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Preparation and characterization of dummy-template molecularly imprinted polymers as potential sorbents for the recognition of selected polybrominated diphenyl ethers

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ABSTRACT

The main aim of this work was to conduct the preliminary/basic research concerning the preparation process of a new dummy molecularly imprinted polymer (DMIP) materials. Developed DMIPs were proposed as a sorption material in solid-phase extraction (SPE) technique for recognition of selected low mass polybrominated diphenyl ethers (PBDEs) – PBDE-47 and PBDE-99. Four new DMIPs were synthesized employing bulky polymerization technique by application of structural analogue of low mass PBDEs - 4,4′-Dihydroxydiphenyl ether, as a dummy template. The DMIPs and corresponding non-imprinted polymers were prepared using different functional monomers: methacrylic acid; methyl methacrylate and different porogen agents: acetonitrile and tetrahydrofuran. The polymerization reaction was thermally initiated with 1,1′-azobis (cyclohexanecarbonitryle). Ethylene glycol dimethacrylate was applied as a cross-linker. To optimize geometries and to calculate energies of the respective template-monomer complexes, the computational molecular modeling method was employed. The particles morphology and physicochemical characteristics of developed DMIPs and their equivalent NIPs were performed using nitrogen sorption porosimetry, scanning electron microscopy, and Fourier transform infrared spectroscopy. The sorption capacities of prepared DMIPs and corresponding NIPs were studied using standard binding test. The adsorption capability studies give a possibility to assess the imprinting factor (IF) values, which were in the range from 1.1 to 4.0, depending on the DMIP type. The recovery values of PBDE-47 and PBDE-99 from prepared organic solutions were in the range from 43 to 92%, depending on the studied DMIP. Performed basic laboratory studies give a possibility to select the optimal DMIP material which might be applied in the environmental samples preparation process as a potential sorbent for the recognition of low mass PBDEs.

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Alphabetical list of abbreviations

ACHN	1,1′-azobis(cyclohexanecarbonitryle)
ACN	acetonitrile
BET	Brauner-Emmet-Teller
BFRs	brominated flame retardants
BJH	Barret-Joyner-Halenda
BSSE	basis set superposition error
CPCM	conductor-like polarizable continuum model
DCM	dichloromethane
DFT	density functional theory
DLLME	dispersive liquid liquid microextraction
DMIP	dummy molecularly imprinted polymer
EGDMA	ethylene glycol dimethacrylate
ESTD	external standard
FR	flame retardants
FT-IR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC-EIMS	gas chromatography with electron impact mass spectrometry
HPLC	high performance liquid chromatography
IF	imprinting factor
IUPAC	International Union of Pure and Applied Chemistry
LOD	limit of detection
LOQ	limit of quantification
MAA	methacrylic acid
MAE	microwave-assisted extraction
MIP	molecularly imprinted polymer
MISPE	molecularly imprinted solid-phase extraction
MMA	methyl methacrylate
MSD	mass selective detector
NIP	non-imprinted polymers
PBDEs	polybrominated diphenyl ethers
PCB	polychlorinated biphenyl
PLE	pressurized liquid extraction
PM	particulate matter
POPs	persistent organic pollutants

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PS-DVB	polystyrene-divinylbenzene copolymer
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
SBSE	stir bar sorptive extraction
SCRF	self-consistent reaction field theory
SDME	single drop microextraction
SEM	scanning electron microscopy
SIM	selective ion monitoring
SPE	solid-phase extraction
SPME	solid phase microextraction
SVOCs	semivolatile organic compounds
THF	tetrahydrofuran
UV	ultraviolet

1. Introduction

One of the main group of chemical compounds classified and widely used in the industry as flame retardants (FRs) are polybrominated diphenyl ethers (PBDEs), defined also as a brominated flame retardants (BFRs). The main purpose of adding PBDE compounds during the manufacturing process of indoor elements is to prevent and to reduce to the minimum the possibility of fire spread in indoor environment. The PBDE compounds were introduced into a general industrial circulation in the early 1970s. Since then, they have been commonly used as additives at the manufacturing stage of various types of plastic materials, such as personal electronic devices, furniture elements, floor coverings, electric cable insulation, water and sewage pipes made of PVC or accessories in cars and planes [1–4]. Nevertheless, it should be mentioned that, despite the addition of these chemical compounds during the manufacturing process of various types of plastics, the PBDEs are not chemically bonded to the structure of the indoor material. As a consequence, they might be transported to the indoor environment from indoor materials – directly to the gaseous phase or through adsorption on the surface of house dust or suspended particulate matter (PM). Moreover, the manufacturing process itself might be considered as direct emission source of PBDEs, affecting the quality of atmospheric air, soil, groundwater and bottom sediment [5–8]. In the beginning of 21st century (in 2009) the chemical compounds classified as PBDEs were listed by the international experts from Stockholm Convention as persistent organic pollutants (POPs) [9,10].

Chemical structure of PBDEs includes several bromine atoms attached to each of the two aromatic rings. The phenyl rings are connected by an ether bond. Theoretically, the PBDEs family might include 209 of possible congeners, which were defined and numbered by the International Union of Pure and Applied Chemistry (IUPAC) [11,12]. Considering the literature information about the PBDE congeners, it might be noticed that the most commonly employed in the industry PBDE compounds are as follows: (i) pentabromodiphenyl ethers defined as penta-BDE (containing PBDE-47 and PBDE-99), (ii) octabromodiphenyl ethers defined as octa-BDE (mixture consists of hexa-to decaPBDE) and (iii) decabromodiphenyl ether defined as deca-BDE (mainly consists of PBDE-209 alongside and nonaPBDEs) [13–15]. As for the penta- and octa-BDE compounds, according to the international low regulations (Directive, 2003/11/EC, NICNAS, 2007 and U.S. EPA, 2010 regulations) their use during the manufacturing process have been banned or radically limited [16–21].

Taking into account the information published in the scientific literature, PBDEs are characterized by a lipophilic nature (logK_{ow} values from 5.9 to 10), long life time in the environment and might undergo bioaccumulation and biomagnification processes [1,22–25]. The most commonly determined PBDE congeners determined in a wide spectrum of environmental and biological samples are: BDE-47, BDE -99, BDE -100, BDE -153, BDE -154, and BDE-209, including their metabolites - hydroxylated- (OH-PBDEs) and methoxylated-PBDEs (MeO-PBDEs) [11,26–28]. According to the comprehensive data reported by Berton et al. (2016), over the last decade the PBDE-47 and PBDE-99 were characterized by the highest frequency of all PBDEs congeners analyzed using various types of analytical methodologies [28]. Moreover, based on the information published by Vonderheide (2009), even in a case, when the type and the quantity of PBDE congeners fluctuations depends on the sampling region, one of the main congener that was determined in most of the environmental samples was PBDE-47 [29]. Given the above, still there is an urgent need to conduct studies aimed at the identification and quantitative determination of PBDE compounds in the environmental (plant species, sediments and soils) and biological (fatty animal tissues) samples, due to the fact that they might be considered as toxic compounds and might negatively affect animals and human health (mainly, an adverse effect on the hormonal balance, e.g. thyroid hormone, kidneys and liver function) [30–33].

Taking into consideration the data available in the scientific literature published over the last decade in the field of monitoring and analysis of PBDEs in environmental and biological samples, it can be noticed that the most commonly applied extraction techniques, are as follows: (i) classical liquid-liquid or solid-liquid extraction - Soxhlet extraction device; (ii) accelerated/assisted extraction techniques (e.g. microwave-assisted extraction - MAE or pressurized liquid extraction - PLE); (iii) liquid phase microextraction techniques (e.g. single drop microextraction – SDME, or dispersive liquid liquid microextraction - DLLME); (iv) extraction with alternative solvents such as ionic liquids or supercritical fluids and (v) solid-phase based extraction techniques (e.g. classical SPE, mainly silica gel with the surface modified by specific functional groups such as: –C8, -C18, PS-DVB, CN, -NH2, etc., solid phase microextraction – SPME, or stir bar sorptive extraction - SBSE) [8,28,34–36].

