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Effect of the Core/Shell Particle Synthesis Method on the Physico–Chemical Properties of Their Shell and Sensory Properties of 3D-Ordered Films

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Abstract: In this work, we investigated the influence of the synthetic conditions of core/shell particles on physico–chemical properties of their shells, the process of self-assembly of particles into 3D-ordered structures, and the sensitivity of films based on these particles to the presence of ethanol and temperature changes. The core/shell particles were prepared by two methods: seed emulsion copolymerization and semi-batch emulsion copolymerization. The cores consisted of polystyrene or its copolymer with methyl methacrylate. Polymer shells of the particles were obtained by copolymerization of methyl methacrylate with several acrylate comonomers: butyl acrylate, butyl methacrylate, propyl acrylate, and ethyl acrylate. The photonic crystal films with the highest sensitivity to ethanol vapors were obtained on the basis of the core/shell particles synthesized by semi-batch emulsion polymerization. It was also established that introducing butyl acrylate or propyl acrylate units into shell copolymers led to an increase in the sensitivity of the resulting photonic crystal films. The films demonstrated a pronounced thermosensitivity only when the corresponding core/shell particles were synthesized as follows: the shell comonomers (methyl methacrylate and butyl acrylate) were introduced into the reaction system during the semi-batch emulsion process in a single step. The intensity of the photonic band gap (PBG) peak for these films decreased by 100% at around 42 °C.

Keywords: thermoresponsive; ethanol-responsive; core/shell particle; photonic crystal; reversible sensor



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1. Introduction

The synthesis of core/shell polymer particles with diameters ranging from 50 nm to 500 nm and the controlled structure of the surface layer is an interesting task both from the theoretical and practical viewpoints. Eventually, these particles may find various applications, such as the development of anti-fouling coatings [1], synthesis of drug carriers [2–6], separation of biologically active or organic substances [7], and purification of biological fluids and wastewater [8]. Another interesting field of application of monodisperse core/shell polymer particles is the development of thin film sensor materials based on photonic crystals (PCs) [9–15]. The fundamental property of a PC is that its permittivity varies periodically in space with a period comparable to optical wavelength. The presence of periodicity in the PC structure leads to the appearance of the photonic band gap (PBG), or the energy range in which propagation of light in a crystal is forbidden in several or all directions. The literature contains many publications concerning the synthesis of core/shell polymer particles and the formation of the PC on the basis of these particles [16–20]. Varying the nature of the shell polymer and the shell thickness makes it possible to obtain the so-called stimuli-responsive 3D-ordered structures, where the position of PBG will be determined not only by the value of core diameter but also by the physico–chemical properties of the

particle shell [21–24]. It should be noted that the sensitivity and selectivity of film-like PC with respect to certain external influences (pressure, temperature, pH, etc.) are based on two processes. First, the physico-chemical properties of the polymer chains localized in particle shells are changed under the action of external factors (that is, chains swell, undergo transition to viscoelastic state, etc.), which leads to changes in either the size of the core/shell particles or in the refractive index of a shell polymer. These processes cause a change in the lattice constant of a photonic crystal structure; as a result, the position of PBG shifts. Varying the lattice constant of PC leads to visual changes in the color of a photonic crystal film [25–28] if the diameter of core/shell particles lies in the 150–350 nm range. In the last decade, particular attention has been paid to the methods of preparation of stimuli-responsive 3D-ordered structures based on core/shell particles with shells containing acrylate comonomers. Pillai et al. [29] described the preparation of polymer PCs of polystyrene@poly(methyl methacrylate-co-acrylic acid)-based core/shell particles. The authors reported that the 3D-ordered film structures obtained on the basis of the synthesized particles demonstrated selective solvatochromic properties in the presence of acetone molecules. Pillai showed that despite the use of a crosslinking agent (ethylene glycol dimethacrylate) in the synthesis of particle shells, this shell swelled selectively (only in the presence of acetone), and the particle size increased by 30 nm. Jianzhong et al. [30] synthesized and studied polystyrene@poly(methyl methacrylate-co-butyl acrylate) core/shell particles. The authors found that the 3D-ordered films based on these particles exhibited solvatochromic properties; they changed color in the presence of ethanol, methanol, and cyclohexane. Over the course of synthesis, various crosslinking agents were introduced both into the cores and shells of the particles. Jianzhong also stated that the effect responsible for solvatochromic properties was based on the change in particle core diameter. Wang et al. described the synthesis of the core/shell particles intended for the preparation of thermosensitive 3D-ordered films [31]. To this end, the core/shell particles with shells containing crosslinked copolymer chains of poly(ethyl acrylate-co-isobutyl methacrylate) were synthesized. The glass transition temperature of polymer chains was determined by the ratio between monomers (ethyl acrylate and isobutyl methacrylate). Wang demonstrated that the developed particles could be used in the development of “smart” labels that change color in the case of improper transportation of food or medical supplies. Schäfer et al. [32] investigated the synthesis of polymer PC that changed their photonic crystal properties under extension. To achieve this, they synthesized the particles with the “core-intermediate layer-shell” structure. Poly(styrene-co-butanediol diacrylate) was selected as a core polymer; the intermediate layer consisted of poly(ethyl acrylate-co-allyl methacrylate), and the shell polymer was poly(ethyl acrylate-co-isobutyl methacrylate-co-hydroxyethyl acrylate). It was shown that extension up to 90% led to a considerable change in Bragg reflection color, which was caused by the transition from the (111) lattice plane to the (200) plane. Zhuoying et al. [33] proposed a simple path to pattern photonic crystals by the clickable photonic crystals built by vinyl-modified sub-micrometer silica particles. Depending on the difference in surface chemical properties, different structure color patterns were revealed under the soaking of the gradient concentration of an ethanol aqueous solution. Zhu et al. [34] investigated the self-organization of thermo-responsive poly(styrene-co-N-isopropylacrylamide) core/shell microspheres. Wei Ma et al. [35] demonstrated that the high-sensitive copolymer-based sensor comprising poly(styrene-ethylene glycol dimethacrylate-acrylic acid) and TiO₂ may be promising for visual detecting and discriminating liquid aromatics—benzene, toluene, ethylbenzene, and xylene. Xia et al. [36] developed a simple and scalable method to realize hydrogel fibers with a dynamic structural color using soft and thermoresponsive microgels as photonic blocks.

Thus, the analysis of the literary data shows the interest of researchers in the topic of synthesis of ordered film structures that are “sensitive” to the external environment. However, at the moment, it is not possible to draw a conclusion about the influence of the conditions of the polymerization process during the formation of both the core and the shell on the physico-chemical properties of the resulting core/shell particles.

Previously, we have studied in detail the process of the synthesis of core/shell particles and the formation of films with a 3D-ordered structure on their basis [37,38]. It was shown that when using a mixture of methyl methacrylate and butyl acrylate as shell comonomers, particles with different surface layer morphology were formed: particles with a homogeneous surface layer or golf-ball-like particles. The composition of the polymer chains forming the cores (based on a copolymer of styrene with methacrylic acid or its terpolymer with methyl methacrylate) affects the shell formation process and determines the localization region of the second-stage monomers in the seed cores, the thermodynamic compatibility of the resulting polymer chains of the shell with the polymer chains of the core, etc. Obviously, varying the nature of the second-stage monomers, as well as the conditions of the core/shell particle formation process, has a significant effect on the physico-chemical properties of the particles. Understanding the composition-property relationship in the formation of thin 3D-ordered films will allow the preparation of “smart” labels with specified properties. For example, such “smart” labels can be used to detect changes in the temperature or composition of the environment.

In this work, a systematic study of the synthesis of core/shell polymer particles was performed. The cores were based on polystyrene or copolymer poly(styrene-co-methyl methacrylate); the shells consisted of copolymers of methyl methacrylate with a number of acrylate comonomers: butyl acrylate, butyl methacrylate, propyl acrylate, and ethyl acrylate. All the synthesized particles were characterized by scanning electron microscopy. It was demonstrated that both the core preparation (seed polymerization that includes the isolation and purification of core or semi-batch polymerization conducted without additional isolation of the core followed by the formation of the shell) and the shell preparation techniques (dropwise addition of shell-forming monomers or one-step addition; preliminary emulsification of monomers in a solution of sodium dodecyl sulfate) significantly affect the physico-chemical properties of the formed shell. As a result, the choice of synthetic method for core/shell particles has a great effect on the solvent sensitivity and temperature sensitivity of the obtained PC films. The novelty of this study is that the method of introducing comonomers in the second stage (seed polymerization or sequential emulsion polymerization) affects the composition of the forming polymer chains of the shell is shown for the first time. The method of shell formation determines the sensitivity of films based on the synthesized particles despite the same composition of the monomer phase of the shell.

