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Dedicated to V. F. Mironov on His 60th Anniversary

Hyperbranched Polyester Poly[3-(morpholin-4-yl)propionates] and Their Copper(II) Complexes

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Abstract—Novel polydentate ligands on the basis of second- and third-generation hyperbranched polyesters containing terminal poly[3-(morpholin-4-yl)propionate] groups and their 6 : 1 and 13 : 1 polynuclear copper(II) complexes were synthesized. The degree of functionalization of the polyesters with morpholine increases in going from the second (56%) to third generation (68%). According to IR and electronic spectroscopy data, each coordination entity in the complexes is an isolated paramagnetic center of the formula $CuN_2O_2Solv_2$ (Solv = H_2O, DMSO).

Keywords: hyperbranched polyester poly[3-(morpholin-4-yl)propionates], copper(II) complexes, ionization, complex formation, electronic absorption spectroscopy

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Chelate ligands containing a few several different donor centers (morpholine, thiomorpholine, and piprazine) are among the most important pharmacophoric compounds [1–3]. Heterocyclic compounds containing nitrogen, oxygen, and sulfur are subunits of biologically active macromolecules [4–6] used as antidepressants [7] and antifungal agents [8, 9]. Metal complexes of such heterocycles have found application as catalysis for the production of polyurethanes, polyamides, epoxide resins, and polyesters [10].

Surface modification of nontoxic hyperbranched polyester polyols with heterocyclic compounds can provide novel functional materials, including therapeutic polymers with desired properties. With this in mind, we synthesized second- and third-generation hyperbranched polyester poly[(3-morpholin-4-yl)-propionates] groups and their copper(II) complexes. The present work continues our research aimed at preparing polydentate macro ligands and polynuclear metal complexes on the basis of hyperbranched polyesters. Earlier we used the hyperbranched polyester polyol platform to synthesize polyamines [11–14], polyester polycarboxylic acids [15–17], and poly-(*N*-phenylcarbamate) [18] capable for self-arrangement and complex formation with *d*-metal ions and drug substrates [13–15, 17, 19, 20].

As the starting compounds we used hyperbranched polyester polyols **1** and **2** containing 16 and 32 hydroxyl groups, respectively. The synthesis of hyperbranched polyester polyols with terminal morpholine fragments involved two stages. First compounds **1** and **2** were reacted with acrylic acid chloride to obtain polyacrylates **3** and **4** (Scheme 1, route *a*). The second stage involved the aza-Michael addition morpholine to polyacrylates **3** and **4** to form hyperbranched polyester poly[3-(morpholin-4-yl)propionates] **5** and **6** (Scheme 1, route *b*).

Analysis of the IR spectra of the starting hyperbranched polyester polyols and synthesized com-