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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

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

A. Yu. Men'shikova[a], Yu. E. Moskalenko[a], A. V. Gribanov[a], N. N. Shevchenko[a], V. B. Faraonova[a], A. V. Yakimanskii[a], M. Ya. Goikhman[a], N. L. Loretsyan[a], A. V. Koshkin[b], and M. V. Alfimov[b]

[a] *Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia*
[b] *Photochemistry Center, Russian Academy of Sciences, Moscow, Russia*

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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.

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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 ^{1}H and ^{13}C 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

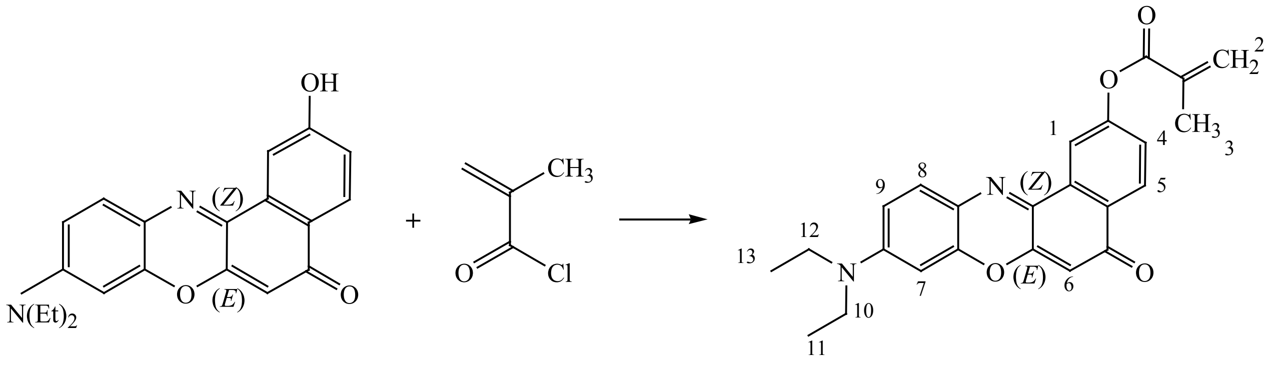
The monomers, styrene (Akros, St. Petersburg) and MAA (98.5%, BASF, Germany), were purified by distillation following standard procedures. Divinylbenzene (DVB, 80%, Aldrich, Germany), polyvinylpyrrolidone of molecular weight 35000 ± 5000 (Farmakon, St. Petersburg), and sodium dodecyl sulfate (Serva, Germany) were used without additional purification. The initiators were purified by double recrystallization: $K_2S_2O_8$, from water with washing with ethanol; benzoyl peroxide (BP), from chloroform into methanol; 2,2'-azobis(isobutyronitrile) (AIBN), from ethanol. Analytically pure grade $Na_2S_2O_3 \cdot 5H_2O$ was used without additional purification. As luminophore-containing comonomers we used fluorescein dimethacrylate (MFl), 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-5*H*-benzo[*a*]phenoxazin-5-one (NR–OH) (Scheme 1).