In the field of extraction of PBDEs from environmental and biological samples, still the most popular solution is Soxhlet extraction using organic solvents. However, this solution is very time consuming and requires significant amounts of organic solvents. Taking into consideration the philosophy of “green analytical chemistry”, the most appropriate extraction techniques for PBDEs isolation from samples of interest are solid-phase based extraction techniques and accelerated/assisted extraction techniques.

The optimal solution is the application of SPE technique using glass columns filled with appropriate type and amount of sorption material. Nowadays, in sample preparation process it is especially required that a sorption medium is characterized by high selectivity to defined type of analytes. In addition, the application of a new type of sorption material should also significantly improve the efficiency of isolation and/or preconcentration process of selected compound or group of chemical compounds from investigated samples. Sorption materials fulfilling above mentioned requirements are molecularly imprinted polymers – MIPs. The synthesis, characteristics and application of these polymeric sorbents in environmental analysis were first described in 1994 by B. Sellergren [37]. The popularity and dynamic development of new MIPs sorption materials, which might be employed as a sorption medium in SPE technique (MISPE) results from the fact, that their application significantly improve the selectivity and efficiency of isolation and/or preconcentration process in analytical procedures [38–41].

The preparation procedure of new type of MIP sorbents is not complicated and requires no advanced laboratory equipment or large

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financial outlays. To synthesize desired MIP sorbent it is obliged to use the following reagents with early assessed molar ratios: the template, mainly reference substance; functional monomer; porogen agent (solvent); cross-linker and reaction initiator - the polymerization reaction might be performed employing appropriate values of temperature (generally defined by the initiator decomposing temperature) or UV radiation. To obtain a preferred MIP sorption material, which is characterized by desired morphological and physicochemical properties, there are several polymerization techniques frequently used in laboratory practice. The valuable properties of MIPs, such as high thermal, mechanical and chemical stability (resistance to organic solvents and wide working range of pH values) are the main reason why analytical chemists applied them in many analytical procedures which concerns the environmental, biological, food and pharmaceutical samples [42–46].

In a case when the template substance is expensive, difficult in synthesis or is not soluble in commonly used porogen agents, the best solution is the application of its structural analogue defined as dummy template – a chemical compound characterized by a similar physicochemical properties to desired template substance (a dummy molecularly imprinted polymer – DMIP). A good example of appropriate selection of dummy template considering its similar physicochemical properties to the desired group of chemical compounds, is the case described by Liang et al. (2015). The authors proposed the 4,4-dihydroxybiphenyl as a dummy template for hydroxylated polychlorinated biphenyls (OH-PCBs). It was noticed that proposed new type of DMIP applied as a sorption medium in SPE technique might be considered as valuable analytical tool to determine the OH-PCBs in the water samples present on the very low content level. Moreover, it was shown that the appropriate prepared DMIP sorption material was characterized by high selectivity and desired values of recovery (from 89 to 110%) [47].

Recently, one of the most novel approaches in this field is the use of the computer molecular modeling methods. The application of suitable software (commercial or freeware) is an effective analytical tool, which gives a possibility to perform a series of complicated calculations and simulations to select optimal chemical compound, which might be considered as structural analogue. Due to this fact, it is possible to reject unsuitable functional monomers or proposed structural analogues and to save time and significantly reduce the use of organic solvents and reagents during MIP or DMIP materials preparation process [48].

This work refers to the basic preliminary studies aimed at the preparation under laboratory conditions of new type of DMIPs sorption materials considering 4,4′-Dihydroxydiphenyl Ether as dummy template. To gain an insight into the intermolecular interactions between the proposed dummy template molecule (structural analogue of low mass PBDE compounds) and selected functional monomers, the density functional calculations were performed. The solvent/porogen agent effect was also assessed in calculation system using the conductor-like polarizable continuum model. Due to this it was possible to assess and to locate the stable dummy template – functional monomer complexes. The implementation of molecular modeling in analytical practice contains a novel solution to reduce the number of reagents and organic solvents used during the new type of MIP sorption materials preparation process, which is consistent with the demands associated with a green analytical chemistry philosophy.

The main aim of the following paper was to suggest the solution to obtain the sorption material, which might be applied in analytical methods at the isolation and/or preconcentration stage of selected low mass PBDEs - PBDE-47 and PBDE-99 from environmental samples. The conducted preliminary studies concerns the preparation process of polymeric sorption materials based on the bulky polymerization technique (selection of the type and amount of reagents used in polymers synthesis) and the evaluation of particles surface morphological and physicochemical parameters, as well as sorption abilities and sorption efficiency of prepared DMIP materials and their equivalent non-imprinted polymers (NIPs) used as a sorbents in SPE technique. The described issue illustrates an interdisciplinary studies associated with polymer chemistry, physical chemistry, environmental chemistry and analytical chemistry, which might be successfully employed in the field of MIP sorption materials developing process.

2. Materials and methods

2.1. Materials, chemicals and reagents

Methacrylic acid - MAA (contains 250 ppm MEHQ as inhibitor, 99%) and methyl methacrylate – MMA (contains ≤ 30 ppm MEHQ as inhibitor, 99%) used in DMIPs and their parallel non-imprinted polymers (NIPs) synthesis as a functional monomers were purchased from *Sigma Aldrich* (*St. Louis, MO, USA*). In each case, the ethylene glycol dimethacrylate – EGDMA (98%, contains 90–110 ppm monomethyl ether hydroquinone as inhibitor) was used as a cross-linker and 1,1′-azobis (cyclohexanecarbonitryle) - ACHN (98%) was used as an initiator of polymerization reaction. The cross-linker and initiator were also obtained from *Sigma Aldrich* (*St. Louis, MO, USA*). The porogen agents used in the DMIPs and their parallel NIPs synthesis – acetonitrile – ACN (isocratic grade for liquid chromatography *LiChrosolv*®) and tetrahydrofuran – THF (HPLC grade, ≥99.9%, inhibitor-free) were purchased from *Merck KGaA, Germany*. At this point it should be mentioned, that before DMIPs and NIPs polymerization process, the vacuum distillation process was performed to remove the polymerization inhibitors from selected functional monomers. As for the EGDMA, to remove the polymerization inhibitor, the liquid–liquid extraction was performed, using 10% solution of sodium hydroxide (*POCH, Gliwice, Poland*) and then dried using anhydrous magnesium sulfate (*Eurochem, BGD, Tarnów, Poland*).

In a case of other organic solvents used in described research protocol, the 2,2,4-trimethylpentane (>99%) was supplied by *ThermoFisher, GmbH, Germany*, methanol (for liquid chromatography *LiChrosolv*®) was delivered by *Merck KGaA, Germany*, toluene (CHROMASOLV™ for HPLC) was purchased from *Honeywell Riedel-de Haën*™, hexane (pure p. a., 99.9%) and dichloromethane (CHROMASOLV™, for HPLC, ≥99.8%) were acquired from *POCH, Gliwice, Poland* and *Honeywell Riedel-de Haën*™, respectively.

