Synthesis of polyamidines based on 1,4-dicyanobenzene and 4,4´-diaminodiphenyl oxide in ionic liquids

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1,4-Dicyanobenzene and 4,4´-diaminodiphenyl oxide at 190—200 °C in ionic liquids form polyamidines of different molecular weights, whose $T_{10\%}$ in air is in the range 250—270 °C.

Key words: polyamidines, ionic liquids, polymerization.

In recent decades, polymers have found wide application in the creation of optical storage media: light-sensitive materials, electrophotographic and photothermoplastic recording media.[1] The photosensitive polymer systems can be obtained upon formation of supramolecular ensembles of photoactive components that are formed due to the system of ordered hydrogen bonds between fragments of macromolecules. Among these polymers are polyamidines (PAD), which can be involved in effective bicentral binding to form cyclic and linear supramolecular ensembles.[1,2] At the same time, PAD are comparatively new class of polymers; methods of synthesis of these compounds which are scarce. Usually, PAD are obtained by reaction of aromatic diamines with ortho esters.[3] This approach has substantial shortcomings associated with the formation of relatively low-molecular polymers; besides, ethanol is liberated during the polycondensation. Thus, the search for the methods of synthesis of high-molecular aromatic polyamidines by the reactions free from secondary products is certainly of great interest.

The purpose of the present work was the study of a possibility of synthesis of PAD on the basis of 1,4-dicyanobenzene and 4,4´-diaminodiphenyl oxide in ionic liquids (IL).

It is known[4] that the reactions of aromatic dinitriles with diamines are acid-catalyzed additions in which Lewis acids are widely used. Acidic IL on the basis of metal halides can be regarded as an alternative for the traditional heterogeneous and homogeneous catalysts, in particular $AlCl_3$.[5] Besides, the efficacy of IL in the synthesis of different polyheteroarylenes was shown.[6,7] These data altogether in combination with the ability of IL to dissolve different organic compounds (in particular, amines and nitriles) served as the basis for studying the possibility of synthesis of PAD in the ionic media. 1-Alkyl-3-methyl- and 1-butyl-2,3-dimethylimidazolium salts with anions Cl^-, Br^-, $AlCl_4^-$, $Al_2Cl_7^-$, and BF_4^- were used as solvents (Table 1).

The reaction of 1,4-dicyanobenzene with 4,4´-diaminodiphenyl oxide served as a model (Scheme 1).

It was found that in the reactions in mixtures [bmim]Cl/$AlCl_3$ containing 0—1 equiv. of $AlCl_3$, which are, in essence, eutectic mixtures of [bmim]Cl and [bmim]$AlCl_4$, relatively low-molecular products are formed (0.07—0.11 dL g^{-1}, H_2SO_4, 20 °C).

The polymerization rate significantly increases in systems containing 2 equiv. of $AlCl_3$, *i.e.*, under the conditions where it is in fact strongly acidic IL [bmim]Al_2Cl_7 generated from [bmim]$AlCl_4$ and $AlCl_3$ that serves as the reaction medium (Fig. 1).[8]

The reduced viscosity of the obtained PAD depends on the temperature and concentration of the starting monomers. The temperature of 200 °C and the concentration of monomers 1.0 mol L^{-1} are optimal (Fig. 2). Further increase in the temperature and the concentration of the monomers results in noticeable reduction of the molecular weight of PAD.

Under the optimal conditions, the polymerization also occurs in other studied IL (see Table 1). The PAD with the highest molecular weight (η_{sp}) is formed in [bmim]Br and [bmim]Al_2Cl_7, while the η_{sp} of PAD obtained in the

Table 1. The influence of the structure of alkyl substituents in imidazolium cation and the anion nature on η_{sp} of PAD[a]

IL[b]	η_{sp}[c]/dL g^{-1}	IL[b]	η_{sp}[c]/dL g^{-1}
[bmim]Cl	0.07	[bdmim]Al_2Cl_7	0.30
[bmim]Al_2Cl_7	0.55	[bmim]Br	0.59
[emim]Al_2Cl_7	0.19	[bmim]BF_4	0.23

[a] T = 200 °C, 16 h, monomers concentration (C_{mon}) 1 mol L^{-1}.
[b] bmim is 1-butyl-3-methylimidazolium, emim is 1-ethyl-3-methylimidazolium, bdmim is 1-butyl-2,3-dimethylimidazolium.
[c] The reduced viscosity values (η_{sp}) for solutions of polymer (0.05 g) in H_2SO_4 (10 mL) at 20 °C.

