene. Diacid dichloride **10** was prepared in carbon tetrachloride solution in the presence of a slight excess of thionyl chloride and traces of DMF. The monomer was recrystallized from hexane. At first we attempted to prepare polyamide **14** from monomer **4** and *p*-phenylenediamine in *N*-MP solution but the polymer was insoluble in this solvent and was precipitated from the reaction mixture during the course of the reaction.

A homogeneous solution was formed when polycondensation was carried out in a 5% LiCl solution of *N*-MP. The resulting polymer was insoluble in *N*-MP but was soluble in LiCl or CaCl$_2$ *N*-MP solutions. We failed to prepare high molecular weight polymer **14** ($\eta_{inh} = 520$ cm^3 g^{-1}) probably because of poor diacid dichloride solubility in the reaction media. Nor could we prepare films from solution because salt precipitation took place before film had formed when a polymer solution was cast into a 5% LiCl–*N*-MP mixture. If we compare the solubility of polymer **14** with that of the polymers described in ref. 1, which contain only one side group in the terephthalic acid core, one can see a decrease in polymer solubility upon introducing a second group into the terephthalic acid moiety. We believe that above-mentioned phenomenon arises from symmetrical disposition of the substituents in the polymer **14** unlike the unsymmetrical distribution in the polymers described in ref. 1. Polyester **13** prepared from monomer **4** and hydroquinone was synthesized by two methods. The first one was a high-temperature polycondensation (200–250°C) in diphenyl ether solution to give an insoluble and non-fusible polymer which was gradually precipitated from the reaction mixture. We assume that cross-linking *via* transesterification took place during the high-temperature polycondensation. The second polycondensation method was a low-temperature solution polycondensation carried out in pyridine at 50°C for several hours. Polymer was precipitated from solution in the course of the reaction simultaneously with diacid dichloride **4** dissolution. The obtained polymer **13** had a low molecular weight ($\eta_{inh} = 220$ cm^3 g^{-1}) and was soluble in CF$_3$COOH–CH$_2$Cl$_2$ mixtures. The low molecular weight of polymer **13** was attributed to poor polymer solubility in pyridine.

More processable polymers were prepared on the basis of monosubstituted derivatives of terephthalic acid **10**. Polyamide **12** prepared according to Scheme 1 in *N*-MP at 0°C was very soluble in *N*-MP. Flexible and tough films were prepared by casting a polymer solution in *N*-MP onto a glass slide. The tensile and strength modulus of such films were found to be 4 GPa and 104 MPa, respectively. Polyester **11** was prepared by low-temperature polycondensation in 1,1,2,2-tetrachloroethane (TCE) in the presence of triethylamine. Polymer **11** was insoluble in reaction media and was precipitated from the solution as a gel in the course of polycondensation. Polymer **11** was soluble in CF$_3$COOH–CH$_2$Cl$_2$; η_{inh} 500 cm^3 g^{-1}. The comparatively low viscosity of polymer **11** was caused by poor solubility of polymer **11** in the reaction media.

In the IR spectra of all polymers synthesized an absorption band due to ester carbonyl at 1735 cm^{-1} is present and an absorption band at 1690 cm^{-1} corresponding to carboxy end groups is absent. In the IR spectra of polyamides **12** and **14** a

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† *Experimental procedure.* 2,5-*Bis*[(4-*benzoyloxy*)*benzoyloxy*]*terephthalic acid* **3**. A mixture of pyridine (10 ml), *N*-MP (17 ml) and 2,5-dihydroxyterephthalic acid **1** (0.68 g, 3.43 mmol) was heated to 60°C so as to obtain a clear solution. The mixture was cooled to −10°C and acid chloride **2** (1.79 g, 0.687 mmol) was added at once with stirring and the reaction was allowed to continue for 5 h at 0°C. The reaction mixture was poured into water and the resulting precipitate was filtered off and recrystallized from dioxane–acetic acid (1:1). Yield 62%, m.p. 260–261°C (decomp.) (Found: C, 66.43; H, 3.86. Calc. for $C_{36}H_{22}O_{12}$: C, 66.87; H, 3.43%).

2,5-*Bis*[(4-*benzoyloxy*)*benzoyloxy*]*terephthaloyl dichloride* **4**. Diacid **3** (3.5 g), freshly distilled thionyl chloride (50 ml) and several drops of DMF were refluxed for 3 h. The obtained precipitate was filtered off under argon flow and recrystallized from xylene. Yield 44%, m.p. 212–215°C. (Found: C, 63.21; H, 3.01. Calc. for $C_{36}H_{20}O_{10}Cl_2$: C, 63.27; H, 2.95%).