As for the standard solutions which were used during the polymeric sorption material preparation process, the 4,4′-Dihydroxydiphenyl Ether (4,4′-Oxydiphenol, >98%) was used as a dummy template (as a structural analogue proposal for low mass PBDEs) and was delivered by *TCI, Japan*. The PBDE-47 (2,2′,4,4′-Tetrabromodiphenyl ether, 50 μg mL^{-1} in Nonane), PBDE-99 (2,2′,4,4′,5-Pentabromodiphenyl ether, 50 μg mL^{-1} in Nonane) and PCB 209 (Decachlorobiphenyl, 10 μg mL^{-1} in heptane) standard solutions were purchased from *LGC Standards (Teddington, United Kingdom)* and *Sigma Aldrich (St. Louis, MO, USA)*, respectively. All reagents, solutions and analytical standards were stored in accordance with the manufacturer's instructions. The empty 3 mL glass SPE columns and appropriate PTFE frits (polytetrafluoroethylene, 20 μm porosity) were purchased from *Sigma Aldrich (St. Louis, MO, USA).* As for the commercially available SPE tubes filled with appropriate sorption material (*SupelMIP*® *SPE – PAHs,* bed wt. 50 mg and *Discovery*® *DSC-Si SPE Tube,* bed wt. 500 mg), used for comparison with the de-

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veloped DMIP sorbents, they were acquired from *Sigma Aldrich (St. Louis, MO, USA)*. It is important not to use the plastic SPE tubes or any synthetic materials in a case of analyzing the PBDE compounds in environmental samples. It is caused by the fact, that those compounds might be present in employed plastic analytical tools and impact on the final determination results.

2.2. Simulation methodology – computer-assisted molecular modeling

The optimized geometries and energies of dummy template molecule (4,4′-Dihydroxydiphenyl Ether), functional monomer molecules (MAA, MMA) and the respective template-monomer complexes were calculated using the density functional theory (DFT). The B3LYP functional with 6-31 + G (d,p) basis set was used [49–51]. The conductor-like polarizable continuum model (CPCM) of the self-consistent reaction field theory (SCRF) was used to simulate a solvent/porogen agent environment (ACN or THF) [52,53]. The structure of dummy template, functional monomers and template-monomer complexes were initially optimized in the gaseous phase and next re-optimized within the CPCM model. All calculated structures exhibited no negative vibration frequencies, thus, all of them were taken as structures corresponding to local energetic minima.

All calculations have been carried out using the Gaussian 09v.D1 (Gaussian Inc., Wallingford, CT) program package [54]. The program HyperChem 8 (Hypercube, Gainesville, FL) was applied to the preparation of input data and for visualization of computed results.

The computational method was used to locate the most stable dummy template – monomer complexes and to calculate their interaction energy (ΔE) according to the following equation (1):

$$\Delta E = E_{complex} - \left(E_{template} + \sum E_{monomer}\right) \tag{1}$$

where $E_{complex}$, $E_{template}$, and $E_{monomer}$ is total energy of the complex, energy of the template, and energy of the monomer, respectively. The interaction energy of template-monomer complexes have been corrected for the basis set superposition error (BSSE) using the standard counterpoise method [55].

2.3. Preparation protocol of dummy imprinted and non-imprinted polymers

Four different dummy molecularly imprinted polymers and their proper non-imprinted polymers (DMIPs and corresponding NIPs) were synthesized by bulk polymerization technique using the non-covalent approach. The home-made glass reaction container/vessel was plugged into the vacuum-nitrogen stream line. To remove oxygen and potential contaminants which might occur inside the reaction container gaseous phase, the glass reaction vessel was purged by vacuum for 20 min and then by stream of inert gas - nitrogen for 5 min. After completion of this step, the selected reagents were introduced into the reaction container/vessel. Then, reaction container/vessel was tightly closed and the polymerization mixture was purged with nitrogen stream for another 5 min. Due to this, the whole polymer sorption materials preparation process (synthesis of DMIP and proper NIPs) was conducted in an inert gas atmosphere. During the whole polymerization process the time and reaction temperature were monitored.

The selected DMIPs were synthesized according to the following general protocol: in the glass container/vessel, 1 mmol (203 mg) of the 4,4′-Dihydroxydiphenyl Ether (dummy template molecule) was dissolved in 15 mL of selected porogen agent (ACN or THF). Then, into this solution, 4 mmol of the appropriate functional monomer – MAA (345 mg) or MMA (401 mg) and 20 mmol of cross-linker (3.9644 g EGDMA) were added. Next, all mentioned components were precisely mixed and the interior of the reaction container/vessel was once again purged by nitrogen gas stream. After this, the appropriate amount of the initiator was added into the solution (ACHN, 1% expressed as the percentage by mass) and once again the interior of the reaction container/vessel was purged by nitrogen stream. At the end, the glass reaction container/vessel was tightly sealed and placed in heated oil bath. The reaction was initiated by the temperature, due to this the oil bath temperature was set to 82 ± 1 °C. The polymerization reaction was carried out by 24 h.

After a defined period of time has elapsed, the polymerization process was completed and the glass reaction container/vessel was put out of the oil bath. Next, the obtained solid polymeric material was removed from the reaction container/vessel, placed on a Petri dish and dried at the room temperature. Then, the solid polymeric material was crushed, ground and sieved through a 250 μm mesh. As for the synthesis of equivalent non-imprinted polymers, also defined as a control blank polymers, the preparation protocol and polymerization conditions of those solid materials were similar, excluding the addition of dummy template molecule - 4,4′-Dihydroxydiphenyl Ether. The final stage of the DMIPs preparation process was to remove the template molecules from the polymeric material particles. Obtained polymeric sorption materials were transferred to the glass 100 mL bottles and 60 mL of methanol was added. Next, such mixture was shaken for 24 h under room temperature. After this, the mixture was filtered and the purified DMIP (without dummy template molecules) was dried at 60 °C. To assess the effectiveness of 4,4′-Dihydroxydiphenyl Ether removal, 150 mg of developed sorbents were placed inside an empty glass SPE column (between two PTFE frit). After this, the solid sorption material was washed using 5 mL of methanol. Then, the extracts were taken to a glass vials after the washing process, evaporated to 1 mL of methanol solution, transferred with a glass pipette to the GC amber glass vials, crimped and analyzed using GC-MS technique.

2.4. Characteristic of GC-MS analysis

The separation, identification and final determination process of analytical standards solutions and prepared real samples was performed applying gas chromatography technique (*Agilent Technologies 7890A GC System*) coupled with mass spectrometer (*Agilent Technologies 5977A MSD system* working in a selective ion monitoring mode – SIM mode) with quadrupole mass analyzer and connected with *Agilent 7693* autosampler. The applied injection system was as follows: pulsed splitless injector initial temperature was set to 300 °C, the injection pulse pressure was 25 psi until 1.5 min. The ZB-Semi-Volatiles, 20 m × 0.18 mm x 0.18 μm capillary chromatographic column (*Zebron, Phenomenex Inc., USA*) was applied for the analysis of selected low mass PBDE compounds and 4,4′-Dihydroxydiphenyl Ether. The GC oven temperature programme for the selected organic compounds separation was as follows: initial temperature was set to 90 °C and held for 1 min, then increased at a rate of 20 °C min^{-1} up to 300 °C, and held for 10 min. Gas flow (helium, 5.0) was operated in the constant flow mode – 0.8 mL min^{-1}. The MSD source temperature was set to 250 °C, the MSD quad temperature was set to 150 °C and the MSD transfer line temperature was set to 300 °C. The identification ions *m/z* for measured organic compounds were as follows: for PBDE-47 – 324, 326, 486, 488, for PBDE-99 – 404, 406, 564, 566, for PCB 209–496, 498, 500 and for 4,4′-Dihydroxydiphenyl

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Ether – 109, 202, 203. Each time 1 μL of analyzed sample (analytical standard or sample solution) was automatically injected onto column in splitless mode. The more information and detailed description of chromatographic analysis of PBDEs compounds might be found in previous literature data [8,14,32].