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

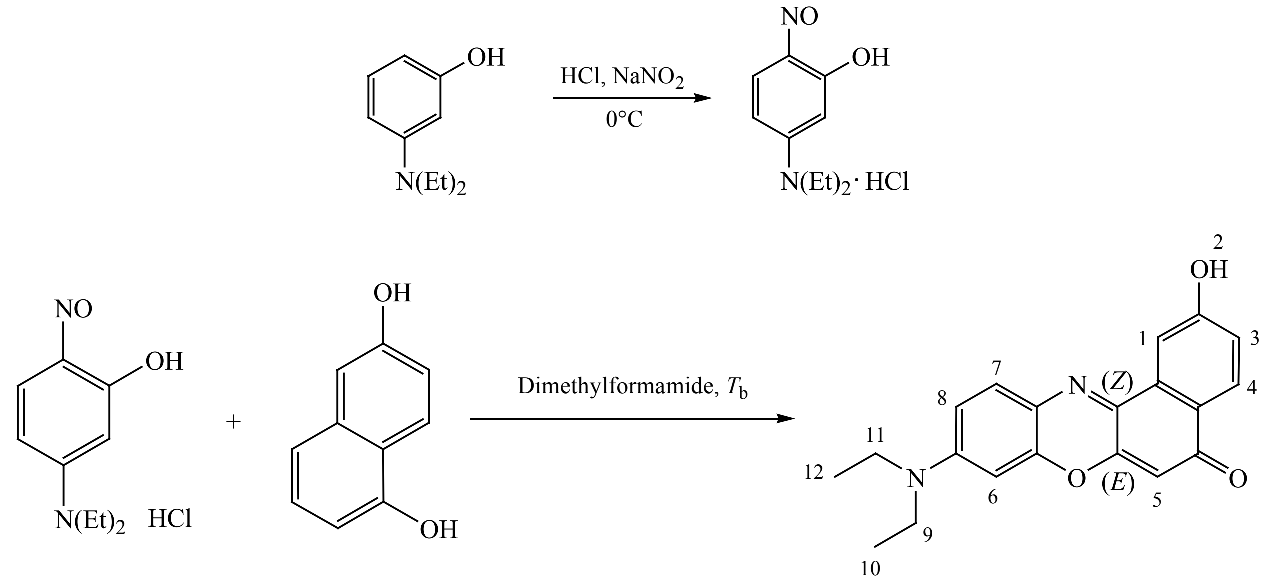
The ^{1}H NMR spectra, recorded with an Avance-400 NMR spectrometer (Bruker, Germany) at 20°C from 10% solutions in DMSO-d_6, contain a set of signals unambiguously confirming the structure of NR–OH and MNR. The NR–OH spectrum contains a broadened singlet in the region of 10.42 ppm, corresponding to 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

Scheme 1.



Scheme 2.



atmosphere. In the first step, following the procedure described previously [16], we formed seeds (Table 1). In so doing, as the main monomer we used hydrophobic styrene ensuring rapid particle nucleation in the course of emulsifier-free emulsion copolymerization and thus formation of polymer dispersion with a narrow particle-size distribution (PSD). In the first step, as functional comonomer we used MAA, which enhanced the aggregative stability of the resulting dispersions in alkaline and neutral solutions owing to ionization of carboxy groups of MAA units in the surface layer of the particles. As cross-linking agent we used DVB. In the first step of the synthesis, its content in the monomer mixture was varied in the interval 5–20 wt % relative to styrene, and in the second step it was increased to 50 wt %, so as to form a rigidly cross-linked polymer matrix and thus to fix the structure of the molecular imprints formed. As aromatic templates we used aromatic impurities present in commercial DVB (20 wt %, mainly diethylbenzenes). As a result, the content of aromatic impurities was 10 wt % of the monomers forming the shell. In the second step, we also introduced into the monomer

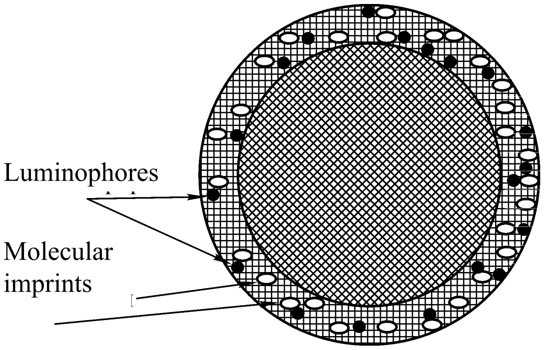


Fig. 1. Scheme of the structure of a core–shell polymer particle with molecular imprints of organic compounds and covalently bonded luminophores in the shell.

Table 1. Synthesis conditions and size of monodisperse seeds

Sample	Copolymerization conditions						D, nm
	T, °C	$(MAA + St)/H_2O$	MAA /St	DVB/St	initiator/monomers	pH_0	
		wt %					
A[a]	80	10	3.6	5	$K_2S_2O_8$, 1.67	10.7	265
B	80	5.5	2.0	20	$K_2S_2O_8$, 2.45; BP, 0.05	11.2	270

[a] Synthesis was performed in the presence of a chain-terminating agent, *o*-diaminodiphenyl disulfide, 0.155 mol % relative to styrene [16].

