MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Sorption of Vapors of Aromatic Compounds by Cross-Linked Polymer Particles Containing Luminophores: A Spectroscopic Study


Received August 24, 2010

Abstract—Monodispersed core–shell particles 290–315 nm in diameter were prepared by seed emulsion copolymerization of styrene with divinylbenzene in the presence of luminophore-containing comonomers. The capability of the particles obtained to sorb toluene vapor was shown by solid-state $^1$H and $^{13}$C NMR spectroscopy.

DOI: 10.1134/S1070427210110200

Growing attention to the development of sensor materials for highly selective detection of organic substances is dictated by the necessity for ensuring safety at chemical enterprises and laboratories, for monitoring of harmful impurities in the atmosphere and in air of inhabited rooms, and also for medical diagnostics [1, 2]. Introduction into relatively cheap polymer matrices of luminophores whose fluorescence spectrum changes upon complexation with organic compounds (solvatochromic effect) is a promising approach to the development of sensor materials with an optical response on the presence of volatile organic compounds in the gas phase [3–11]. Today the technology of molecular imprinting has already been suggested for the development of a new generation of highly selective polymeric sorbents. In the process, template molecules (target analyte or a structurally similar substance) are introduced into the reaction mixture in the step of formation of the cross-linked polymer matrix [5, 12]. Owing to various noncovalent interactions, these molecules are fixed in the polymer matrix and, after the synthesis completion, can be removed from it with the formation of molecular imprints (molecular recognition sites) complementary in the size, shape, and chemical structure to definite organic molecules and hence capable of their selective binding [13, 14].

To enhance the selectivity of sensor polymeric materials with optical response on the presence of an analyte, it seems appropriate to combine both these approaches, i.e., to apply the molecular imprinting technology to make molecular imprints with the participation of luminophore-containing comonomers. In this case, the radical copolymerization should involve the formation of a complex of a template with the luminophore which, in turn, is fixed in the cross-linked polymer matrix owing to incorporation in the polymer chain. After the synthesis completion and template removal, an empty sensor site remains in the immediate vicinity of the luminophore. Molecules structurally similar to the template, when getting into this site from the environment, can be detected by changes in the fluorescence spectrum of the polymer material. Two alternative approaches can be used for the formation of a sensor polymer layer in the presence of a template: polymerization of the monomers in a thin layer directly on the detector of a sensor device [3–5] or preparation of dispersions of particles uniform in size, containing molecular imprints and luminophores, by heterophase polymerization methods, followed by application of these particles onto a sensor panel by jet printing [14]. The latter approach seems to be more technologically efficient, because it makes possible
large-scale production and formation of a bank of polymer particles differing in the size, polymer matrix, type of the incorporated luminophore, and nature of the template used in the synthesis.

The principally important points in the development of sensor materials with optical response on vapors of volatile organic substances are the accessibility of the pore space of the polymer matrix to sorption of analyte molecules and the occurrence of detectable changes in the fluorescence spectrum of the indicator luminophore incorporated in the polymer matrix upon interaction with these molecules. In this connection, our goal was to synthesize luminophore-containing cross-linked monodisperse polymer particles using the molecular imprinting technique, to study the capability of the particles prepared for sorption of vapors of aromatic compounds (with toluene as example) by solid-state ¹H and ¹³C NMR spectroscopy, and to compare the results obtained with the data on changes in the fluorescence of the layers of the same particles in benzene vapor.

EXPERIMENTAL

The monomers, styrene (Akros, St. Petersburg) and MAA (98.5%, BASF, Germany), were purified by distillation following standard procedures. Divinylbenzene (DVB, 80%, Aldrich, Germany), polyvinylpyrrolidone of molecular weight 35000 ± 5000 (Farmakon, St. Petersburg), and sodium dodecyl sulfate (Serva, Germany) were used without additional purification. The initiators were purified by double recrystallization: K₂S₂O₈, from water with washing with ethanol; benzoyl peroxide (BP), from chloroform into methanol; 2,2'-azobis(isobutyronitrile) (AIBN), from ethanol. Analytically pure grade Na₂S₂O₃·5H₂O was used without additional purification. As luminophore-containing comonomers we used fluorescein dimethacrylate (MFI), methacryloyloxyethylthiocarbamoyl Rhodamine B (MRB, Aldrich, Germany), and 2-methacryloyloxy derivative of Nile Red (MNR), prepared by the reaction of methacryloyl chloride with 2-OH derivative of Nile Red, 9-diethylamino-2-hydroxy-5H-benzo[a]phenoxazin-5-one (NR–OH) (Scheme 1).

NR–OH was prepared by the procedure described previously [15] (Scheme 2).

The ¹H NMR spectra, recorded with an Avance-400 NMR spectrometer (Bruker, Germany) at 20°C from 10% solutions in DMSO-d₆, contain a set of signals unambiguously confirming the structure of NR–OH and MNR. The NR–OH spectrum contains a broadened singlet in the region of 10.42 ppm, corresponding to the H-2 proton of OH group, two doublets of equal intensity at 7.96 and 7.87 ppm, belonging to H-4 and H-1 protons, respectively, doublets at 7.08, 7.55, and 6.77 ppm, belonging to H-3, H-7, and H-8 protons, respectively, and a singlet at 6.61 ppm, belonging to the H-6 proton. The aliphatic moiety of NR–OH is manifested as a quartet at 3.48 ppm of 4H intensity, belonging to four H-9 and H-11 protons, and a triplet at 1.15 ppm of 6H intensity, belonging to six H-10 and H-12 protons. In the MNR spectrum, the signals corresponding to hydrogen atoms of the aromatic system and –N(Et)₂ group do not change appreciably their position compared to the related signals in the NR spectrum. In addition, new signals appear: two singlets at 5.9 and 6.1 ppm of 1H intensity and a singlet at 2.0 ppm of 3H intensity, belonging to protons of the methylene (H-2) and methyl (H-3) fragments of the methacrylate group, respectively.

Cross-linked monodisperse core–shell particles with imprints of aromatic molecules and covalently bonded luminophores in the surface layer (Fig. 1) were prepared by seed emulsion copolymerization in an argon...