2. Materials and Methods

Materials. The synthesis of the core/shell particles was carried out using the following monomers: methacrylic acid (MAA), methyl methacrylate (MMA), butyl acrylate (BA), ethyl acrylate (EA), propyl acrylate (PA), butyl methacrylate (BMA), and styrene (St) (all purchased from Sigma-Aldrich (Darmstadt, Germany)). Ethylene glycol dimethacrylate (EGDM) and trimethylolpropane trimethacrylate (TMPTM) were used as crosslinking agents (all purchased from Sigma-Aldrich (Germany)). Thioglycolic acid (TGA), utilized as a chain regulator in the synthesis of polystyrene cores, was used without additional purification (Vekton LLC, St. Petersburg, Russia). Monomers and crosslinkers were purified using standard procedures [37]. Water-soluble potassium persulfate was used as an initiator ($K_2S_2O_8$) (Vekton LLC, Russia), and the initiator was purified by recrystallization from water. N,N,N,N-tetramethylethylenediamine (TEMED) (Sigma-Aldrich (Germany)) was used without further purification. Sodium dodecyl sulfate (SERVA (Heidelberg, Germany)) was used without additional purification. Ethanol (96% vol.) was manufactured by Vekton LLC (Russia) and used without additional purification. Double-distilled deionized water was used to prepare solutions and carry out heterophase polymerization (conductivity not above $0.12 \mu S/cm$ (deionization system VODOLEI-M, Russia)). NaOH solutions were obtained by dissolving NaOH tablets (analytical grade, Vekton LLC, Russia) in double-distilled water after preliminary washing with sodium bicarbonate ($NaHCO_3$), which negatively affects the polymerization process. The exact concentration of NaOH solutions

was determined with conductometric titration (Seven Multi conductivity meter (Metler Toledo, Greifensee, Switzerland)) with a standard HCl solution (analytical grade, Vekton LLC, Russia). NaOH solutions were used for no more than two weeks since during long-term storage they absorb CO₂ from the air.

Synthesis of core/shell particles. The synthesis of the core was carried out using previously published methods [12,32]. The synthesis of core/shell particles was carried out either by semi-batch polymerization or by seed emulsion polymerization.

The synthesis was carried out under a nitrogen atmosphere in a 100 mL flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. Degassed deionized water with an initiator dissolved in it was placed in a glass flask. With constant stirring, half the volumes of MAA and the calculated amount of NaOH solution were added to the flask. After this, a mixture of monomers (St, MMA, and the remaining amount of MAA and TGA (if necessary)) was added to the reaction system. Using a water bath, the required temperature was set. The polymerization process was carried out for 2 h, maintaining the temperature in the reactor constant. The emulsion polymerization conditions of P(St-MAA) and P(St-MMA-MAA) core particles and their characteristics are presented in Table 1.

Table 1. Conditions for the synthesis of P(St-MAA) or P(St-MMA-MAA) core particles.

Acronym	Core-Forming Comonomers	Mn/H ₂ O wt. %	K ₂ S ₂ O ₈ /H ₂ O wt. %	T °C	D *, nm/PDI
Y1	St-MAA	6	2.4	90	260/0.03
Y2	St-MMA-MAA	8	1.3	75	200/0.01
Y3	St-MMA-MAA	8.6	1.3	75	190/0.04

* according to DLS.

The formation of a shell containing acrylate comonomer units was carried out in two ways: semi-batch polymerization or seed emulsion polymerization. During semi-batch polymerization, monomers of the second stage were introduced into the reaction system (dropwise at a rate of 0.2 mL/min) (with the exception of experiment Y3/C8, Table 2) immediately after the synthesis of the core without isolating and purification of the core. The content of second-stage monomers was 50 wt.% relative to the core (the ratio of methyl methacrylate to acrylate comonomer was 1:2.5 wt/wt, 0.5 wt.% crosslinking agent EGDM (or TMPTM) relative to shell monomers). In addition, an aqueous solution of the initiator K₂S₂O₈ (1.2 wt.% relative to the shell monomers) was also additionally introduced into the reaction system. Polymerization was carried out for 2 h. The choice of conditions for the polymerization process is based on previously conducted studies that determine the optimal process parameters [38].

In addition, the formation of core/shell particles was carried out by seed polymerization in two stages. In the first stage, using the method described earlier, P(St-MAA) or P(St-MMA-MAA) cores were formed. The obtained particle cores were cooled to room temperature and further purified from unreacted monomers and water-soluble oligomers. Next, the purified dispersion of particle core (5 wt.%) was placed in a flask and heated in a water bath. After keeping the particle dispersion for 30 min, a mixture of monomers forming the shell was added. After 30 min of swelling, a redox-initiating system K₂S₂O₈–TEMED was introduced (TEMED was not added to the reaction system when the process was conducted at 90 °C). The reaction mixture was kept under heating for no more than 15 min, after which it was cooled to room temperature.

After the polymerization process, unreacted monomers were removed by evaporation under reduced pressure (Rotary Evaporator Laborota4011, Heidolph, Germany). The polymer dispersion of particles was purified from water-soluble oligomers by triple sequential cycles of “centrifugation-redispersion” in bidistilled water (Centrifuge 5804, Eppendorf, Germany).

Table 2. Seed emulsion polymerization conditions for preparation of core/shell particles and their characteristics.

Acronym	The Composition of the Reaction System				Characteristics of Obtained Polymer Core/Shell Particles				Recovery of the Optical Density of PBG After Drying **, %
	Shell-Forming Acrylate Comonomer	Cross-Linker/Mn wt. %	K ₂ S ₂ O ₈ /Mn wt. %	DSNa *	D, nm, (DLS)	PDI	ξ-Potential mV (10 ^{−2} M NaCl)	h, nm	
Y1/C1	BA	TMPTM—0.5	1.2	—	320	0.08	−77	30	83
Y1/C2	BA	EGDM 0.5	1.2	—	315	0.04	−71	30	71
Y2/C3	BA	EGDM 0.5	2	1 CCM	250	0.04	−67	25	100
Y2/C4	EA	EGDM 0.5	2	1 CCM	260	0.03	−53	30	0
Y2/C5	BMA	EGDM 0.5	2	1 CCM	270	0.05	−73	35	6
Y2/C6	PA	EGDM 0.5	2	1 CCM	260	0.01	−61	30	83

h—thickness of the formed shell. Shell synthesis temperature is 50 °C (samples Y2/C3–Y2/C6) and 90 °C (samples Y1/C1 and Y1/C2), 1:2.5 shell monomer ratio (wt.). * Shell monomers were introduced after the preliminary formation of the emulsion. ** Recovery of the photonic band gap of 3D-ordered films after exposure to ethanol followed by drying.

Characterization

Particle size. Particle size and surface morphology were studied using scanning electron microscopy (SUPRA 55 VP microscope, ZEISS AG, Oberkochen, Germany). Measurements of the hydrodynamic diameter of particles using the dynamic light scattering (DLS) method and their ζ-potential were carried out on an analyzer Zetasizer Nano-ZS (Malvern Instruments Limited, Worcestershire, UK). The particles were equilibrated for 2 h before measurements.

ATR-FTIR spectroscopy. Chemical characterization of the dried particles was performed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) using IR-Affinity-1S spectrometer (Shimadzu, Kyoto, Japan). All the spectra were recorded in the range of 400–2000 cm^{−1} and represented an average of 30 scans taken.

Conductometric titration. The concentration of surface functional groups was determined by reverse conductometric titration. Titration was carried out for polymer dispersions purified from water-soluble impurities using a conductometer SevenMulti (Mettler-Toledo GmbH, Greifensee, Switzerland). To determine the concentration of functional groups, an excess of HCl of a known concentration was added to the dispersion of polymer particles and then successively titrated with a 0.01 M NaOH aqueous solution [15].

Preparation of films based on the particles obtained. Three-dimensional-ordered films were obtained based on the synthesized composite particles. A diluted aqueous dispersion of core/shell particles was deposited into a previously cleaned glass substrate and slowly dried in air.

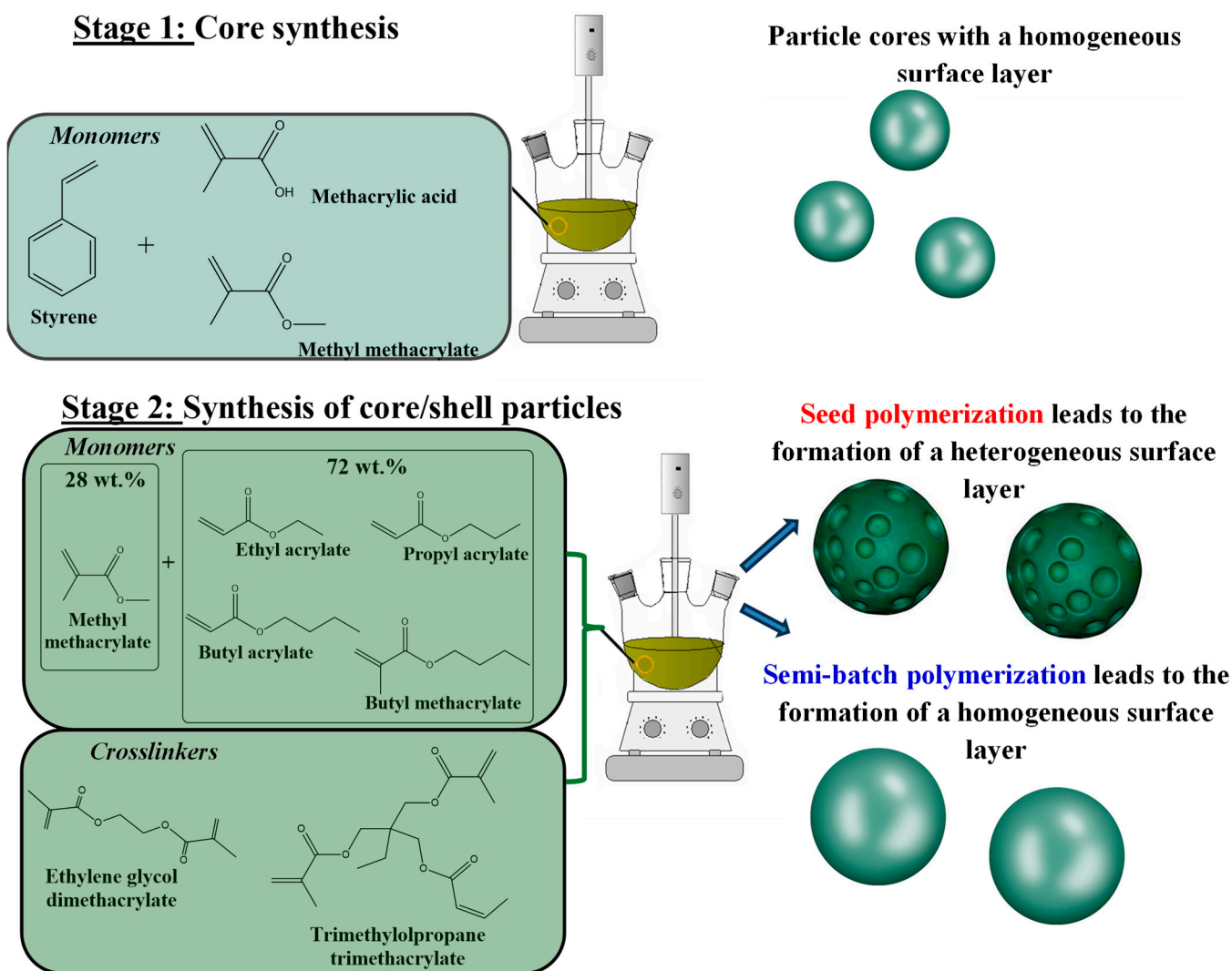
Study of solvatochromic and thermochromic properties. The obtained 3D-ordered films were placed in a quartz cuvette for spectrophotometry, and then an aqueous solution of ethanol was added to the cuvette and it was covered with a lid. Optical absorbance spectra were recorded on a spectrophotometer UV-1900i (Shimadzu, Japan). Absorption spectra of polymer 3D-ordered films depending on temperature change were studied using a spectrophotometer QE65000 (Ocean Optics, Orlando, FL, USA). For this purpose, a special temperature-controlled cell with real-time temperature control was designed. In the cell, the temperature was changed by 1 °C every 2 min. It was previously established that the achievement of an equilibrium state of the film with a temperature change of 1 °C is achieved within 1 min.