Table 2. Synthesis conditions and size of cross-linked luminophore-containing core–shell particles

Sample	*T*, °C	Luminophore/shell	Initiator/monomers	Alcohol/water, vol %	pH_0	*D*	*h*
		wt %				nm	
A-1	40	MFl, 0.12	$K_2S_2O_8$, 2.0 $Na_2S_2O_3\cdot 5H_2O$, 1.85	Ethanol, 20	6.8	290	13
A-2	40	MRB, 0.12	$K_2S_2O_8$, 2.0 $Na_2S_2O_3\cdot 5H_2O$, 1.8	Ethanol, 5	6.7	290	13
B-1	70	MNR, 0.12	BP, 2.0	Ethanol, 20	6.8	310	20
B-2	60	MNR, 0.12	AIBN, 2.0	Methanol, 20	6.8	315	22

mixture 0.12 wt % luminophore-containing comonomer (Table 2). The core-to-shell weight ratio was 70 : 30, which was optimal for forming a continuous cross-linked surface layer. Low shell thickness reduces to a minimum the consumption of the luminophore-containing comonomer and makes the sensor sites formed with its participation more accessible to the analyte. In all the experiments, using an ultrasonic bath, we preliminarily prepared a thin emulsion of the monomer mixture in an aqueous solution containing 2 wt % polyvinylpyrrolidone, effective as a steric stabilizer in heterophase polymerization, and 0.234 wt % sodium dodecyl sulfate as anionic emulsifier. To facilitate mass transfer of the monomers of the second step from the emulsion drops to the surface layer of the seeds through the aqueous medium, 5–20 vol % ethanol was added. In the second step of the synthesis, the ratio of the comonomer mixture to the aqueous ethanol phase was 5 wt%. After each step of the synthesis, the residual monomers and aromatic impurities (diethylbenzene) were removed by steam distillation, and then the polymeric dispersion was purified to remove water-soluble impurities by threefold successive centrifugation and redispersion of the particles in double-distilled water.

The diameter of the particles obtained was determined by electron microscopy (JEM 100 S microscope, JEOL, Japan) (Fig. 2).

To examine the structure of the particles obtained

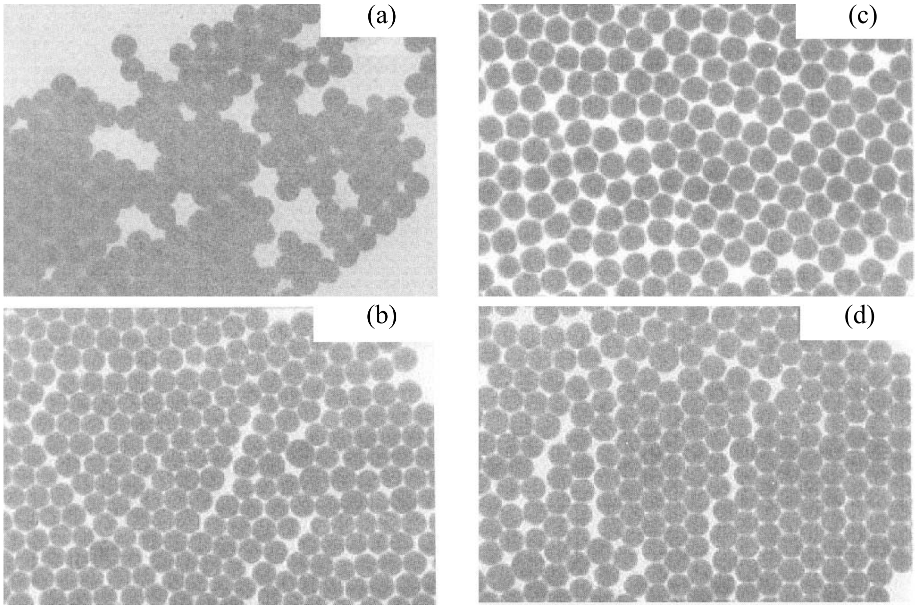


Fig. 2. Electron micrographs of seeds (a) A and (b) B (Table 1) and core–shell particles (c) A-2 and (d) B-1 prepared on their basis (Table 2).

and their sorption power toward aromatic compounds (with toluene as example), we used solid-state ^{1}H and ^{13}C NMR spectroscopy. The NMR spectra were recorded with an Avance II-500 NMR spectrometer (Bruker, Germany) operating at 500 MHz for ^{1}H and 125.7 MHz for ^{13}C. Polymer samples were packed in zirconium rotors 4 mm in diameter. The spectra were recorded at 20°C at a spinning frequency of 8 or 10 kHz. The magic angle was adjusted with KBr, and the chemical shifts were determined relative to external adamantane. The ^{13}C MAS NMR spectra were recorded following the standard program of single-pulse excitation with 6 s delays between $\pi/2$ pulses and proton decoupling. The $^1\text{H}\rightarrow{}^{13}\text{C}$ CP–MAS NMR spectra were taken at a contact time of 4 ms. The composite lines were resolved into components using DMFIT program [17] on the basis of mathematical simulation in which the ratio of the Gauss and Lorentz functions $x\text{G}/(1\text{–}x)\text{L}$ was taken equal to 0.5 for high-resolution lines and to 0.8 for broad lines.