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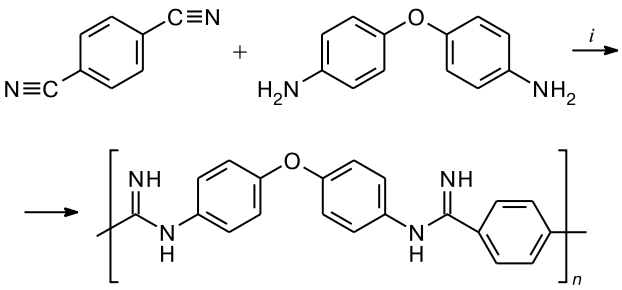
Scheme 1



i. IL, 190—200 °C, 15—17 h.

traditional solvents (nitrobenzene, sulfolan) does not exceed 0.13 dL g^{-1}.

The polymers are completely soluble in concentrated sulfuric and formic acids, as well as in DMF and DMAA under gentle heating. The obtained PAD form brittle films from solutions in HCOOH. According to TGA data (5 °C min^{-1}, air, 10% weight loss), their thermal resistance is 250—270 °C.

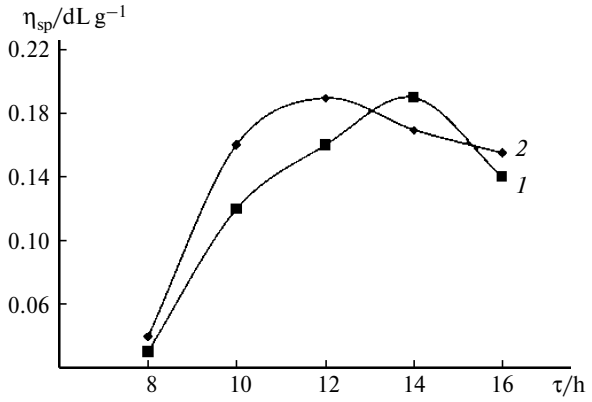


Fig. 1. Dependence of the reduced viscosity of PAD on the IL composition and duration of synthesis; T = 160 °C, C_{mon} = = 0.6 mol L^{-1}, [bmim]Cl : $AlCl_3$ = 1 : 1.1 (*1*) and 1 : 2 (*2*).

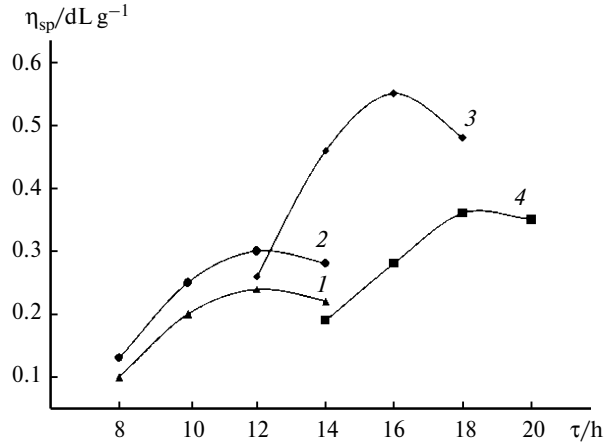


Fig. 2. Dependence of the reduced viscosity of PAD on the monomer concentration and duration of synthesis; T = 200 °C, [bmim]Al_2Cl_7, C_{mon} = 0.6 (*1*), 0.8 (*2*), 1.0 (*3*), and 1.2 mol L^{-1} (*4*).

Experimental

1,4-Dicyanobenzene, 4,4′-diaminodiphenyl oxide, and the IL (Aldrich and Merck) were used without additional purification.

IR spectra were recorded on an Excalibur FTS 3000NX spectrometer (Varian) in the range 4000—400 cm^{-1} in KBr pellets. Proton-noise-decoupled ^{13}C and ^{1}H NMR spectra of polymers were recorded on a Varian VXR-500S spectrometer with working frequency 400 MHz in DMSO-d_6 at a concentration of 10—15 mass.%. The internal standard was Me_4Si.

The reduced viscosity was measured on the Ostwald viscosimeter, diameter 1.31 mm, H_2SO_4, 20 °C; DTA was carried out on an STA 449 C14/G Jupiter TG-DTA/DSC instrument (Netzsch) in air at the heating rate of 5 °C min^{-1}.

Synthesis of polymers. Loading of [bmim]Cl (1.1625 g, 6.6619 mmol), aluminum chloride (1.7787 g, 13.3236 mmol), 1,4-dicyanobenzene (0.12 g, 0.9375 mmol), and 4,4′-diaminodiphenyl oxide (0.18 g, 0.9375 mmol) in a 50-mL flask with a stirrer was carried out under an argon atmosphere. The reaction mixture was vigorously stirred for 16 h at 200 °C, then it was poured into a weakly alkaline solution. The product was filtered out, washed with water, and dried *in vacuo* at 60 °C to constant weight. The polymer yield was quantitative. IR, ν/cm^{-1}: 3400, 3050 (N—H); 1600 (C=N). ^{1}H NMR, δ: 7.2 (C=NH); 7.3 (C—NH). ^{13}C NMR, δ: 149.6 (C=NH).

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