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The Mumm—Hesse rearrangement in the synthesis of *N*-phenyl-substituted polydiacylamines

V. G. Kotlyarov, V. F. Burdukovskii,★ and D. M. Mognonov

Baikal Institute of Nature,
Siberian Branch of the Russian Academy of Sciences,
6 ul. Sakh´yanovoi, 670047 Ulan-Ude, Russian Federation.
Fax: +7 (301) 243 4259. E-mail: kot666abu@mail.ru, burdvit@mail.ru

Aromatic polydiacylamines (acyclic polyimides) are extremely interesting, but poorly studied class of polymers. It is obvious that *N*-phenyl-substituted analogs are more promising than unsubstituted polymers, first of all, due to their better solubility, thermal stability, and simple recycling.[1] We have shown for the first time a possibility to synthesize *N*-phenyl-substituted polydiacylamines **1** through the Mumm—Hesse rearrangement of polycarboxyimidates **2** (Scheme 1).[2]

It was found that the reaction of imidoyl chloride with aromatic dicarboxylic acid at 70 °C in *N*-methyl-2-pyrrolidone (*N*-MP) for 6—8 h leads to the intermediate polycarboxyimidate, which during further thermal treatment at 150 °C over 10 h is converted to compound **1**. If the reaction is carried out at 120 °C, the target product is directly formed already within 6—8 h. Obviously, in such a method of synthesis compound **2** is transformed to product **1** in the moment of formation.

The structures of *N*-phenyl-substituted polydiacylamines obtained by different methods have no considerable differences and were confirmed by IR and ^{13}C NMR spectroscopic data.[3] The IR spectrum of product **1** (KBr) exhibits an absorption band for C=O at 1791 cm^{-1}, whereas an absorption band for the azomethine group C=N (at 1687 cm^{-1}) is virtually absent. The ^{13}C NMR spectrum (DMSO-d$_6$) of compound **2** exhibits signals for both the azomethine carbon atom C(1) (δ 139.5), and the carbonyl carbon atom C(2) (δ 164.4), whereas in the spectrum of compound **1** an increase in intensity of the signal for the carbon atoms of the carbonyl groups C(2), C(2´) (δ 165.1) is observed, while the signal for the azomethine carbon atom C(1) is absent.

An exothermic effect registered on the DSC curve at 141.9 °C can serve as an indirect confirmation of the rearrangement of polymers.

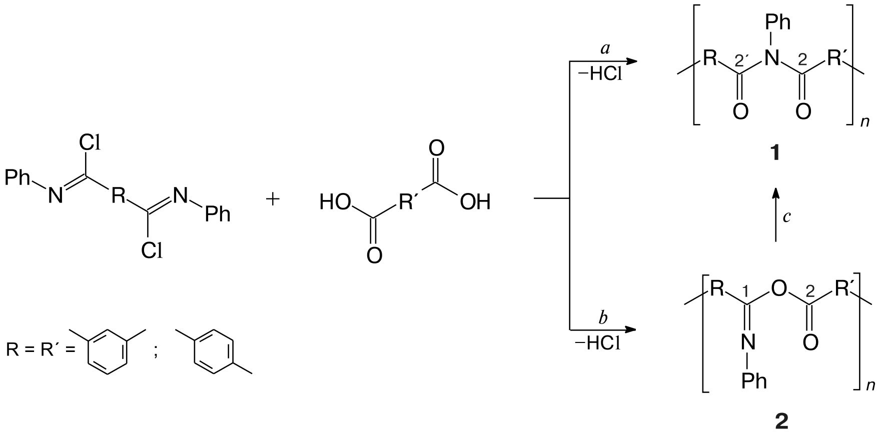
The obtained polymers **1** and **2** are completely soluble without heating in sulfuric and formic acids, as well as in amide solvents (DMF, DMAA, and DMSO).