Statistics. The experiments were performed with $n = 3–4$.

3. Results

3.1. Synthesis of Core/Shell Particles

In the first series of experiments, the core/shell particles with shells based on methyl methacrylate-butyl acrylate copolymer were obtained. These core/shell polymer particles were synthesized by seed polymerization (Table 2, Scheme 1) according to the technique described in the Section 2. In this method, followed by the synthesis of the core particles, the reaction system is cooled, and the particles are purified from unreacted monomers and water-soluble oligomers. The subsequent formation of the shell occurs on the purified cores, which are placed in the reaction flask together with the monomers of the second stage.



Scheme 1. Formation of core/shell particles.

The first step included the preparation of the cores (Table 1). The diameters of synthesized cores measured by DLS were equal to 260 and 190 nm for P(St-MAA) and P(St-MMA-MAA), respectively (the dispersity of particle core diameters did not exceed 0.04).

The SEM studies showed that the cores of P(St-MAA) and P(St-MMA-MAA) particles were monodisperse spherical particles with a smooth surface layer (Figure 1a–c). The second step consisted of the formation of a shell. Note that in the course of the synthesis of particles Y2/C3 ÷ Y2/C6, methyl methacrylate was introduced both during the formation of a core and a shell. MMA is necessary to provide better compatibility between the forming polyacrylate chains and the polystyrene core. However, as evidenced by the SEM data, the surface layer of particles after polymerization of shell monomers contains a certain

amount of “dents” (“golf ball-like” particles; Figure 1d,e,f). The successful formation of core/shell particles was confirmed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Figure S1).

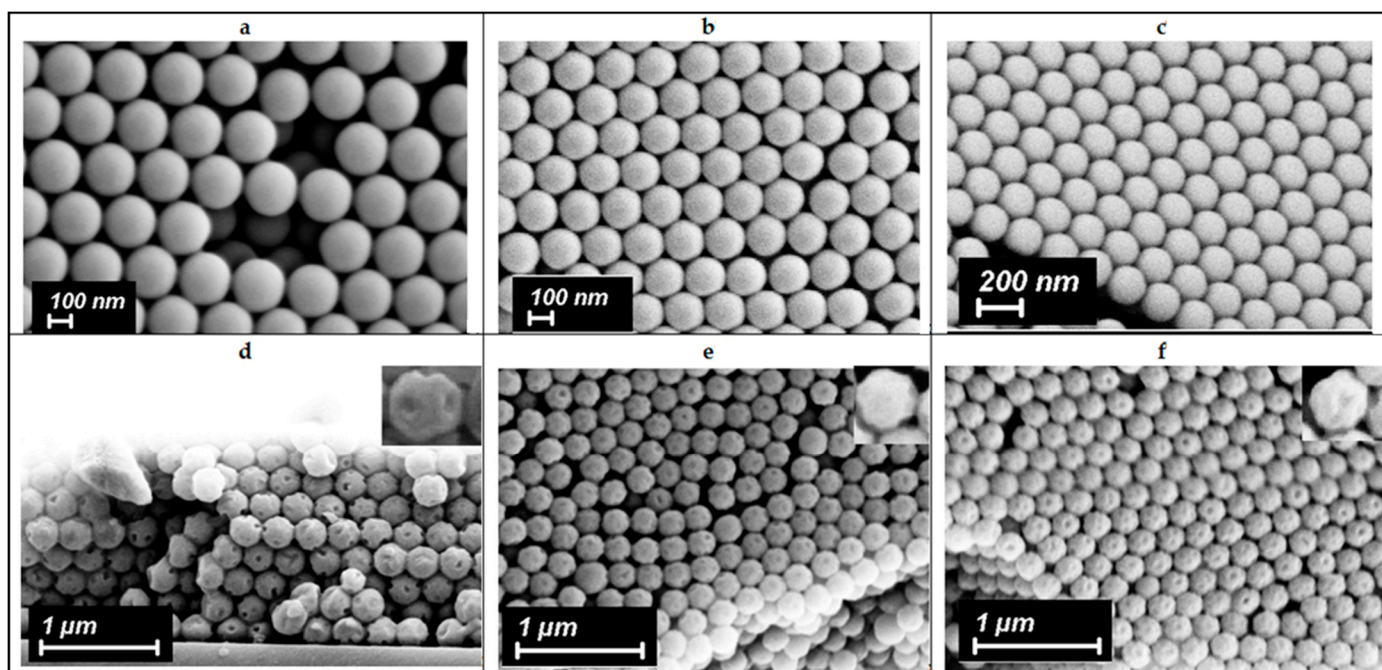


Figure 1. SEM images of core particles Y1 P(St-MAA) (a), Y2 P(St-MMA-MAA) (b), Y3 P(St-MMA-MAA) (c), as well as core/shell particles Y1/C1 (d), Y2/C3 (e), and Y2/C6 (f). The inset shows an enlarged image of the particle.

The variation of such parameters of the reaction system as the nature of the crosslinking agent, reaction temperature, and emulsification condition (introduction of an emulsifier, sodium dodecyl sulfate) does not have an influence on the structure of the surface layer of the formed particles; all particles have dents in the surface layer and differ only in their amount. It was demonstrated that the shell thicknesses (h , nm) in all samples were equal to 25–35 nm. Next, we traced the influence of the nature of the shell-forming acrylate comonomer added to methyl methacrylate on the morphology of the prepared core/shell particles.

Several monomers were investigated: butyl acrylate, butyl methacrylate, propyl acrylate, and ethyl acrylate. It was shown that varying the nature of acrylate comonomer did not result in any significant changes in shell morphology. In all experiments, monodisperse core/shell particles with diameters ranging from 250 to 270 nm with a golf ball-like structure of the surface layer were obtained (Y2/C3, Y2/C4, Y2/C5, and Y2/C6). However, as will be shown in Sections 3.2 and 3.3, the nature of the functional comonomer introduced during the formation of the shell, as well as the composition of the polymer chains of the core, have a significant effect on the physico-chemical properties of films formed on the basis of the synthesized core/shell particles, and consequently on the properties of 3D-ordered films when the composition or temperature of the environment changes.

In the first series of experiments, the use of butyl acrylate in seed polymerization led to the formation of core/shell particles with the most heterogeneous structure of the surface layer. In the second series of experiments, we investigated semi-batch emulsion copolymerization and butyl acrylate also acted as the main comonomer of the second stage. In this method, the formed particle cores were not purified from the formed reaction products (mainly water-soluble oligomers), and the second-stage monomers were added dropwise to the hot cores (0.2 mL/min) (Table 3). It is apparent that, similarly to the first series of experiments, the surface layer of the cores has a homogeneous structure

(Figure 1a,c). It was shown that the variation of such parameters as the composition of the polymer chains of the seed cores, the core/shell mass ratio, and the nature of the crosslinking agent during copolymerization of the shell monomers did not affect the morphology of the formed core/shell particles (Figure 2). The surface layers of the obtained particles Y1/C4, Y1/C5, Y3/C6, and Y3/C7 demonstrate a homogeneous structure. Thus, the formation of core/shell particles by semi-batch emulsion polymerization under the described experimental conditions does not lead to the formation of the “golf-ball like” morphology of the surface layer. It should be noted that in the presence of a crosslinking agent (TMPTM) in the reaction system, a thinner shell was formed (Y3/C6 particles with 10 nm shell layer (according to the DLS data)).