2.5. Characterization of the particles morphology

The specific surface areas of the developed DMIPs and proper NIPs were estimated using BET (Brauner-Emmet-Teller) nitrogen adsorption/desorption analysis. To assess the average pore sizes, pore diameters and pore volumes of the developed DMIP sorbents and their equivalent NIPs, the BJH (Barret-Joyner-Halenda) technique was applied. All above pointed analysis were performed with the use of Accelerated Surface Area and Porosimetry Analyzer (*Micromeritics, model ASAP, 2020*).

In order to characterize the chemical structure of the developed polymer sorbents (DMIPs and corresponding NIPs) the Fourier transform infrared spectroscopy (FT-IR) analysis with a KBr pellet formation method was performed. The amount of analyzed samples was 2.3 ± 0.3 mg. The DMIPs and NIPs samples were analyzed using *Philips PU9800* spectrometer (*Philips Analytical, Cambridge, UK*). The wave numbers of FT-IR analysis were collected at one data point per 2 $\mathrm{cm^{-1}}$ and ranged from 4000 to 500 $\mathrm{cm^{-1}}$.

The images of all DMIPs (after structural analogue removal) and one of the non-imprinted material (NIP_4) surfaces were taken by scanning electron microscopy technique (SEM) - *Hitachi TM3000 (Hitachi, Japan).* In order to present the characteristic of surface morphology of obtained polymeric sorption materials, the images of particles were taken in a different magnifications to show the distribution of DMIPs and selected NIP particles in an optimal way. Each time, before taking images of the surface of obtained sorption materials, the selected samples of DMIPs and NIP_4 were smoothly placed on the surface of carbon discs/rings as a suspension in ethanol solution. Then, the samples of studied polymer materials were covered with thin gold film, and during the sorption materials surface characteristic studies the electron beam was accelerated to 15 kV [56,57].

2.6. Solid-phase extraction with DMIP sorbent

The extraction was performed using commercially available SPE BAKER stationary system equipped with 12-position manifold and appropriate vacuum pump (vol. 15 L $\mathrm{min^{-1}}$). The DMIPs and their parallel non-imprinted material containers were prepared by placing 150 mg of defined polymer directly into the empty 3 mL SPE glass columns. It is important not to use the plastic SPE tubes in a case of analyzing the PBDE compounds in environmental samples, due to the fact that those compounds might be present in used plastic analytical tools and significantly impact on the final determination results. Defined amount of polymeric sorption material was packed between two frits made of PTFE. Firstly, the DMIP sorption material was once again rinsed by 5 mL of methanol solution, to fully removed potential remains of template molecules. Next, the sorption material was conditioned with 5 mL of isooctane: toluene solution (90: 10) and 5 mL of hexane: DCM solution (50: 50). Then, 1.5 mL of the sample (0.5 μg $\mathrm{mL^{-1}}$ hexane: DCM (50: 50) solution of mixture of PBDE-47 and PBDE-99) was introduced onto the SPE glass column. After this, the adsorbed analytes (PBDE compounds) were eluted with the use of 2 mL of hexane: DCM (50: 50) solution and 3 mL of isooctane: toluene (90: 10) solution. Next, the eluant was collected using glass tubes and evaporated under stream of nitrogen gas to 1 mL. Finally, defined volume of eluant was transferred to the amber glass chromatographic vials using glass Pasteur pipette, crimped with aluminum caps with PTFE membrane and analyzed using GC-EIMS system. Each SPE process was repeated four times for every DMIP sorbent and their corresponding NIPs. At this point it should be mentioned, that using SPE technique it is important to prevent the drying of the sorption bed on each step of SPE protocol. Similar analytical protocol was also applied in a case of selected SPE columns filled with commercially available sorption medium used for comparison with the developed DMIP sorbents.

2.7. Binding/adsorption studies

Taking into account the information enclosed in the scientific literature, the average numerical values of adsorption capacity (Q_t) [ng $\mathrm{mg^{-1}}$], in both static and dynamic adsorption tests, were evaluated employing the following equation (2) [58–60]:

$$Q_t = \frac{C_0 - C_t \times V}{m} \tag{2}$$

where:

C_0 - the initial concentration of the selected low mass PBDE in the prepared reference solution [μg $\mathrm{mL^{-1}}$];
C_t - the final concentration of selected low mass PBDE in the prepared reference solution [μg $\mathrm{mL^{-1}}$];
V – volume of solution [mL];
m - the mass of sorption materials placed in the SPE glass column [mg].

Briefly, the binging/adsorption capacity of developed DMIPs and their equivalent NIPs, defined as a blank samples, was estimated by calculating the difference of selected low mass PBDEs concentration in the initial reference solution (defined concentration of selected low mass PBDE compound), and their concentration measured in supernatant, after defining period of mixing time.

2.7.1. Static binding/adsorption tests

The static binding/adsorption tests of developed DMIP sorbents and their parallel NIPs were performed according to the following laboratory protocol: (i) approx. 21 mg of selected DMIP (the average mass of all studied DMIPs was 21.16 ± 0.76 mg) and appropriate NIPs (the average mass of all studied NIPs was 21.31 ± 0.72 mg) was weighted in 1.8 mL amber glass chromatographic vials; (ii) to each glass vials containing defined amount of sorption material, 0.5 mL of solvent hexane: DCM (50:50) was added; (iii) the PBDE-47 (c = 50 μg $\mathrm{mL^{-1}}$ in nonane) and PBDE-99 (c = 50 μg $\mathrm{mL^{-1}}$ in nonane) standard solutions were added with a different concentrations (ranged from 0.025 μg $\mathrm{mL^{-1}}$ to 0.150 μg $\mathrm{mL^{-1}}$) to each type of DMIPs and NIPs; (iv) every glass vial containing prepared mixture was shaken (220 rpm) vigorously for 6 h at room temperature; (v) the solution was separated from the sorption material, every supernatant was filtered and the concentration of selected low mass PBDE compounds in supernatant was measured by GC-MS system employing previously defined working parameters.

2.7.2. Dynamic binding/adsorption tests

The dynamic binding/adsorption tests of developed DMIP sorbents and their parallel NIPs were performed according to the following laboratory protocol: (i) approx. 21 mg of selected DMIP (the average mass of all studied DMIPs was 20.97 ± 0.85 mg) and appropriate NIP (the average mass of all studied NIPs was 21.64 ± 0.98 mg) was weighted in 1.8 mL amber glass chromatographic vials; (ii) to

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each glass vials containing defined amount of sorption material, 0.5 mL of solvent hexane: DCM (50: 50) was added; (iii) the PBDE-47 ($c = 50\,\mu g\,mL^{-1}$ in nonane) and PBDE-99 ($c = 50\,\mu g\,mL^{-1}$ in nonane) standard solutions were added at defined concentration $0.100\,\mu g\,mL^{-1}$ to each type of DMIPs and their equivalent NIPs; (iv) every glass vial containing prepared mixture was shaken (220 rpm) vigorously for different time intervals: 15 min, 30 min, 60 min, 120 min, 240 min, 300 min, 420 min at room temperature; (v) the solution was separated from the sorption material, every supernatant was filtered and the concentration of added low mass PBDEs in supernatant was measured by GC-MS system employing previously defined working parameters.

2.7.3. The recovery and imprinting efficiency studies

To conduct the recovery preliminary studies, the 150 mg of every DMIP sorption materials and their equivalent NIPs were placed inside the SPE glass tube, between two PTFE frits. After this, the extraction processes of selected low mass PBDEs (PBDE-47 and PBDE-99) from the reference hexane: DCM (50: 50) solutions at a concentration of $0.50\,\mu g\,mL^{-1}$ were conducted. The SPE procedure was performed similar to the protocol described in the previous section 2.5. This kind of studies gives another possibility to estimate the impact of selected reagents used during polymer synthesis on the morphological and physicochemical properties of developed sorption materials.