Sorption of toluene vapor on polymeric particles was performed by keeping it in a desiccator with an open vessel with toluene for 24 h. The sorbed toluene was detected by the appearance of the corresponding high-resolution signals in the ^{1}H and ^{13}C NMR spectra. For quantitative interpretation of the sorption values, the intensities of the signals of the toluene CH_3 groups (2 ppm in the ^{1}H spectrum and 21 ppm in the ^{13}C NMR spectrum) were compared with those of the signals of the CH and CH_2 groups in the polymer backbone (0–3 ppm for ^{1}H and 35–57 ppm for ^{13}C).

To prepare layers of polymer particles, onto cover glass (Menzel–Glaser, 24 × 24 mm) we applied a drop (20 μl) of a 1 wt % polymer dispersion. The sample was left at 20°C for 24 h, which was sufficient for complete drying.

To measure the fluorescence response on vapors of organic compounds, the cover glass with a layer of polymer particles was placed in a dark box of volume 1.73 l together with a porous support wetted with a volatile analyte (benzene, methanol, ethanol), so that the concentration of its vapor was of the order of 100 ppm. The sample was kept in the presence of the anlayte vapor for 5–10 min, after which the support with the analyte was withdrawn and the box was purged with a fan. The optical response on the anlayte was recorded by the fluorescence method with an SD2000 fiber optic spectrofluorimeter (Ocean Optics, USA). The excitation light of wavelength 390 nm was transmitted to the sample with a fiber optic system.

Electron-microscopic examination of the polymer particles obtained showed that narrow PSD was attained already in the step of formation of seeds (Figs. 2a, 2b). The same distribution was preserved after synthesis of a rigidly cross-linked shell on them (Table 2; Figs. 2c, 2d). Comparison of the diameters of particles obtained in the first and second steps of the synthesis allowed estimation of the shell thickness, which varied in the range 13–22 nm (Fig. 2, Table 2).

As initiator in the synthesis of samples A-1 and A-2 we used the redox system $K_2S_2O_8/Na_2S_2O_3$ allowing the radical polymerization to be performed at a relatively low temperature (40°C), which increased the probability of complex formation by the template and luminophore in the second step of the synthesis and could ensure the reaction of primary radicals with the luminophore-containing monomers MFl and MRB already in the dispersion medium, with the subsequent capture of the propagating radicals by the seeds. However, A-1 particles did not have the characteristic yellow color, and their layer exhibited no fluorescence. Apparently, under the synthesis conditions the adsorption of MFl (present as the monomer or incorporated in a propagating radical) by seeds is hindered, because MFl is capable of ionization with the formation of carboxylate ion having the like charge with the particle surface. On the contrary, under the conditions of the synthesis of A-2 particles, MRB cations were efficiently incorporated in the shell of negatively charged particles, which is confirmed by fluorescence of their layer in the region characteristic of Rhodamine B.

In synthesis of B-1 and B-2 samples with the participation of a hydrophobic luminophore-containing monomer, MNR, we used oil-soluble initiators BP and AIBN, effecting polymerization only in the organic phase, particle shell, which ensures the preset particle morphology and excludes formation of new nanoparticles not bonded to the seeds. Indeed, samples B-1 and B-2 had thicker shell than samples A-1 and A-2 (Table 2). However, with the peroxy initiator BP, the capability of B-1 particle layer for fluorescence decreased by an order of magnitude and the fluorescence maximum shifted toward shorter wavelengths (Table 3, samples B-1, B-2). This fact indicates that the synthesis under the action of BP can be accompanied by oxidation of the luminophore with the break of its conjugation system. Thus, the use of a peroxy initiator in combination with luminophore-

Table 3. Optical responses of layers of core–shell particles on organic solvent vapors

Sample	Luminophore-containing comonomer	Alcohol in reaction mixture, vol %	Fluorescence maximum wavelength, nm	Fluorescence maximum intensity, arb. units	Response maximum wavelength, nm	Response maximum intensity, arb. units
A-2	MRB	EtOH, 5	580	1565	602, benzene	+175
B-1	MNR	EtOH, 20	582	155	561, benzene	+18
B-2	MHK	MeOH, 20	603	1798	624, benzene	+92
				1884	553, methanol	–74
				1884	553, ethanol	–86

containing comonomers is not appropriate, whereas the azo initiator used in the synthesis of B-2 particles appeared to be quite efficient.