Table 3. Semi-batch emulsion polymerization conditions of core/shell particles and their characteristics.

Acronym	Composition of the Reaction System			Characteristics of Obtained Polymer Core/Shell Particles				Recovery of the Optical Density of PBG After Drying ^{***} , %
	Core:Shell wt. %	(MMA + BA) wt. %	Cross-Linker/Mn wt. %	D, nm, DLS/SEM	PDI	h, nm	ξ -Potential mV (10^{-2} M NaCl)	
Y1/C4	50:50	1:2.5 *	EGDM 0.5	370/330	0.04	77/35	−81	21
Y1/C5	65:35	1:2.5 *	EGDM 0.5	310/220 ÷ 325	0.06	45/32	−80	100
Y3/C6	50:50	1:2.5 *	TMPTM—0.5	230/220	0.03	20/15	−78	77
Y3/C7	50:50	1:2.5 *	EGDM 0.5	309/250	0.03	60/30	−70	78
Y3/C8	50:50	1:2.5 **	EGDM 0.5	270/240	0.01	40/25	−84	0

h—thickness of the formed shell. Shell synthesis temperature is 90 °C (samples Y1/C4, Y1/C5) and 75 °C (samples Y3/C6, Y3/C7 and Y3/C8); concentration of $K_2S_2O_8$ /Mn—1.3 wt.%. *—monomers were added dropwise. **—monomers were added in a single step. *** Recovery of the photonic band gap of 3D-ordered films after exposure to ethanol followed by drying.

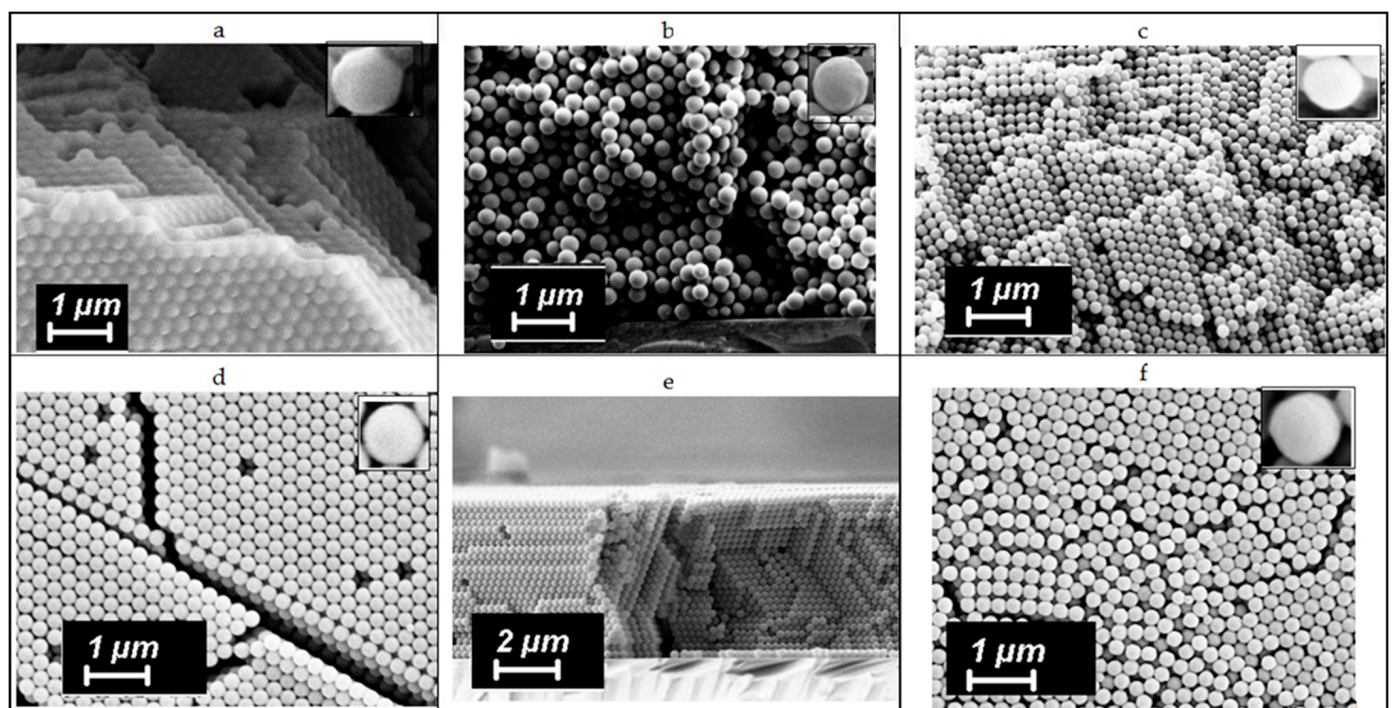


Figure 2. SEM images of core/shell particles Y1/C4 (a), Y1/C5 (b), Y3/C6 (c), Y3/C7 (d,e), and Y3/C8 (f). The inset shows an enlarged image of the particle.

At the same time, the shell thickness for all other synthesized particles (when EGDMA was used as a crosslinking agent) was at least two times higher (Table 3). As seen from the SEM images, the conditions of experiment Y1/C5 yielded particles that were characterized by wide size distribution with a slight inhomogeneous surface (Figure 2b).

Obviously, the formation of such surface layer morphology is caused by two factors. Firstly, at an elevated temperature (90 °C), the copolymerization reaction proceeds rapidly, and the monomers of the second stage do not have sufficient time to diffuse into the surface layer of the core/shell particles. Secondly, the synthesis of the Y1/C5 particles is carried out at a lower concentration of the second-stage monomers (35 wt.%), which also results in the formation of inhomogeneous shells.

The synthesis of core/shell particles Y3/C6 and Y3/C7 at 75 °C resulted in the formation of particles with smooth surfaces (Figure 2c,d). When the shell monomers were introduced in a single step (experiment Y3/C8), the formed particles, on the one hand, had minimum diameter dispersion values, and, on the other hand, slight inhomogeneity of the surface layer (Figure 2e). Only particles Y3/C7 were suitable for the preparation of 3D-ordered structures with thicknesses of up to 60 monolayers (Figure 2d). In the Supporting Information file, Figure S1 shows FTIR spectra of both particle cores and core/shell particles, and characteristic peaks of FTIR spectra are described in the table. It should be noted that the obtained data allow us to confirm the inclusion of comonomers introduced into the reaction system into the polymer chains.

Thus, semi-batch emulsion polymerization allows for the formation of core/shell particles with a more homogeneous morphology of the surface layer. Similarly to particles obtained by seed emulsion polymerization, the shell thickness of the particles obtained in the second series (in the semi-batch polymerization process) of experiments is 25–35 nm. In addition, all core/shell particles obtained in this work are characterized by high values of the surface layer zeta potential (more than -50 mV).

3.2. Study of Solvatochromic Properties of Films

In Section 3.1, it is shown that thin 3D-ordered films can be formed on the basis of the synthesized core/shell particles. The presence of periodicity in the films leads to the appearance of photonic band gap (PBG); as a result, such film structures become “sensitive” to external influence (provided that the physico-chemical properties of the polymer chains of the shell can be changed by varying the environmental parameters). The variation of the photonic crystal properties of the films based on the synthesized core/shell particles depending on ethanol concentration was studied (Figure 3). Since all the studied core/shell particles had comparable diameters (from 250 nm to 310 nm) and shell thicknesses (25–30 nm), it was concluded that the photonic crystal properties of 3D-ordered films during the adsorption of ethanol vapors would be influenced only by the nature and structure of the surface layers of these particles. It should be noted that the PBG of the obtained films lies in the range of 450 to 750 nm (depending on the diameter of the initial cores; see Table 1), which allows for detecting the influence of ethanol vapors not only with the help of spectrophotometer but also visually. Firstly, the properties of core/shell particles synthesized by seed emulsion polymerization were studied.

We started with the study of the influence of ethanol concentration on the properties of 3D-ordered films formed by Y1 and Y2 seed cores (Figure 3). As can be seen, at an ethanol content of 15 vol.%, there is a gradual decrease in the PBG peak intensity accompanied by a bathochromic shift. In the scientific literature, the bathochromic shift of the PBG of 3D-ordered films in the presence of volatile organic molecules is explained by the swelling of the particles. Obviously, the degree of swelling of the Y2 particle is higher compared to that of Y1 because their polymer chains include units of less hydrophobic MMA comonomer. As a result, a sharper decrease in the peak intensity is observed for these films (Figure 3). The decrease in the peak intensity in the spectra of 3D-ordered films can be attributed to two factors. First, there is a decrease in the degree of ordering of the three-dimensional structure caused by the non-uniform swelling of polymer particles.

The main factor influencing this process is the non-uniform condensation of molecules of volatile organic solvents in the three-dimensional structure. Second, the reduced difference between the refractive index values of the surrounding medium (air, $n^{25} = 1.0003$) and the polymer matrix is observed. Since the average value of the refractive index of polystyrene is 1.588, the refractive index decreases upon adsorption of ethanol molecules ($n^{25} = 1.361$). At ethanol vapor content equal to 20 vol.%, the pore space in the 3D structure becomes filled with ethanol molecules. In the case of the Y2 particles, further increase in the ethanol content does not lead to a change in the photonic crystal properties of the films, which indicates that no diffusion of ethanol molecules into the particles occurs. On the contrary, for the cores of the Y1 particles, an increase in the PBG peak intensity is observed with increasing ethanol content (more than 20 vol.%). This result is obviously related to the increasing degree of ordering of the 3D film. As can be seen from the data presented in Figure 3, no bathochromic shift in the PBG peak position is observed at ethanol contents from 20 to 40 vol.%. Apparently, the increase in the degree of order is due to the filling of cracks with ethanol; a certain number of cracks is always present in photonic crystal films based on polystyrene particles.