One of the most commonly used analytical procedures to evaluate the imprinting efficiency is to estimate the numerical values of parameter defined as imprinting factor (*IF*). Based on the application of developed DMIP sorption materials and their corresponding non-imprinted polymers, to assess the imprinting efficiency, which also estimates the presence of binding sites, the IF numerical values for each of developed DMIP sorption materials were calculated, employing the following equation [58,61,62] (3):

$$IF = \frac{Q_{tDMIP}}{Q_{tNIP}} \tag{3}$$

where:

Q_{tDMIP} – is the adsorption capacity of developed DMIP on the selected low mass PBDE compound;
Q_{tNIP} – adsorption capacity of appropriate non-imprinted material (NIP) on the selected low mass PBDE compound

As for the recovery values (*R*) of selected low mass PBDE compounds, they were calculated based on the following equation (4):

$$R = \frac{m_i}{m_0} \times 100\% \tag{4}$$

where:

m_i – the mass of selected analyte retained on the sorption medium [ng];
m_0 – the initial mass of selected analyte present in the studied sample [ng]

2.8. Evaluation of the QA/QC basic parameters

The calibration of GC-EIMS system was performed based on the external standard method (ESTD). In order to carry out the calibration process, for each of PBDEs (PBDE-47 and PBDE-99 reference standard solutions; $c = 50\,\mu g\,mL^{-1}$) a 6 calibration standard solution mixtures were set. Mentioned solutions were prepared in the amber glass chromatographic vials in which 1 mL of isooctane: toluene solution (90: 10) had been placed. Developed calibration standard solutions for PBDE-47 and PBDE-99 were ranging from 0.10 to $1.5\,ng\,mL^{-1}$. In every case, from each of prepared standard mixture the 1 μL was injected onto the GC-EIMS system starting from the solution containing the lowest concentration of selected PBDE compounds and analyzed using previously described equipment parameters. The injection procedure was repeated six times for each point on the curve. The calculated correlation coefficients (R^2) of the obtained calibration curves were as follows: for PBDE-47 – 0.999; for PBDE-99 – 0.998. The numerical values of standard deviation for each point on the developed calibration curves, ranged from 8.1 to 13.2%. In order to ensure the appropriate quality of obtained results, investigate the potential shifts between retention times of analyzed compounds and to reduce the influence of EIMS sensitivity on the obtained results, the PCB-209 was used as an injection standard. In the scientific literature mentioned PCB compound is also defined as an internal standard in some analytical protocols due to its comparable properties and similar behaves to the investigated organic compounds.

As for the other basic QA/QC parameters, to assess the basic validation parameters, which are the limit of detection (LOD) and the limit of quantification (LOQ), for applied GC-MS system, the calculation method based on the determination of the standard deviation of the collection of signals (defined by MS detector response) and the directional coefficient of the evaluated calibration curves was used. To estimate the numerical value of the LOD parameter for the GC-MS system used in the described studies, the following equation was employed [63](5):

$$LOD = \frac{3.3 \times \sigma}{b} \tag{5}$$

where:

σ - the standard deviation of the detector response (MSD) determined on the basis of the lowest concentration of the PBDEs compounds,
b - the directional coefficient of the calibration curve for individual PBDEs.

As for the values of LOQ parameter, it was determined as a triple value of the previously-assessed values of LOD: LOQ = 3 *x* LOD. Moreover, the estimated values of LOD parameter were investigated to approve the accuracy of the calculated parameter, verifying the following relationship: $10\ x\ LOD > m_{min}$ and $LOD < m_{min}$. It was noticed, that calculated values of LOD parameters meet the requirements of this equation. The assessed values of the LOD parameter for applied GC-MS technique were as follows: for PBDE-47 – 0.0302 ng; for PBDE-99 – 0.0315 ng.

3. Results and discussions

3.1. Composition of DMIP reaction mixture – molecular modeling studies

The new types of dummy molecularly imprinted polymer (DMIPs) sorption materials were prepared based on the laboratory protocol described in section 2.3. Considering the physicochemical properties of reagents and solubility of proposed structural analogue in the commonly employed in the synthesis porogen solvents, the THF and ACN were selected for further studies. The MAA functional

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monomer was selected as a representative of acid functional monomers group, and the MMA was picked up as a representative of inert functional monomers group. Detailed information about acronyms of the developed DMIP sorption materials, non-imprinted polymers and their chemical composition was listed in Table 1. The implementation of advanced mathematical calculations, combined with appropriate software, in the field of preparation of desired polymer sorption materials gives a possibility to significantly reduce the number of synthesis that might fail or receiving an unsuitable final product (reduction of the amount of organic solvents and mostly very expensive reference chemical compounds - templates). Relying on knowledge about the basic physicochemical properties of individual reagents, it is possible to narrow the search spectrum and to reduce the input data, which is needed to conduct the calculations concerning desired polymer material.

Table 1
The type and chemical composition of synthesized dummy molecularly imprinted polymers (DMIPs) and corresponding non-imprinted materials (NIPs).

Polymer acronym	Porogen	Functional monomer	Crosslinker	Dummy Templete
NIP_1	THF	MMA	EGDMA [20 mmol]	–
NIP_2	THF	MAA		–
NIP_3	ACN	MMA		–
NIP_4	ACN	MAA		–
DMIP_1	THF	MMA		4,4′-Oxydiphenol [1 mmol]
DMIP_2	THF	MAA		
DMIP_3	ACN	MMA		
DMIP_4	ACN	MAA		

Table 2
Results of B3LYP/6-31 + G (d,p) energies calculations of the most stable template–functional monomer complexes for 1:1, 1:2, 1:3 and 1:4 ratios calculated at the B3LYP/6-31 + G (d,p) level of theory in the gaseous phase.

molecules	E[a] (hartree)	BSSE[b] (kJ·mol^{-1})	ΔE[c] (kJ·mol^{-1})
template	−688.802962	–	–
MAA	−306.413053	–	–
MMA	−345.689354	–	–
template-(MAA)$_1$	−995.230041	3.50	−33.33
template-(MAA)$_2$	−1301.664579	7.93	−85.31
template-(MAA)$_3$	−1608.091676	11.40	−118.70
template-(MAA)$_4$	−1914.526164	15.84	−170.54
template-(MMA)$_1$	−1034.502779	2.42	−25.05
template-(MMA)$_2$	−1380.201616	4.61	−47.76
template-(MMA)$_3$	−1725.895027	6.48	−56.54
template-(MMA)$_4$	−2071.588333	8.20	−65.20

[a] Sum of electronic and zero point energies.
[b] Basis set superposition error.
[c] Energy of interaction with BSSE correction.

A theoretical study on the interaction of the dummy template molecule (4,4′-Dihydroxydiphenyl Ether) with functional monomers (MAA, MMA) in the formation process of a molecularly imprinted polymer was investigated by DFT method at the B3LYP/6-31 + G (d,p) level. The possible configurations of template - (functional monomer)$_n$ complexes, where “n” is from 1 to 4, were optimized in the gaseous phase. The calculated energies of the most stable complexes in the gaseous phase are listed in Table 2.

It can be seen from Table 2 that the dummy template – functional monomer complexes obtained for the 1:4 ratio of dummy template – monomer complexes (in comparison with the ratios 1:1, 1:2 and 1:3) have the highest interaction energy (ΔE). The optimized structures of the most stable complexes in a 1:4 stoichiometry are presented in Fig. 1. Furthermore, the template-(MAA)$_4$ complex is the most stable, than the template-(MMA)$_4$ complex. The high value of the interaction energy in the template-(MAA)$_4$ complex results from the formation the cyclic hydrogen-bonded structures in which MAA molecules form hydrogen bonds with the template molecule and between each other (see Fig. 1).