Typical ^{13}C and ^{1}H NMR spectra of the polymer particles obtained are shown in Figs. 3 and 4. The characteristic regions are those of the resonance of the aromatic groups of the polymer (6–8 ppm for ^{1}H and 110–150 ppm for ^{13}C) and aliphatic groups (0–5 and 10–50 ppm, respectively). Comparative analysis of the structure of the weakly cross-linked core (A) and of core-shell particles (A-1, A-2) was performed using the ^{1}H NMR spectra (Fig. 4, spectra *1*–*3*). Notably, in the spectrum of A-1 particles there are high-resolution signals in the range 3.6–5.3 ppm (half-width 25 Hz), whereas A-2 particles are characterized by the presence of high-resolution signals at approximately 1 ppm (half-width 40 Hz). Such small half-widths of lines are typical of highly mobile fragments of organic compounds. Comparative analysis of the ^{13}C NMR spectra also revealed the presence of highly mobile groups manifested

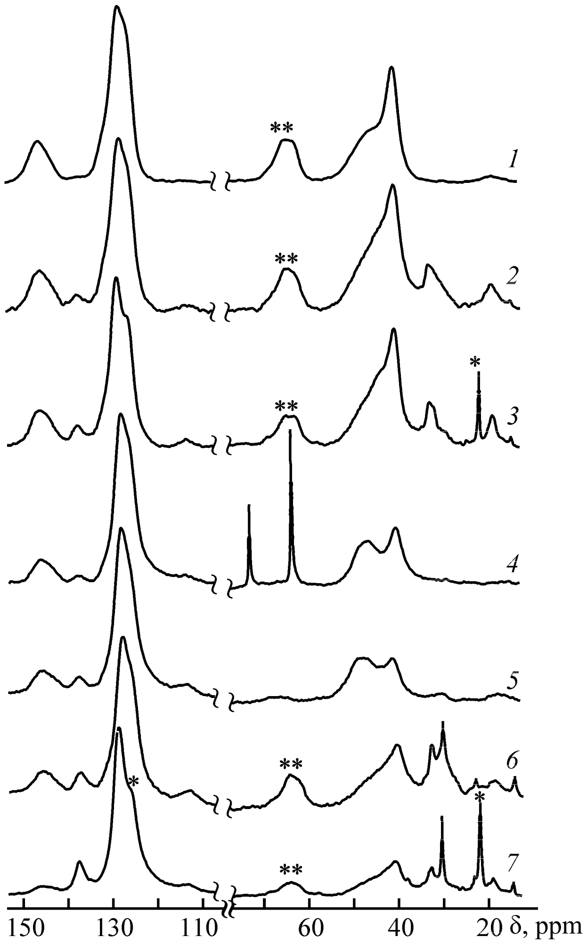


Fig. 3. ^{13}C (*1*–*3*) CP–MAS and (*4*–*7*) MAS NMR spectra of polymer particles: (*1*) seeds A; A-2 core–shell particles (*2, 6*) before and (*3, 7*) after sorption of toluene; (*4*) A-1 and (5) B-1 core–shell particles. Toluene signals (21 and 126 ppm) are marked with one asterisk, and side signals at a rotation rate of 8 kHz, with two asterisks.