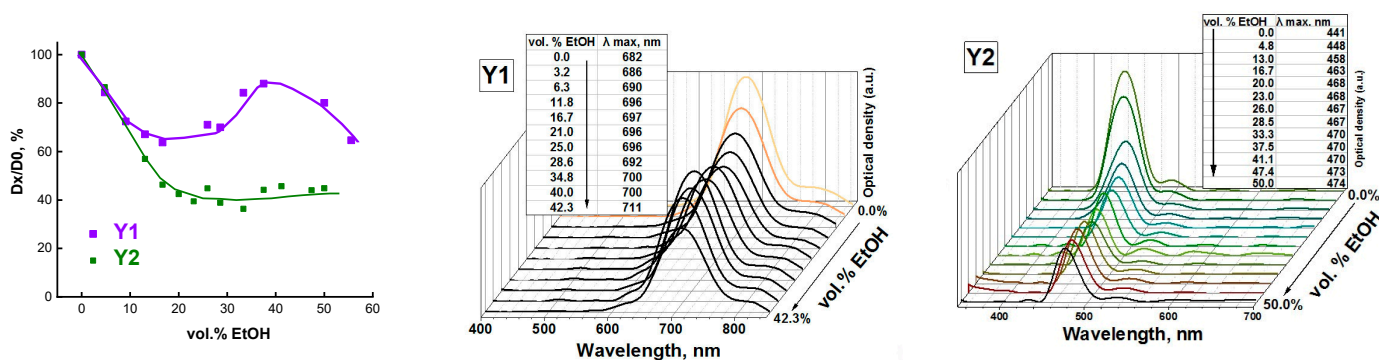


Figure 3. The influence of ethanol concentration on the PBG maximum intensity of the films based on the obtained core particles.

Next, we investigated the dependence of the photonic crystal properties of films based on Y1/C1 and Y1/C2 on the ethanol vapor concentration. Figure 4 shows the data on the change in the position of the PBG maximum. In both cases, there is a gradual bathochromic shift of 30 nm. However, the photonic crystal properties of the 3D films are different due to the difference in the physico-chemical properties of the particle shells. The compositions of the shell polymer chains are similar and differ only in the degree of crosslinking (Table 1). It was shown that the presence of the branched crosslinking agent TMPTM (the Y1/C1 particles) in the reaction system leads to less dense crosslinking of polymer chains of the shell; as a result, ethanol vapors can diffuse more easily into the surface layer, while the PBG peak intensity is reduced by 80%. However, the shell of the Y1/C2 particles is formed in the presence of the EGDMA crosslinking agent; as a result, at ethanol content up to 30 vol.%, both swelling of the particle shell and reduction in the PBG peak intensity are insignificant (no more than 10%, Figure 4). It should be noted that the maximum reduction in the photonic band gap of films based on the Y1/C1 and Y1/C2 particles is 80%; therefore, these core/shell particles cannot be considered promising for the development of ethanol vapor sensors.

The next series of core/shell particles Y2/C3 ÷ Y2/C6 was obtained on the basis of the Y2 seed cores containing methyl methacrylate units. It was supposed that the presence of MMA units in the core would improve the copolymerization of shell monomers in their surface layer. The influence of the nature of comonomers (butyl acrylate, butyl methacrylate, propyl acrylate, and ethyl acrylate) on the physico-chemical properties of the shell and photonic crystal properties of films based on the synthesized particles in the presence of ethanol vapors was traced. As shown in Figure 5, the Y2/C3 and Y2/C6 particles, which were synthesized in the presence of butyl acrylate and propyl acrylate, respectively, are

promising for the formation of 3D films sensitive to ethanol vapors. The intensity of the PBG peak of the films based on the Y2/C3 particles decreases by 60% at an ethanol content of 5 vol.%; the PBG peak intensity of the films based on the Y2/C6 particles decreases by 100% at an ethanol content of 40 vol.%. In addition, the films based on the obtained core/shell particles Y2/C3 ÷ Y2/C6 are characterized by a stronger bathochromic shift (more than 60 nm). This indicates that the shell of such particles swells more strongly, which leads to an increase in the size of the core/shell particles. The butyl methacrylate units in the polymer chains of the particle shells limit their conformational mobility; as a result, the bathochromic shift of the maximum PBG of films based on such particles changes insignificantly (by no more than 20 nm). At the same time, when increasing the ethanol content up to 30 vol.%, the maximum PBG peak decreases by no more than 20%. However, at the ethanol concentration equal to 41 vol.%, the films become transparent and do not restore their photonic crystal properties after the evaporation of ethanol molecules (Table 1). The films based on the Y2/C3 particles demonstrate 100% recovery of photonic crystal properties, while for the films based on the Y2/C6 particles, only 80% of the PBG peak intensity is recovered. Figure 5 displays the optical images of PC films before exposure to ethanol, immediately after ethanol exposure, and after 5 min of air drying.

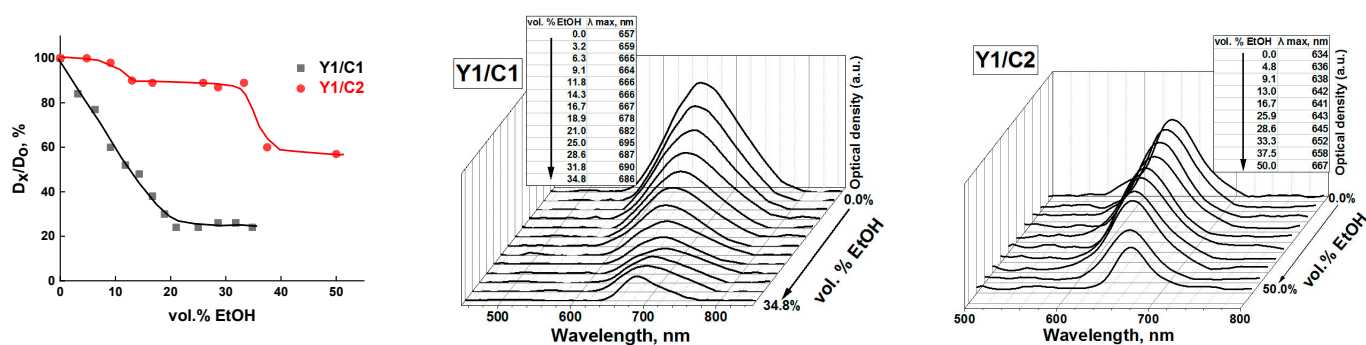


Figure 4. The influence of ethanol concentration on the change in the PBG maximum intensity of the films based on the obtained core/shell particles.

Note that upon the removal of ethanol, some films do not recover their photonic crystal properties (Tables 1 and 2). The PBG of the films based on core/shell particles Y2/C3 is fully recovered (100%), the films based on the Y2/C6 particles recover only 80% of their PBG, and the films based on particles Y2/C4 do not recover the initial PBG at all. Apparently, depending on the physico-chemical properties of the shell polymer chains, the ethanol molecule can diffuse to different depths of the shell polymer chains. As a result, either reversible or irreversible changes occur in the structure of the surface layer of particles.

Thus, it was shown that core/shell particles that are promising for the detection of ethanol vapors in the environment can be obtained by seed emulsion polymerization. The formation of the shell by pre-emulsification of the monomers of the second stage in the presence of a surfactant (sodium dodecyl sulfate) promotes the formation of a polymer shell enriched with acrylate comonomer units. The introduction of methyl methacrylate units into the polymer chains of the core is a necessary condition for the formation of a more “sensitive” shell. In addition, it was shown that the introduction of butyl acrylate units into the polymer chains of the shell of the Y2/C3 particles facilitates the formation of mobile polymer chains that efficiently adsorb ethanol molecules. As a result, the bathochromic shift of the PBG peak of films based on the Y2/C3 particles is maximal and amounts to 60 nm. Figure 6 displays the results of the study of the solvatochromic properties of films based on the core/shell particles synthesized by semi-batch emulsion polymerization. In this series of experiments, all particle shells are composed of poly(methyl methacrylate-co-butyl acrylate) copolymer. It was shown that the physico-chemical properties of the shells depend on the nature of the crosslinking agent and the method of the addition of

a monomer in the second stage. In turn, physico-chemical properties have a significant influence on the sensitivity of PC films to ethanol.

Thus, the thickness of the P(MMA-BA) shell of the Y1/C4 particles is equal to 77 nm (Table 2) as measured by the DLS method; even the presence of 5 vol.% ethanol is sufficient to achieve a considerable decrease in the PBG peak intensity (more than 90%, Figure 6, experiment Y1/C4). It was found that only 20% of the photonic crystal properties of these films were recovered after 5 min of air drying after exposure (Table 3). This indicates good adsorption of ethanol molecules by the polymer chains of the shell and high chain mobility. At the same time, the PC films based on Y1/C5 core/shell particles (with a shell thickness of 45 nm) are less sensitive to ethanol vapors.