The synthesis of appropriate MIP sorption materials involves the formation of a complex between dummy template molecules (or its structural analogues) and the functional monomers in an appropriate solvent defined also as a porogen agent. Therefore, it must be taken into account the solvent effect on the stability of the template – functional monomer complexes. The conductor-like polarizable continuum model (CPCM) was used to study the effect of solvent (ACN, THF) on the effectiveness of dummy template – functional monomer interaction. The interaction energies of template – functional monomer complexes for 1:1, 1:2, 1:3 and 1:4 ratios in two corresponding solvents are shown in Table 3.

As it might be observed from Table 3, the template – functional monomer complexes are the most stable in the presence of THF as the solvent. Moreover, the interaction energies in the complexes of template-MAA are higher than in the template-MMA complexes. The template-MAA complexes formed with 1:4 stoichiometry (see Fig. 1), stabilized by cyclic hydrogen bonds, are the most stable in comparison with the mole ratios 1:1, 1:2 and 1:3. However, in the case of complexes with MMA, the most stable are complexes in which the monomer molecules form hydrogen bonds with the template molecule, i.e. containing two molecules of MMA (1:2). Subsequent MMA molecules do not form hydrogen bonds with the template molecule, whereas they form van der Waals interactions between the template and monomer molecule as well as between the monomer molecules (see Fig. 1). The lower interaction energies in the 1:3 and 1:4 complexes as compared with those in the 1:1 and 1:2 complexes are the

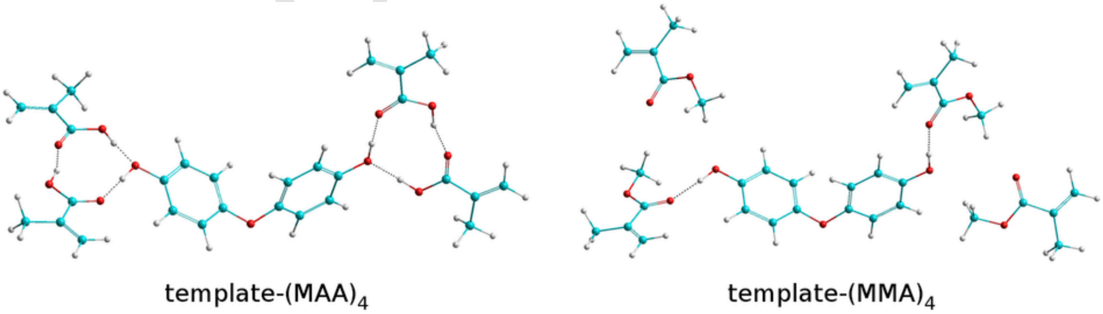
template-(MAA)$_4$ template-(MMA)$_4$

Fig. 1. The most stable template – functional monomer complexes calculated at the B3LYP/6-31 + G (d,p) level of theory in the gaseous phase. Hydrogen bonds are indicated by dashed lines.

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Table 3
Interaction energies with the BSSE correction (ΔE) of the most stable template–monomer complexes for 1:1, 1:2, 1:3 and 1:4 ratios calculated at the B3LYP/6-31 + G (d,p) level of theory in a simulated solvent environment (CPCM model).

functional monomer	solvent	$\Delta E_{1:1}$	$\Delta E_{1:2}$	$\Delta E_{1:3}$	$\Delta E_{1:4}$
		(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})	(kJ·mol^{-1})
MAA	ACN	−15.18	−51.14	−65.95	−102.12
	THF	−17.37	−55.16	−72.33	−110.25
MMA	ACN	−13.91	−27.14	−25.69	−24.42
	THF	−15.06	−29.57	−29.33	−29.15

effect of competition between van der Waals interactions with the solvent and the existing 1:2 complex. As a result, the complex of two molecules of MMA more likely to interact with the solvent molecules than with MMA, which contributes to decrease interactions in the complexes of 1: 3 and 1: 4. The calculated results of the interactions between template and MAA or MMA indicate that both functional monomers form stable complexes with the template molecule in the solvents considered. The hydrogen bonds formed between the template molecule and monomer play a major role in the complex stability. The best complexes, which means the most stable one, is achieved with MAA functional monomer and with THF as the solvent.

3.2. The DMIPs and NIPs FT-IR structure investigation

The general information about the result of FT-IR surface analysis of developed DMIPs and their equivalent NIP materials was presented on Fig. 2. Taking into account presented data it might be concluded that IR spectrum (the position, shape and intensity of the major bands) of developed DMIPs and their parallel NIPs were similar. This confirms mostly physical interactions between template molecules and polymer matrix [58]. The presence of this phenomenon might be caused by the fact, that the template molecules were probably completely washed out from the backbone structure of developed imprinted polymer materials. As it can be noticed, in several cases there were some differences in a signal intensity comparing NIPs and DMIPs FT-IR spectra. Moreover, minor shifts of some NIPs and DMIPs signals were observed. In general, the absorptions signals linked to stretching vibrations of hydrogen bond O-H for non-imprinted material were detected at 3434 cm^{-1}, but for developed DMIPs sorption materials (from no. 1 to no. 4) the adsorption signals were in the range from 3437 to 3442 cm^{-1}. The specific adsorption signals which corresponds to the stretching vibration of C=O, C-O and C-O bonds (which proves the application of the EDGMA as the cross-linker in polymer preparation process) for non-imprinted material, DMIP_1, DMIP_3 and DMIP_4 were observed at 1733 cm^{-1} and in the range from 1260 to 1254 cm^{-1} and from 1153 to 1155 cm^{-1} [57,64]. For DMIP_2 the specific adsorption peaks of C=O, C-O and C-O bonds were identified at 1731, 1257 and 1157 cm^{-1}, respectively. The methylene or methyl characteristic peaks for asymmetric stretching vibrations were detected for non-imprinted material and DMIPs sorption materials at the range from 2952 to 2991 cm^{-1}.

3.3. Morphological characteristic of polymeric sorption materials

Performing the BET nitrogen adsorption/desorption analysis and using BJH technique it is possible to obtain the valuable information about the morphological characteristic of the prepared sorption materials - DMIPs by defining the particles pore volume, specific surface area and pore size distribution. Interpretation of the obtained results of the nitrogen adsorption/desorption analysis of the developed DMIPs sorbents gives a possibility to assess the most important polymerization reaction factors influencing the applicability of the prepared polymer material as a sorption medium and the basic factors which might affect the sorption abilities. Based on the results of BET and BJH analysis, the general information about the relationship between the basic parameters characterized the surface morphology of developed DMIP sorption materials and their equivalent non-imprinted polymers (NIPs) were presented on Fig. 3 and 4. The discussion about the data which concerns the surface morphological charac-