(4-*Biphenylcarbonyloxy*)*terephthalic acid* **9**. To a mixture of pyridine (20 ml), *N*-MP (20 ml) and hydroxyterephthalic acid **8** (2 mmol) was added acid chloride **7** (2 mmol) with stirring at 0°C. After being stirred for 48 h at 0°C, the reaction was poured into a cold 5% solution of sulphuric acid. The precipitate was filtered off and washed with water to pH 7. Yield 93%, m.p. 257–260°C from acetic acid–dioxane (1:1). (Found: C, 69.29; H, 3.92. Calc. for $C_{21}H_{14}O_6$: C, 69.61; H, 3.89%).

(4-*Biphenylcarbonyloxy*)*terephthaloyl dichloride* **10**. Diacid **9** (1.81 g) was refluxed in a mixture of carbon tetrachloride (5 ml) and thionyl chloride (3 ml) in the presence of several drops of DMF for 10 h. The solution was filtered and solvent was evaporated under reduced pressure. Residue was recrystallized from dry hexane under argon flow. Yield 98%, m.p. 85–87°C. (Found: C, 64.03; H, 2.98. Calc. for $C_{21}H_{12}O_4Cl_2$: C, 63.18; H, 3.03%). In the IR spectra of all acid dichlorides synthesized an absorption band at 1780 cm^{-1} corresponding to the acid chloride carbonyl group was observed and an absorption band at 1690 cm^{-1} corresponding to carboxylic carbonyl was absent.

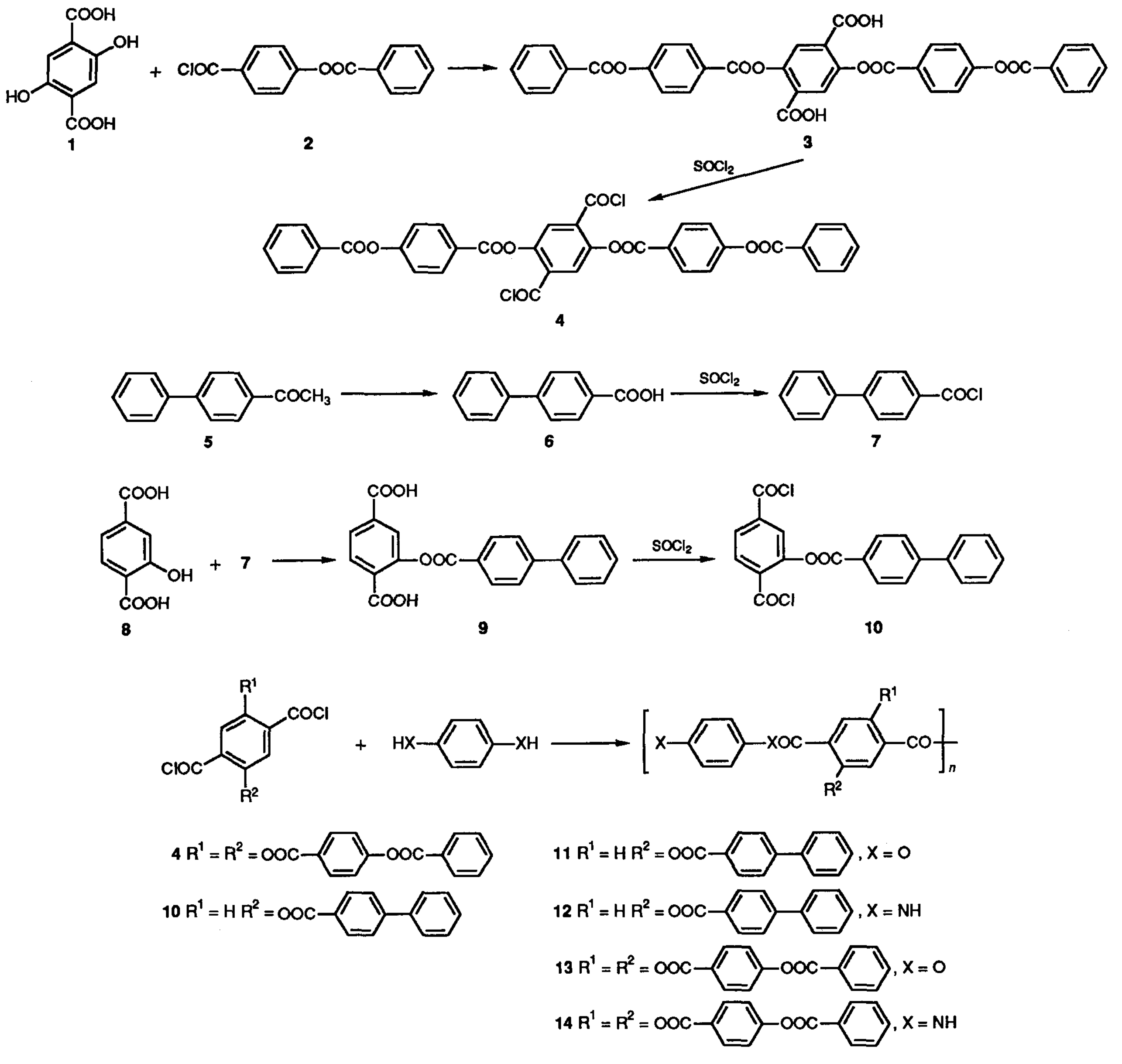
Polyamide **14**. LiCl (0.18 g), dried *in vacuo* at 300°C, and *p*-phenylenediamine (0.2003 g) were dissolved in *N*-MP (9 ml) under argon flow, after which diacid dichloride **4** (1.2656 g) was added at once with stirring at −5°C. The reaction was allowed to continue for 5 h at room temperature. Polymer was precipitated with water, filtered off and dried *in vacuo* at 100°C. Yield 93%, $\eta_{inh} = 520$ cm^3 g^{-1} at 25°C in a 0.5% solution in *N*-MP containing 5% LiCl. [Found: C, 69.18; H, 4.05, N, 4.13. Calc. for $(C_{42}H_{26}N_2O_{10})_n$: C, 70.19; H, 3.65; N, 3.90%].