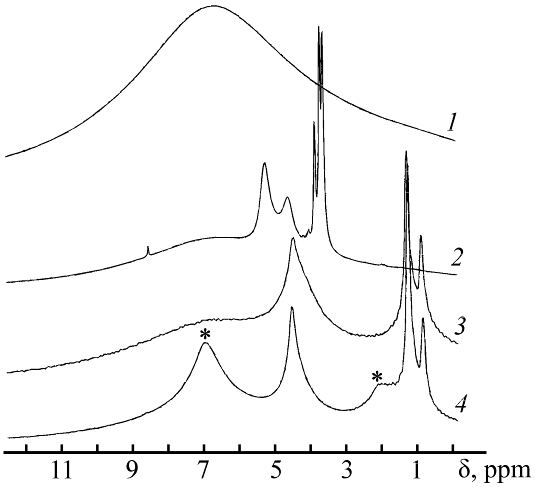
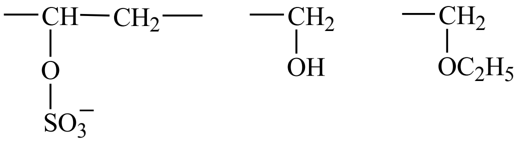


Fig. 4. ^{1}H NMR spectra of polymer particles: (*1*) seeds A; (*2*) A-1 and (*3, 4*) A-2 core–shell particles (*2, 3*) before and (*4*) after toluene sorption. The toluene signals (2 and 7 ppm) are marked with an asterisk.

in the spectra of samples A-1 and A-2 in the ranges 60–70 and 20–30 ppm, respectively (Fig. 3, spectra *4*, *6*). It should be noted that these signals practically are not observed in the ^{13}C CP–MAS NMR spectrum but are well resolved in the ^{13}C MAS NMR spectrum recorded by the standard single-pulse excitation program. This can also be accounted for by relatively high mobility of the corresponding groups. To rule out the possible assignment of these signals to organic solvents sorbed from air, we additionally dried sample A-2 over NaOH, after which the ^{13}C MAS NMR spectrum did not change. This fact suggests that the mobile groups detected are bonded to the polymer matrix. It is known from the literature [18] that high DVB content (about 50%) in copolymerization with styrene ensures only 30–35% effective cross-links. Thus, better resolution of the ^1H and ^{13}C MAS NMR spectra of A-1 and A-2 particles relative to the spectrum of weakly cross-linked A cores may be due to larger amount of terminal groups in branched and cross-linked polymer chains of the shell.

The groups giving in the ^{13}C MAS NMR spectrum a signal at 60–70 ppm can be formed at the polymer chain termini under the conditions of initiation of the emulsion polymerization with the $K_2S_2O_8/Na_2S_2O_3$ redox system as a result of attack of the monomers with primary $SO_4^{\cdot-}$ radicals or of radical transfer to solvent molecules (water, ethanol), followed by attack of the monomers by $\cdot OH$ or $\cdot OC_2H_5$ radicals:



$$-CH(OSO_3^{-})-CH_2- \qquad -CH_2OH \qquad -CH_2OC_2H_5$$

The decreased content of ethanol in the reaction mixture in synthesis of sample A-2 sample compared to A-1 (Table 2) leads to disappearance of the signals of alcohol and ether groups in the range 60–70 ppm from the ^{13}C NMR spectra as a result of lower probability of formation of terminal ether groups in the polymer and to appearance of high-resolution signals of mobile terminal methyl and methylene groups at 20–30 ppm. In the ^1H NMR spectrum, a change in the nature of terminal groups in going from sample A-1 to A-2 is also manifested as a shift of high-resolution signals from 3.6–5.3 to ~1 ppm (Fig. 4, spectra *2*, *3*).

On the contrary, with an oil-soluble initiator, BP, used in the synthesis of B-1 and B-2 particles, the signals of aliphatic terminal groups are absent from the ^{13}C and ^1H NMR spectra.

It should be noted that introduction into a polymer matrix of small amounts of luminophores was not reflected in the NMR spectra of the polymers. The similarity of the spectral characteristics of the polymers, irrespective of the structure of the photoactive component, allowed us to compare the spectra of different samples.

After the sorption of toluene vapor with polymer particles, toluene signals appear in the ^{13}C NMR spectra: the signal of the methyl group at ~21 ppm and that of the aromatic ring at ~125 ppm (Fig. 3, spectra *3*, *7*). The best resolved and suitable for quantitative treatment are ^{13}C MAS NMR spectra, but application of the MAS technique to recording the spectra from nuclei with a low sensitivity (^{13}C) requires much time for the measurement [19]. Therefore, our data were compared with the results of calculating the toluene sorption from the ^{13}C CP–MAS NMR spectra. This technique allows high resolution to be attained in a relatively short time.