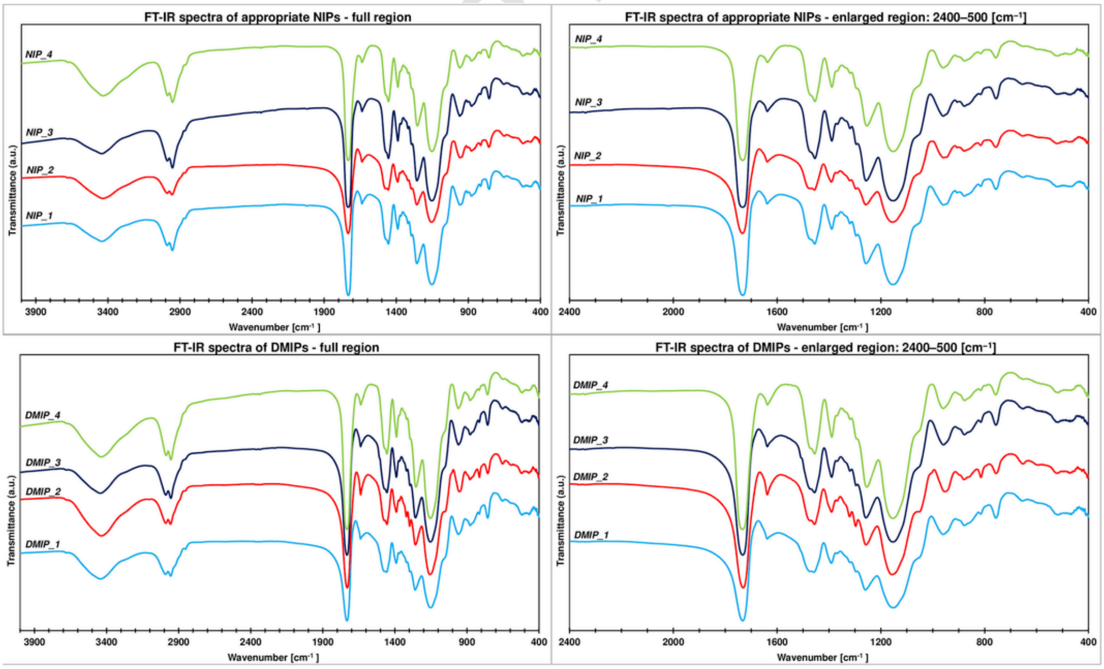

Fig. 2. The general view of FTIR spectra of developed DMIP sorption materials and corresponding non-imprinted polymers (NIPs).

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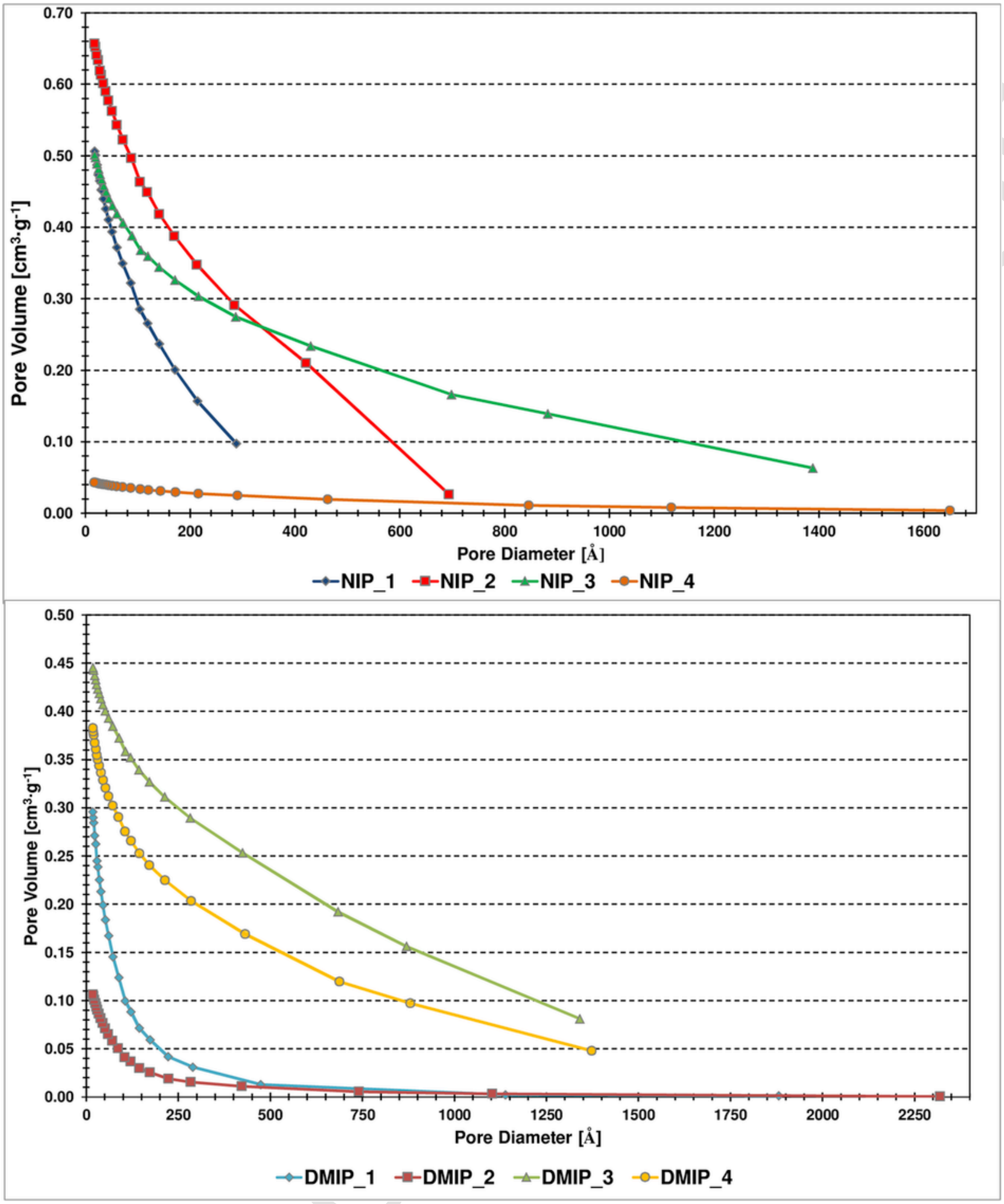

Fig. 3. The relationship between particles pore diameter and pore volume of developed DMIPs and their corresponding NIP materials.

teristic of the developed DMIPs and their equivalent NIPs should be carried out, taking into account the following main aspects: (i) differences between surface morphological characteristic of DMIP sorbents and non-imprinted materials; (ii) the influence of the functional monomer on the obtained DMIPs surface characteristic and (iii) the impact of porogen agent on the developed sorption materials.

Based on the results of BET and BJH analysis it was observed that the prepared DMIP sorption materials were characterized by relatively well-developed pore surface area in the range from 118 for DMIP_2 $m^2 g^{-1}$ to 352 $m^2 g^{-1}$ for DMIP_1. As for the corresponding non-imprinted polymers, the pore surface area was in the range from 17 $m^2 g^{-1}$ for NIP_4 to 398 $m^2 g^{-1}$ for NIP_1. Taking into account this information it might be concluded that prepared non-imprinted polymers are characterized by much more developed pore surface area then DMIPs, due to this they might be considered as a better sorbets for desired low mass PBDE compounds. Probably the well-developed pore surface area of NIPs is caused by the significant amount of nanopores or micropores, whose presence only affects the increase in specific surface area, but not to the availability of binding sites. Confirmation of this can be the information on the amount of mesopores, defined by the numerical value of the S_{micro}/t-plot parameter. In a case of non-imprinted materials the values of mentioned parameter were in the range from 0.64 $m^2 g^{-1}$ for NIP_4 to 29 $m^2 g^{-1}$ for NIP_3. As for the developed DMIP sorption materials the numerical value of the S_{micro}/t-plot parameter were much higher and ranged from 17 $m^2 g^{-1}$ for DMIP_2 to 88 $m^2 g^{-1}$ for DMIP_4. This may lead