Polyester **13**. Method A: diacid dichloride **4** (0.4701 g) and hydroquinone (0.0747 g) were dissolved in 6 ml of freshly-distilled diphenyl ether under argon flow. The reaction mixture was stirred at 150°C for 2 h then at 220°C for 3 h. In the course of the reaction polymer was gradually precipitated from the reaction mixture. After being cooled, the reaction was diluted with methanol, and precipitated polymer was filtered off and dried *in vacuo* at 100°C. The polymer was insoluble in common solvents. (Yield 88%.) [Found: C, 69.54; H, 3.33. Calc. for $(C_{42}H_{24}O_{12})_n$: C, 70.00; H, 3.55%].

Method B: to a solution of hydroquinone (0.1841 g) in pyridine (10 ml) under argon flow, diacid dichloride **4** (1.1370 g) was added, dropwise with stirring. The reaction mixture was heated to 50°C and stirred for 4 h at this temperature. After being cooled, the reaction mixture was diluted with ether, and the precipitated polymer was filtered off, washed with water and acetone and dried at 150°C *in vacuo*. Yield 87%, $\eta_{inh} = 220$ cm^3 g^{-1} in CF$_3$COOH–CH$_2$Cl$_2$ (1:1) at 25°C, 0.5% concentration. [Found: C, 69.82; H, 3.44. Calc. for $(C_{42}H_{24}O_{12})_n$: C, 70.00; H, 3.55%].

Polyamide **12**. To a solution of *p*-phenylenediamine (1.4 mmol) in *N*-MP (5 ml) was added diacid dichloride **10** (1.4 mmol) dropwise with stirring, under argon flow at 0°C. The reaction was allowed to continue for 3 h at room temperature after which the reaction was poured into water in order to precipitate the polymer; this was filtered off and dried *in vacuo* at 50°C to constant weight, yield 96%, $\eta_{inh} = 187$ cm^3 g^{-1} in 0.5% *N*-MP solution at 25°C. [Found: C, 73.23; H, 4.08; N, 6.33. Calc. for $(C_{27}H_{18}N_2O_4)_n$: C, 74.65; H, 4.17; N, 6.45%].

Polyester **11**. To a mixture of hydroquinone (1.295 mmol) and TCE (5 ml) was added triethylamine (0.5 ml) under argon flow. After 5 min acid dichloride **11** (1.295 mmol) was added at once with stirring at 0°C and the reaction allowed to continue for 5 h at room temperature. The mixture was then poured into acetone, and the resulting precipitate was filtered off, washed with water and dried *in vacuo* at 50°C, $\eta_{inh} = 50$ cm^3 g^{-1} in CF$_3$COOH–CH$_2$Cl$_2$ (1:1) at 25°C, 0.5% concentration. [Found: C, 74.01; H, 3.58. Calc. for $(C_{27}H_{16}O_6)_n$: C, 74.31; H, 3.70%].



Scheme 1

new absorption band due to the amide carbonyl group appeared at 1670 cm^{-1} in addition to ester carbonyl absorption.

In conclusion, the symmetrical disposition of substituents drastically decreases the solubility of rigid-rod polymers with rigid-rod side groups (polymers **10** and **13**) as compared to unsymmetrically substituted ones described in ref. 1. This may arise from a difference in crystalline structure of the polymers. An X-ray study is now in progress.

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