As can be seen in Figure 6, the intensity of the maximum PBG decreases gradually with increasing ethanol concentration; these PC films are able to restore their photonic crystal properties (Table 3, Supplementary Information Figure S2). In the series of experiments Y3/C6–Y3/C8, the nature of the crosslinking agent and the method of the addition of shell monomers were varied during the formation of the P(MMA-BA) shell. It turned out that upon the addition of ethanol (up to 10 vol.%), the intensity of the PBG maximum of PC films decreased by 70–80% in all cases. The highest sensitivity was found in the films based on the Y3/C8 particles. The shells of these particles were obtained by the single-step introduction of monomers into the reaction system. When more than 15 vol.% ethanol is added, the PC films based on these particles become transparent; after evaporation of ethanol, photonic crystal properties are not restored (Table 3). On the contrary, the films based on Y3/C6 and Y3/C7 particles recovered up to 80% of their PBG maximum. It should be noted that in contrast to the results reported in Ref. [39], the exposure to ethanol vapors led only to the single shift of the PBG maximum into the long-wavelength region, followed by a decrease in peak intensity (partial or complete discoloration of a film). This behavior was observed for all films obtained in our work.

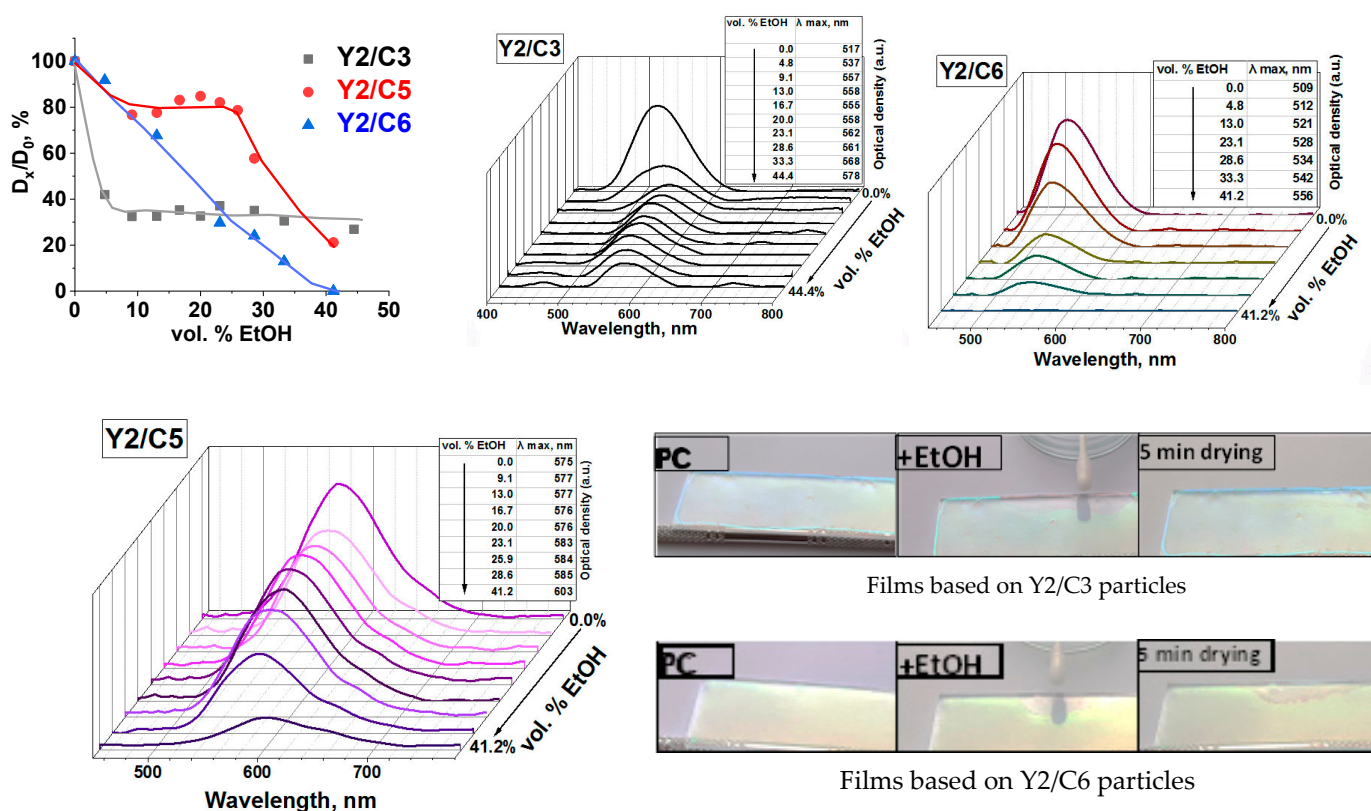


Figure 5. The influence of ethanol concentration on the maximum PBG intensity of the films based on the obtained core/shell particles, as well as photo of films based on Y2/C3 and Y2/C6 particles depending on the ethanol exposure.

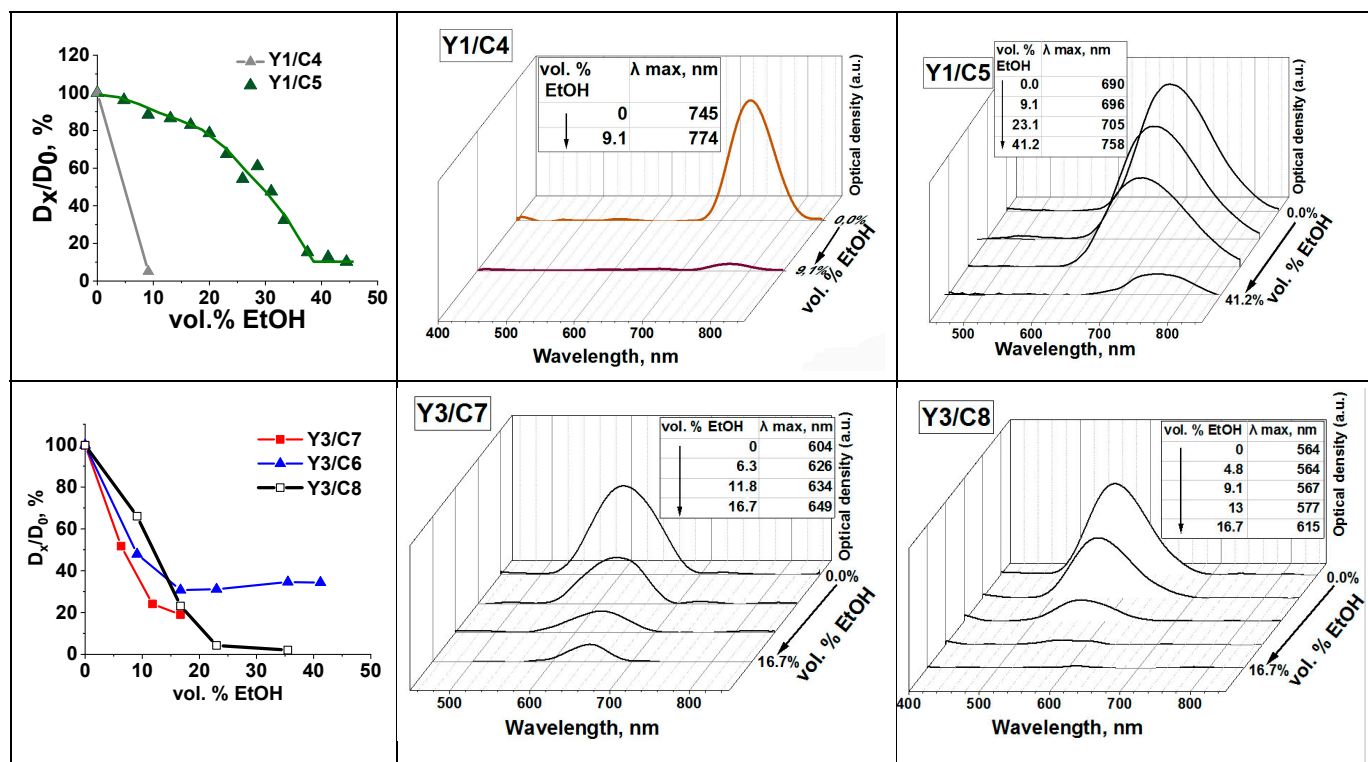


Figure 6. The influence of ethanol concentration on the maximum PBG intensity of the films based on the resulting core/shell particles.

To summarize, when using semi-batch emulsion polymerization for the formation of a shell based on a poly(methyl methacrylate-co-butyl acrylate) copolymer, it is preferable to use cores that do not contain methyl methacrylate units. In addition, optimal properties are observed for films formed on the basis of particles with a greater shell thickness (Table 2). An unexpected result was that with a single-stage introduction of second-stage monomers in the semi-batch emulsion polymerization method, Y3/C8 core/shell particles are formed, the films of which are more sensitive to ethanol compared to Y3/C7 core/shell particles (the shell is obtained in the process of dropwise addition of monomers). Thus, in this present study, the conditions for the formation of core/shell particles of similar composition are found but the sensory properties of films based on such particles can differ by four times: films based on Y1/C4 particles can be used as sensors for a content of 10 vol.% ethanol, films based on Y3/C8 particles—20 vol.% ethanol, films based on Y2/C6 particles—40 vol.% ethanol.

