INTRODUCTION

Since their advent at the end of the 20th century [1], macroporous polymer materials, which are synthesized in block and represent a monolithic matrix, have remained the focus of attention of researchers owing to their use in interphase-mass-transfer techniques (chromatography, solid-phase bioanalysis, etc.) [2–6]. The developed sorbents possess a high efficiency related to the improved mass-transfer mechanism associated with the predominance of convection over diffusion. Moreover, as opposed to swellable network polymers, in which porosity is attained when they are placed in a good solvent, the materials under consideration are characterized by constant porous structure that is formed during synthesis and is preserved in the dry state. In addition, among the indubitable advantages of macroporous monolithic materials are their high chemical resistance and mechanical stability, easy synthesis, and a wide range of tunable physicochemical properties.

Although several publications are devoted to the synthesis of macroporous materials with different chemical natures of the polymer matrix, different kinds of surfaces, and different porous characteristics, considerable interest in these materials persists. This situation is primarily related to widening of the scope of their application areas. Polymer monoliths are as a rule prepared via the free-radical copolymerization of monomer (functional monomer) and divinyl (crosslinking agent) monomers in the presence of thermodynamically poor solvents (porogens) [7]. In this case, the pore-formation process may be described as follows. When an initiator decomposes at the initial stages of polymerization, gel-like oligomer particles (cores) form and begin to precipitate from the organic phase owing to the low solubility in porogenes. Under these conditions, the monomeric part of the organic phase is a better solvent than the phase of porogenes for incipient polymer chains, which is favorable for penetration of monomers into the precipitating insoluble cores and continuation of their participation in polymerization proceeding inside cores that gradually achieve the dimensions of microglobules. Then, growing polymer globules unite into clusters held by polymer chains penetrating neighboring particles. At the final stage of polymerization, the dimensions of clusters become sufficient for their mutual contact; as a result, a solid mass is formed inside the polymerization mixture. The resulting matrix gradually strengthens owing to interglobular crosslinks and persistent polymerization. As a result, porous polymer material forms. At this stage, a porogeneous solvent is an individual organic phase that fills voids of the porous polymer mass. The fraction of voids, or macropores, in the final polymer corresponds to the volume fraction of porogeneous solvents in the initial polymerization mixture [7].

One of the main directions of research involves seeking means of controlling the porous structure and properties of the material as a whole. Specifically, the use of special patterns or templates as pore-forming agents, namely, particles insoluble in the polymerization mixture, has aroused considerable interest. In this...
case, the polymer material forms around the introduced particles. Further removal of inert templates from the polymer materials being formed leads to the appearance of voids, that is, macropores, instead of templates. Several studies deal with the use of inorganic templates for the synthesis of macroporous polymer monoliths [8–10], and only a single publication describes the use of organic gel particles as pore-forming agents [11]. Chirica et al. [8] first used silica gel-based particles 3–10 µm in size for the synthesis of macroporous copolymers based on butyl methacrylate, styrene, and divinylbenzene. After completion of polymerization, the final material was washed with concentrated solution of sodium hydroxide to remove the used particles. On the one hand, the hydrodynamic permeability of the materials increased, and, on the other hand, their specific surface area decreased appreciably. To increase the surface area, Jandera et al. [9] used conventional low-molecular-mass porogenes simultaneously with inorganic particles. In this case, the formation of macropores is associated with the existence of large particles in the system, while the presence of organic solvent ensures the conventional formation of micro-, meso-, and macropores during phase separation. Thus, 1-propanol and 1,4-butanediol were used as low-molecular-mass coporogenes along with silica gel particles for the synthesis of a macroporous monolithic material based on the copolymer of butyl methacrylate and ethylene dimethacrylate.

Another interesting example of using inorganic templates for the formation of macropores was described by Du et al. [10]. Granules of sodium sulfate were used as templates, and several organic solvents were employed as coporogenes. The resulting monolithic materials had macropores with a size of up to 6 µm and provided much better permeability than sorbents prepared solely with the use of porogeneous solvents. At the same time, owing to addition of organic solvents in the reaction mixture, the capacity for the subsequent immobilization of adsorptively active ligands decreased insignificantly.

The goal of this study was to investigate the synthesis of macroporous monolithic materials based on copolymers of glycidyl methacrylate and glycerol dimethacrylate (GDMA) and copolymers of butyl methacrylate and ethylene dimethacrylate through the use of monodisperse polystyrene microspheres as templates. These materials were characterized by scanning-electron microscopy, atomic-force microscopy, mercury intrusion porosimetry (MIP), porosimetry based on the intraporous adsorption and desorption of gases, IR spectroscopy, and solid-state NMR spectroscopy.

**EXPERIMENTAL**

**Materials and Instruments**

Glycidyl methacrylate (GMA), glycerol dimethacrylate (GDMA), butyl methacrylate (BMA), ethylene dimethacrylate (EDMA), styrene, 2-hydroxy-2-methylpropiophenone, 2-methoxy-2-phenylacetophenone, dodecanol, cyclohexanol, 1-propanol, and 1,4-butanediol were purchased from Sigma-Aldrich GmbH (Germany). Toluene, methylene chloride, methanol, ethanol, and other organic solvents were purchased from OOO Vekton (Russia). The azo initiators 4,4’-azo-bis(4-cyanovaleric acid) (CVA) and 2,2’-azo-bis[2-(imidazidinyl-2)propane] dihydrochloride were purchased from Waco Pure Chemical Industries Ltd. (Japan). Polyvinylpyrrolidone (PVP) with $M = 3.5 \times 10^4$ was purchased from OOO Farmakon (Russia).

Microspheres were precipitated with the help of an SM-50 centrifuge (Latvia). In radical polymerization experiments, a Philips 125-W mercury lamp (Netherlands) with a wide emission spectrum and a constant intensity was used as a source of UV radiation. The surface morphology of the materials was examined with a JEOL JSM-35 CF scanning electron microscope (Japan) and a VEECO diNanoScope V atomic-force microscope (United States). The porous characteristics were determined with a Pascal 440 Thermoquest Instrument mercury porosimeter (Italy). The IR and solid-state NMR studies of the samples were performed on a Bruker Fourier Transform Infrared spectrophotometer (Germany) and a Bruker Avance-500 (Germany) spectrometer, respectively.

**Methods**

**Monodisperse microspheres.** Monodisperse PS microspheres with different dimensions and surface