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CHEMISTRY

Dependence of the Properties of Fluorine-Containing Poly(phenylquinoxaline) on the Method of Its Preparation

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Abstract—A method of synthesis of new fluorine-containing tetraamine, 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane, has been developed; the tetraamine has been used as the initial compound for preparing poly(phenylquinoxaline)s in both supercritical carbon dioxide and solution. Thermal characteristics of fluorine-containing poly(phenylquinoxaline)s have been studied. There is a bimodal particle size distribution at the used polymer concentration (C_{pol} = 0.1 wt %) according to dynamic laser light scattering data.

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In recent time, scientists succeeded in the preparation of certain polyheteroarylenes in supercritical carbon dioxide ($scCO_2$) used as a solvent and reaction medium in the synthesis of macromolecular compounds [1, 2]. This method provides the preparation of enhanced purity polymers.

Therefore, it seems reasonable to prepare poly(phenylquinoxaline)s (PPQ) as promising synthetic materials for electrooptical devices [3] and organic light-emitting diodes [4] by alternative synthesis in $scCO_2$ rather than classical solution method.

In continuation of our studies [5] in $scCO_2$, we prepared PPQ based on a new fluorine-containing tetraamine and studied certain properties thereof.

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RESULTS AND DISCUSSION

It is known that introduction of fluorine into polymers imparts them solubility, fire resistance, optical transparency, and improved electrophysical properties [6]. In the context of proposed study, we developed a method of synthesis for new tetraamine, 2,2-bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane (**4**) (Scheme 1).

Such compounds are prepared by multistep and low-efficiency methods from 4-nitrochlorobenzene as initial compound.

The use of 5-chloro-2-nitroaniline (**1**) is more attractive and allows one to decrease considerably the number of stages. This precursor is difficult to employ because of its low reactivity in S_NAr reactions [7]. Ultrasound activation considerably facilitates the reaction of aromatic nucleophilic substitution [8]. We used this fact for the preparation of diaminodinitroarene (**3**) (Scheme 1).

The S_NAr reaction of compound **1** with 2,2-bis(4-hydroxyphenyl)hexafluoropropane (**2**) was carried out in an Elmasonic S 10 H ultrasound bath at 80°C in the presence of K_2CO_3 using DMSO as a solvent. Conversion of **1** was 98% after 2 h. Compound **3** was obtained in 94% yield after crystallization.

$H^{5'',5''}$, $J = 8.8$), 6.92 (d, 4H, $H^{3',3'5',5'}$, $J = 8.5$), 7.24 (d, 4H, $H^{2',2',6',6'}$, $J = 8.4$).

For $C_{27}H_{22}F_6N_4O_2$ anal. calcd. (%): C 59.01; H 4.01; N 10.20. Found (%): C 58.94; H 3.98; N 10.23.

Synthesis of Polymers

Poly(phenylquinoxaline)s were prepared in $scCO_2$ according to the work [5] using the corresponding catalysts, the polymers were obtained in solution according to the work [9].

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“УТВЕРЖДАЮ”

Директор ИНЭОС РАН

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ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

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