3.3. Study of Thermochromic Properties of Films

The change in the photonic crystal properties of the prepared PC films with temperature was studied. In the first series of experiments, the properties of core/shell particles synthesized by seed emulsion polymerization were investigated (Figure 7.). As may be seen from Figure 7, the positions and intensities of PBG peaks of the corresponding polymer PC films based on core particles do not change with temperature. Similar to the process of ethanol sorption, the temperature dependence of photonic crystal properties of films is related to the physico-chemical properties of particle shell. For the PC films based on particles Y1/C1 and Y1/C2 (whose shells were synthesized in the presence of different crosslinking agents), it was found that a decrease in the peak PBG intensity with increasing temperature did not exceed 30%. In this series of experiments, the PC films based on the Y2/C6 particles demonstrate the highest temperature sensitivity. Their shells contain poly(propyl acrylate) units; as a result, at 65 °C, the peak PBG of these films decreases down to 0, and the films become transparent (Figure 7 Y2/C6). It should be noted that all

changes associated with temperature exposure are irreversible, and the films do not restore their photonic crystal properties when the temperature is reduced to room temperature. In the second series of experiments, we studied the temperature dependence of the photonic crystal properties of the films based on the particles obtained by semi-batch emulsion polymerization (Figure 7). As is seen from the experimental data, the shell thickness has a significant influence on the thermal sensitivity of these films. Thus, the thickness of P(MMA-BA) films is equal to 77 nm (particles Y1/C4, Table 2). Already at 30 °C, the intensity of the peak PBG decreased by more than 90% (Figure 7 Y1/C4). As a result, the polymer film became transparent. Thus, increasing the temperature significantly increases the mobility of the polymer chains of the shell, and as a result, the holes in the structure of the photonic crystal disappear due to the gluing of the polymer chains of the shells. At the same time, the PC films based on Y1/C5 particles (shell thickness 45 nm) change their photonic crystal properties only at temperatures exceeding 60 °C.

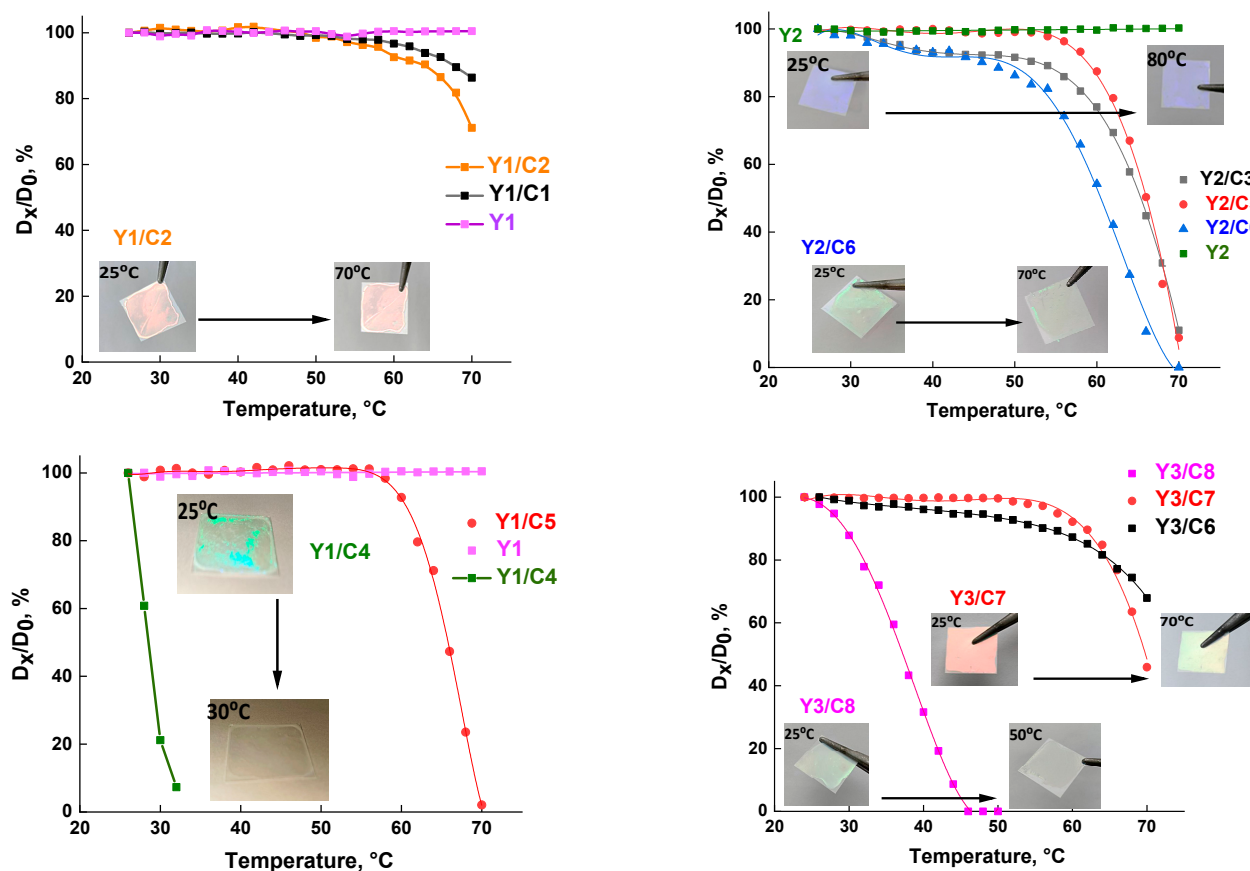


Figure 7. The influence of temperature on the change in the PBG maximum intensity of the films based on the obtained core/shell particles.

In the series of experiments Y3/C6–Y3/C8, the nature of the crosslinking agents and the method of introducing shell monomers were varied during the synthesis of the P(MMA-BA) shell. It turned out that only the films based on particles Y3/C8 demonstrated pronounced thermal sensitivity. The intensity of the PBG maximum of PC films based on these particles decreases by 100% at 42 °C. Thus, it was shown that the conditions of experiments Y1/C5 and Y3/C8 are optimal for the synthesis of core/shell particles and the formation of thermosensitive “smart” PC films that are able to detect temperature changes in the 30–45 °C range.

4. Conclusions

In this work, we demonstrated that in similar compositions of the shell monomer mixture, the method of introduction of monomers and core composition had strong influences on the photonic crystal properties of the films based on core/shell particles. It was found that 3D-ordered structures with minimal amounts of defects can be prepared using Y3/C7 particles (obtained by semi-batch emulsion polymerization, P(St-MMA)@P(MMA-BA) particles with the dropwise addition of shell-forming monomer); the film colloid crystals may reach up to 60 monolayers. The PC films based on the particles synthesized by different methods (seed emulsion polymerization, semi-batch emulsion polymerization) demonstrate solvatochromic properties in the presence of ethanol. The most sensitive films (solvatochromism in the presence of minimal amount of ethanol) were prepared on the basis of particles Y1/C4 (semi-batch emulsion polymerization, shell thickness 77 nm). Further, these films demonstrate temperature sensitivity (the PBG peak disappears completely at 30 °C). If the shell monomers are introduced in a single step during synthesis (and not dropwise), the promising core/shell particles are formed; the films based on these particles exhibit thermal sensitivity (the PBG peak disappears at around 42 °C). FTIR spectroscopy data indicate that when the ratio of peak areas 1730/1492 cm^{−1} (stretching vibrations of C=O bonds of acrylate groups/-stretching vibrations of the PSt aromatic ring) is equal to or greater than 10, photonic crystal films exhibit maximum sensitivity to the presence of ethanol molecules and to temperature changes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/colloids8060067/s1>, Table S1. ATR-FTIR peak analysis. Figure S1. FTIR-spectra of core/shell particles. The ration of peaks at 1730 cm^{−1} (stretching vibrations of C=O bonds of acrylate groups) to 1492 cm^{−1} (stretching vibrations of the PSt aromatic ring) is indicated. Figure S2. Photo of films depending on the addition of ethanol.

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References

1. Leigh, B.L.; Cheng, E.; Xu, L.; Derk, A.; Hansen, M.R.; Guymon, C.A. Antifouling Photograftable Zwitterionic Coatings on PDMS Substrates. *Langmuir* **2018**, *35*, 1100–1110. [CrossRef] [PubMed]
2. Freiberg, S.; Zhu, X.X. Polymer microspheres for controlled drug release. *Int. J. Pharm.* **2004**, *282*, 1–18. [CrossRef] [PubMed]
3. Du, C.G.; Cui, L.Y.; Zhang, Y.Z.H.; Zhao, T.Y.; Wang, J.X.; Song, Y.L.; Jiang, L. Fabrication of Colloidal Crystals with Hierarchical Structure and Its Water Adhesion Properties. *J. Nanosci. Nanotechnol.* **2010**, *10*, 7766–7769. [CrossRef] [PubMed]
4. Kolle, M.; Lee, S. Progress and Opportunities in Soft Photonics and Biologically Inspired. *Opt. Adv. Mater.* **2018**, *30*, 1702669. [CrossRef] [PubMed]
5. Constantin, M.; Bucatariu, S.M.; Doroftei, F.; Fundueanu, G. Smart composite materials based on chitosan microspheres embedded in thermosensitive hydrogel for controlled delivery of drugs. *Carbohydr. Polym.* **2017**, *157*, 493–502. [CrossRef]
6. Zhang, W.; Wei, B.; Li, S. Preparation and Chromatographic Application of β -Cyclodextrin Molecularly Imprinted Microspheres for Paeoniflorin. *Polymers* **2017**, *9*, 214. [CrossRef]
7. Wang, X.D.; Li, Y.; Dai, T.T. Preparation of pectin/poly(m-phenylenediamine) microsphere and its application for Pb²⁺ removal. *Carbohydr. Polymers* **2021**, *260*, 117811.
8. Qi, X.; Tong, X.; Pan, W.; Zeng, Q.; You, S.; Shen, J. Recent advances in polysaccharide-based adsorbents for wastewater treatment. *J. Clean. Product.* **2021**, *321*, 128221. [CrossRef]
9. Shevchenko, N.N.; Shabsel's, B.M.; Iurasova, D.I.; Skurkis, Y.O. Synthesis and Properties of Polymer Photonic Crystals Based on Core-Shell Particles. *Polym. Sci. Ser. C* **2022**, *64*, 245–255. [CrossRef]