The amount of toluene sorbed by A-2 particles, estimated from the ^1H and ^{13}C MAS NMR and ^{13}C CP–MAS NMR spectra, was 0.37, 0.35, and 0.08 molecule per monomeric unit of the polymer chain, respectively. The sorption values calculated from the ^1H and ^{13}C MAS NMR spectra are well consistent, whereas the technique in which the intensity of the ^{13}C NMR signal is determined by the magnetization transfer from protons gives considerably lower value. A similar pattern was observed with samples B-1 and B-2: The toluene sorption, according to ^{13}C MAS NMR data, was 0.26 and 0.30 molecule per monomeric unit, whereas according to ^{13}C CP–MAS NMR data it was as low as 0.03 and 0.06 molecule, respectively. Thus, the NMR data confirm that samples A-2, B-1, and B-2 synthesized using different initiators but having similar nature of the polymer matrix and comparable particle size are characterized by close values of toluene sorption. At the same time, high, according to ^{13}C MAS NMR data, values of toluene sorption by polymer particles that are cross-linked and incapable of swelling seem doubtful. To compare, core–shell particles based on a copolymer of methyl methacrylate with ethylene glycol dimethacrylate sorbed lower alcohols from their saturated vapor in amounts of 0.02–0.08 molecule per monomeric unit, according to ^{13}C NMR data [20]. For various samples, the ratio of the sorption values calculated from the MAS and CP–MAS spectra was in the range 1.03–2.85, whereas for toluene sorption by particles with a polyaromatic matrix this ratio is considerably higher: 4.38–8.67. Apparently, in the system under consideration, toluene sorption was accompanied by toluene condensation from saturated vapor on the surface of particles with the polyaromatic matrix. This assumption is confirmed by the fact that, after the contact with toluene vapor, the samples looked wet. On the contrary, the ^{13}C CP–MAS NMR spectra give more reasonable sorption values close in the order of magnitude to the amount of the template (diethylbenzene) introduced in particle synthesis. However, the ^{13}C CP–MAS NMR data can be used only as estimates, because the magnetization transfer kinetics and, correspondingly, the signal intensities in the spectra are largely determined by the amount of ^{1}H nuclei and by their steric proximity to the ^{13}C nuclei (Overhauser effect).

In the case of samples A-2 and B-2, with sufficient amount of luminophore incorporated in the shell, the layer of particles of these samples also showed optical response on benzene (Table 3). The deviation of the fluorescence intensity from the initial value during 5-min monitoring did not exceed 12%, which is sufficient for detection of this aromatic analyte but, at the same time, suggests its relatively slow diffusion from the gas phase into the cross-linked polymer shell of particles to sites containing luminophore groups. The optical response on benzene of a layer of A-2 particles was appreciably higher than that of a layer of B-2 particles. This may be due to smaller shell thickness, i.e., to better accessibility of molecular imprints in the immediate vicinity of the luminophore to diffusion of the analyte into them. In addition, lower content of ethanol in the reaction mixture in the course of synthesis of A-2 particles decreases the probability of its redistribution from the dispersion medium into the particle shell in the course of the synthesis with the formation of the corresponding molecular recognition sites in accordance with the molecular imprinting technology. The latter assumption was confirmed by detection of the fluorescence response of a layer of B-2 particles on methanol and ethanol in the gas phase (Table 3), whereas the layer of A-2 particles gave no response on lower alcohols. Hence, the presence of a large amount of ethanol in the reaction mixture negatively affects the sensor properties of the particles formed toward the aromatic analyte.

CONCLUSIONS

(1) Seed emulsion copolymerization of styrene with divinylbenzene in the presence of luminophore-containing comonomers allows preparation of core–shell particles of uniform size with the diameter in the submicrometer range, containing in the shell both luminophore groups and molecular imprints of aromatic compounds.

(2) Methods of solid-state ^{1}H and ^{13}C NMR spectroscopy furnish important information both on the structure of the polyaromatic cross-linked particles formed and on their capability to sorb vapors of aromatic compounds (with toluene as example). Increased values of sorption of the aromatic solvent from its saturated vapor, determined by ^{1}H and ^{13}C MAS NMR compared to ^{13}C CP–MAS NMR, may be due to additional condensation of toluene vapor on the particle surface.

(3) Benzene vapor causes changes in the fluorescence of a layer of particles containing luminophore groups in the surface layer. A decrease in the alcohol content in the reaction mixture in the course of formation of particle shells increases the optical response of the particle layer. The particles obtained show promise for the development of sensor materials with optical response on aromatic analytes.

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