The polydiacylamines synthesized exceed polycarboxyimidates in their thermal stability. According to the thermogravimetric analysis data (5 °C min^{-1}, air), the 10% loss in weight is observed at 380—410 °C, *i.e.*, at higher temperature than for the corresponding starting polycarboxyimidates (330—370 °C).

Experimental

***N*,*N*´-Diphenylisophthalimidoyl chloride.** Isophthalic acid dianilide (31.6 g, 100 mmol) and thionyl chloride (14.3—21.5 mL, 200—300 mmol) were placed into a two-neck flask equipped

Scheme 1



Reagents and conditions: *a*. *N*-MP, Et$_3$N, 120 °C, 6—8 h; *b*. *N*-MP, Et$_3$N, 70 °C, 6—8 h; *c*. 150 °C, 10 h.

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with a reflux condenser. The mixture was heated in an oil bath to 70—80 °C and kept for 2 h after complete homogenization of the reaction solution. An excess of thionyl chloride was evaporated. The product was recrystallized from octane or hexane. The yield was 94%, m.p. 81.2—81.8 °C. Found (%): C, 67.94; H, 4.27; N, 8.02. $C_{20}H_{14}N_2Cl_2$. Calculated (%): C, 68.15; H, 4.00; N, 7.94. IR, ν/cm^{-1}: 1636 (C=N); 695 (C—Cl).

Polycarboxyimidates were obtained in a 50-mL two-neck flask equipped with a stirrer, inlet and outlet for argon. An acid (1.66 g, 10 mmol) and *N*-MP were sequentially placed into the flask prior filled with argon. Triethylamine (2.8 mL, 20 mmol) and imidoyl chloride (3.53 g, 10 mmol) were added with vigorous stirring. The mixture was placed into an oil bath, and the temperature of the reaction mixture was elevated to 70—80 °C. After the reaction was completed, the product was precipitated into a 2% aqueous ammonia, sequentially washed with 1% aq. sodium disulfite and water, dried in a vacuum drying oven at 60—70 °C until the weight was constant. Characteristic viscosity (η) was 0.24 dL g^{-1} (an Ostwald viscometer ($\varnothing$ = 0.56 mm), DMF, 20 °C). IR (KBr), ν/cm^{-1}: 1687 (C=N); 1710 (C=O); 1212, 1076 (C—O). ^{13}C NMR (DMSO-d$_6$), δ: 139.5 (C(1)); 164.4 (C(2)); 120.4—135.2 (C_{Ar}).

N*-Phenyl-substituted polydiacylamides.** ***A. A sealed tube with polycarboxyimidate (1 g) was heated for 10 h at 150 °C. A polymer obtained was dissolved in DMF upon heating, then precipitated into water, and dried in a vacuum drying oven at 60—70 °C until the weight was constant. The yield was quantitative. IR (KBr), ν/cm^{-1}: 1791 (C=O). ^{13}C NMR (DMSO-d$_6$), δ: 165.1 (C(2), C(2´)); 120.4—135.4 (C_{Ar}).

B. A one-step synthesis was performed in a 50-mL two-neck flask equipped with a stirrer, inlet and outlet for argon. An acid (1.66 g, 10 mmol) and *N*-MP were sequentially placed into the flask prior filled with argon. Triethylamine (2.8 mL, 20 mmol) and imidoyl chloride (3.53 g, 10 mmol) were added with vigorous stirring. The mixture was placed into an oil bath, and the temperature of the reaction mixture was elevated to 120 °C and kept for 8 h. After the reaction was completed, the product was precipitated into a 2% aq. ammonia, sequentially washed with 1% aq. sodium disulfite and water, dried in a vacuum drying oven at 60—70 °C until the weight was constant. Characteristic viscosity (η) was 0.26 dL g^{-1} (an Ostwald viscometer ($\varnothing$ = 0.56 mm), DMF, 20 °C). The yield was quantitative. IR (KBr), ν/cm^{-1}: 1787 (C=O). ^{13}C NMR (DMSO-d$_6$), δ: 164.5 (C(2), C(2´)); 121.7—134.4 (C_{Ar}).

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