10. Shevchenko, N.; Pankova, G.; Laishevskina, S. Core/shell polymer particles containing derivatives of 1,3-diphenyl- β -diketonate boron difluoride: Synthesis and spectroscopic investigation of toluene vapor sorption. *Colloids Surf. Physicochem. Eng. Asp.* **2019**, *562*, 310–320. [[CrossRef](#)]
11. Ohnuki, R.; Takeoka, Y.; Yoshioka, S. Cross-Sectional Investigations of Spherical Colloidal Clusters from Submicrometer-Sized Silica Particles toward Designing Novel Photonic Materials. *ACS Appl. Nano Mat.* **2023**, *6*, 13137–13147. [[CrossRef](#)]
12. Iakobson, O.; Ivan'kova, E.; Shevchenko, N. Photonic Crystal Films Based on Polymer Particles with a Core/Shell Structure Responding to Ethanol. *Langmuir* **2023**, *39*, 9952–9962. [[CrossRef](#)] [[PubMed](#)]
13. Demirörs, A.F.; Poloni, E.; Chiesa, M. Three-dimensional printing of photonic colloidal glasses into objects with isotropic structural color. *Nat. Commun.* **2022**, *13*, 4397. [[CrossRef](#)] [[PubMed](#)]
14. Goerlitzer, E.S.; Taylor, R.N.; Vogel, N. Bioinspired photonic pigments from colloidal self-assembly. *Adv. Mater.* **2018**, *30*, 1706654. [[CrossRef](#)] [[PubMed](#)]
15. Shevchenko, N.; Tomsik, E.; Laishevskina, S.; Pankova, G. Cross-linked polyelectrolyte microspheres: Preparation and new insights into electro-surface properties. *Soft Matter* **2021**, *17*, 2290–2301. [[CrossRef](#)]
16. Shevchenko, N.; Steinhart, M.; Tomsik, E. Single-step preparation of mono-dispersed sulfur nanoparticles for detention of copper. *J. Nanopart. Res.* **2019**, *21*, 246. [[CrossRef](#)]
17. Fan, J.; Zhang, L.; Wei, S.; Zhang, Z.; Choi, S.-K.; Song, B.; Shi, Y. A review of additive manufacturing of metamaterials and developing trends. *Mater. Today* **2021**, *50*, 303–328. [[CrossRef](#)]
18. Saraswati, B.; Joby, J. Single-step optical realization of bio-inspired dual-periodic motheye and gradient-index-array photonic structures. *Opt. Lett.* **2016**, *41*, 3579–3582.
19. Gopalan, A.-I.; Komathi, S.; Muthuchamy, N.; Lee, K.P.; Whitcombe, M.J.; Lakshmi, D. Functionalized conjugated polymers for sensing and molecular imprinting applications. *Prog. Polym. Sci.* **2019**, *88*, 1–129.
20. Li, W.S.J.; Ladmiral, V.; Takeshima, H.; Satoh, K.; Kamigaito, M.; Semsarilar, M.; Caillol, S. Ferulic acid-based reactive core-shell latex by seeded emulsion polymerization. *Polym. Chem.* **2019**, *10*, 3116–3126. [[CrossRef](#)]
21. Pursiainen, O.L.; Baumberg, J.J.; Winkler, H.; Viel, B.; Spahn, P.; Ruhl, T. Phononic Behavior of Colloidal Systems. *Adv. Mater.* **2008**, *20*, 1484. [[CrossRef](#)]
22. Goh, E.; Stöver, H. Cross-Linked Poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate) Microspheres and Microgels Prepared by Precipitation Polymerization: A Morphology Study. *Macromolecules* **2002**, *35*, 9983–9989. [[CrossRef](#)]
23. Kredel, J.; Dietz, C.; Gallei, M. Fluoropolymer-Containing Opals and Inverse Opals by Melt-Shear Organization. *Molecules* **2019**, *24*, 333. [[CrossRef](#)] [[PubMed](#)]
24. Schäfer, C.G.; Smolin, D.A.; Hellmann, G.P.; Gallei, M. Reversible Light-, Thermo-, and Mechano-Responsive Elastomeric Polymer Opal Films. *Langmuir* **2013**, *29*, 11275–11283. [[CrossRef](#)] [[PubMed](#)]
25. Schäfer, C.G.; Lederle, C.; Zentel, K.; Stühn, B.; Gallei, M. Utilizing Stretch-Tunable Thermochromic Elastomeric Opal Films as Novel Reversible Switchable Photonic Materials. *Macromol. Rapid Commun.* **2014**, *35*, 1852–1860. [[CrossRef](#)]
26. Quan, M.; Yang, B.; Wang, J.; Yu, H.; Cao, X. Simultaneous Microscopic Structure Characteristics of Shape-Memory Effects of Thermo-Responsive Poly(vinylidene fluoride-co-hexafluoropropylene) Inverse Opals. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4243–4249. [[CrossRef](#)]
27. Espinha, A.; Serrano, M.C.; Blanco, Á.; López, C. Hydroxypropyl cellulose photonic architectures by soft nanoimprinting lithography. *Adv. Opt. Mater.* **2014**, *2*, 516–521. [[CrossRef](#)]
28. Fang, Y.; Ni, Y.; Leo, S.Y.; Taylor, C.; Basile, V.; Jiang, P. Reconfigurable photonic crystals enabled by pressure-responsive shape-memory polymers. *Nat. Commun.* **2015**, *6*, 7416. [[CrossRef](#)]
29. Thomas, M.M.; Chandran, P.R.; Vipin, V.V.; Mohamed, A.P.; Kingshott, P.; Pillai, S. Core/shell based responsive colloidal photonic crystals for facile, rapid, visual detection of acetone. *Polymers* **2020**, *158*, 104779. [[CrossRef](#)]
30. Wang, X.H.; Li, Y.C.; Zheng, J.Y.; Li, X.Y.; Liu, G.J.; Zhou, L.; Zhou, W.L.; Shao, J.Z. Polystyrene@poly(methyl methacrylate-butyl acrylate) Core-Shell Nanoparticles for Fabricating Multifunctional Photonic Crystal Films as Mechanochromic and Solvatochromic Sensors. *ACS Appl. Nano Mater.* **2022**, *5*, 729–736. [[CrossRef](#)]
31. Wu, P.; Shen, X.; Schäfer, C.G.; Pan, J.; Guo, J.; Wang, C. Mechanochromic and thermochromic shape memory photonic crystal films based on core/shell nanoparticles for smart monitoring. *Nanoscale* **2019**, *11*, 20015–20023. [[CrossRef](#)] [[PubMed](#)]
32. Vowinkel, S.; Boehm, A.; Schäfer, T.; Gutmann, T.; Ionescu, E.; Gallei, M. Preceramic core-shell particles for the preparation of hybrid colloidal crystal films by melt-shear organization and conversion into porous ceramics. *Mater. Des.* **2018**, *160*, 926–935. [[CrossRef](#)]
33. Chen, J.; Liu, P.; Du, X.; Xie, Z. Clickable Colloidal Photonic Crystals for Structural Color Pattern. *Langmuir* **2018**, *6*, 13219–13224. [[CrossRef](#)] [[PubMed](#)]
34. Bazin, G.; Zhu, X.X. Understanding the thermo-sensitivity of crystalline colloidal arrays formed by poly(styrene-co-N-isopropylacrylamide) core-shell microspheres. *Soft Matter* **2012**, *8*, 1909–1915. [[CrossRef](#)]
35. Kou, D.; Ma, W.; Zhang, S.; Tang, B. Copolymer-Based Photonic Crystal Sensor for Discriminative Detection of Liquid Benzene, Toluene, Ethylbenzene, and Xylene. *ACS Appl. Polym. Mater.* **2020**, *2*, 2–11. [[CrossRef](#)]
36. Kim, S.H.; Son, W.K.; Kim, Y.J.; Kang, E.-G.; Kim, D.-W.; Park, C.W.; Kim, W.-G.; Kim, H.-J. Synthesis of polystyrene/poly(butyl acrylate) core-shell latex and its surface morphology. *J. Appl. Polym. Sci.* **2003**, *88*, 595–601. [[CrossRef](#)]

37. Iakobson, O.D.; Ivan'kova, E.M.; Vaganov, G.V. Synthesis of Composite Polymer Particles by Seeded Emulsion Polymerization and Formation of Photonic Crystals Based on Them. *Polym. Sci. Ser. B* **2023**, *65*, 457–466. [[CrossRef](#)]
38. Iakobson, O.D.; Ivankova, E.M.; Popova, E.N.; Shevchenko, N.N. Surface morphology of core/shell particles and its determining factors. *Coll. Surf. A Physicoch. Eng. Asp.* **2024**, *697*, 134416. [[CrossRef](#)]
39. Dong, X.; Wu, P.; Schaefer, C.G.; Zhang, L.; Finlayson, C.E.; Wang, C. Solvatochromism based on structural color: Smart polymer composites for sensing and security. *Mater. Des.* **2018**, *160*, 417–426. [[CrossRef](#)]

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