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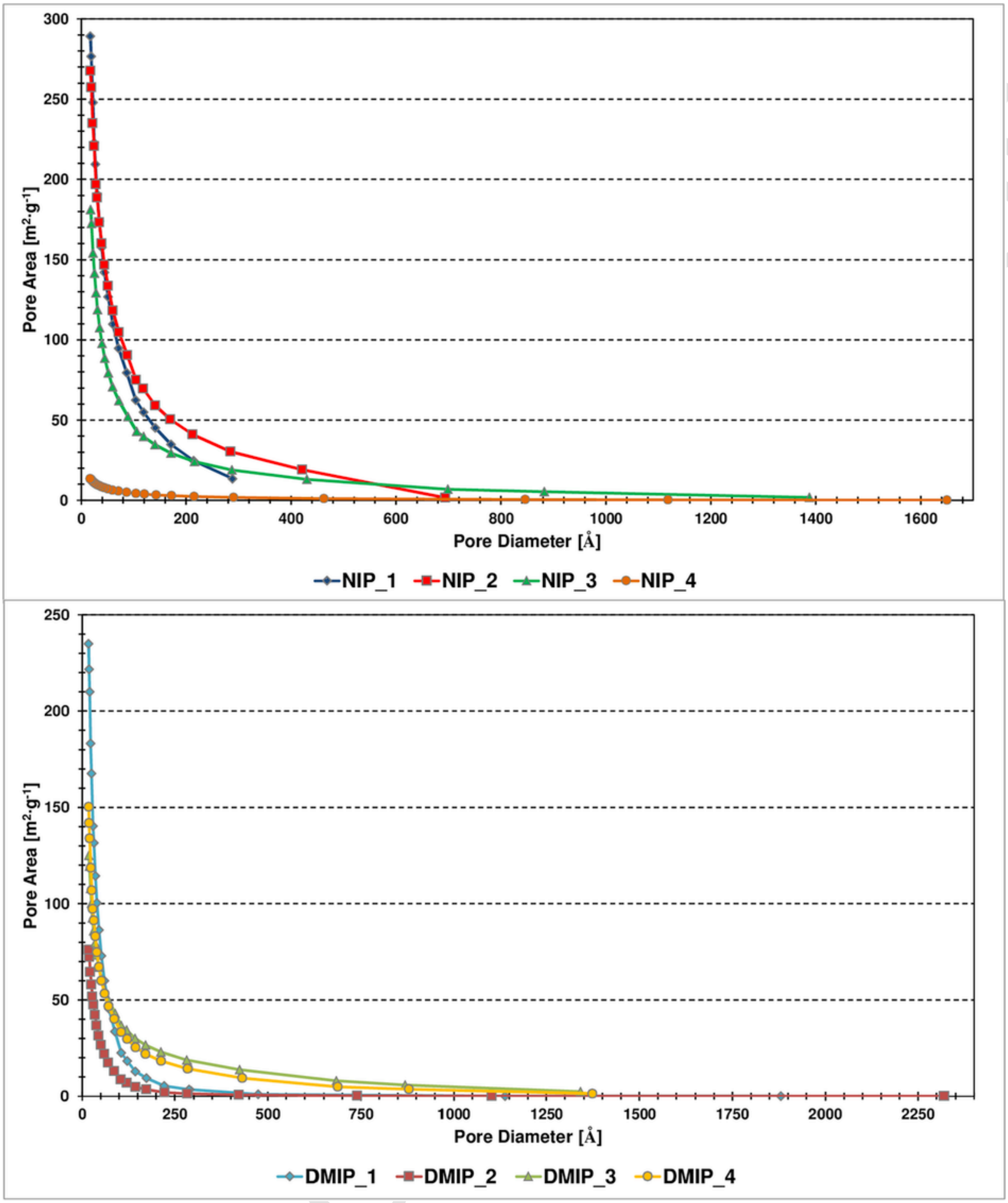

Fig. 4. The relationship between particles pore diameter and pore area of developed DMIPs and their corresponding NIP materials.

to the assumption that the imprinting process changes the surface morphological characteristic by increasing the availability of the porous structure for desired chemical compounds (higher availability of particles defined as mesopores). In addition, the presence of this phenomenon might be explained that in a case of non-imprinted polymers there is a lack of specific binding sites. Furthermore, high level of mesopores is a much desired factor in a case of sorption materials, due to the fact that they are responsible for a suitable surface area of the binding cavities. As a consequence, they support an appropriate identification and binding template molecules or other molecules which are characterized by similar structure. Additionally, the presence of significant amount of mesopores gives a possibility to successfully employ prepared polymer material as a sorption medium in SPE technique. It is caused by the fact, that such type of particles is characterized by good permeable for organic solvents in SPE technique and, because of this application of high pressures during extraction process might be omitted. Taking into account the data presented on Figs. 3 and 4 it might be noticed a clear dissimilarities between DMIP_4 and its corresponding non-imprinted material (NIP_4). In mentioned case, it was observed that non-imprinted material, which corresponds directly to the DMIP_4 (considering the types and amounts of applied polymerization reagents) had larger average pore diameter (approx. 17.5%), significantly smaller pore surface area (approx. 16 times) and much smaller cumulative pore volume (approx. 7 times). This lead to the conclusion that in a described

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case the presence of the dummy template molecule as the main element of the DMIP synthesis affects significantly on the general parameters that characterized the surface morphology of sorption materials.

Taking into account the influence of applied functional monomer during the sorption material preparation process it was observed that the type of functional monomer has an important impact on the cumulative pore volumes of DMIPs. Analyzing the data presented on Figs. 3 and 4, it was noticed that in a situation when the applied porogen solvents were the same, the cumulative pore volumes of investigated DMIPs prepared based on MMA were larger than for MAA. However, the observed difference in a case of DMIPs where the THF was employed as a porogen agent were much more significant than for DMIPs prepared based on ACN as a porogen solvent. The occurrence of this type of relationship might results from different physicochemical properties of applied functional monomers. MAA (logP = 0.831) is classified into the group of acidic monomers, while MMA (logP = 1.4) is defined as neutral functional monomers. There were no clear relationships between the employed type of functional monomer and the average pore diameter or average pore surface area.

Taking into account the impact of the type of porogen solvent on the surface morphological parameters it might be concluded that DMIPs materials prepared based on THF porogen agent were characterized by smaller values of average pore diameters (average value – 4.2 nm) and smaller cumulative pore volumes (average value – 0.22 cm^3 g^{-1}), then DMIPs sorbents developed using ACN as a porogen solvent (average values – 12.7 nm and 0.44 cm^3 g^{-1}, respectively). This kind of relation might results from the differences between the polarity of the employed solvents - the ACN (medium-polarity solvent) is much more polar porogen agent, then THF (moderately polar solvent). The interactions between functional monomer and porogen solvent and the differences between physicochemical properties, has also an important impact on the sorbent surface morphological characteristic.

Gathering all the information about the morphological surface characteristic of developed DMIPs sorption materials in should be highlight that the selection of the optimal porogen solvent for imprinted and non-imprinted materials should be motivated by the economic factors (i.e. ACN is cheaper, then THF) and laboratory safety, considering the physicochemical properties of applied organic solvents – in a described case lower boiling point of THF and the ability to form highly explosive peroxides might not be an optimal solution.

To perform the particles surface morphology studies of developed DMIP sorption materials and selected non-imprinted polymer (NIP_4), scanning electron microscopy (SEM) was applied. The particle surface images of the developed DMIPs sorption materials and NIP_4 were presented on Fig. 5. Analyzing mentioned surface images it was observed that in a case of developed DMIP sorbents, the particles were characterized by irregular shape and a broad distribution of sizes. This result from the fact, that developed DMIP materials after polymerization process were prepared by mechanically grinding the obtained polymer monoliths. However, comparing the images of the particles surfaces of DMIP and NIP materials it might be observed clear morphological differences between prepared polymer materials. In a case of DMIP sorption materials synthesized based on ACN (DMIP_3 and DMIP_4) as a porogen solvent, it might be seen that particles are characterized by more developed irregular surface shape than those prepared employing THF as a porogen agent (DMIP_1 and DMIP_2). Additionally, it was observed that the DMIP_2 particles were characterized by the smoother surface in comparison to other DMIP materials. The smooth surface of particles and wide-range areas of high homogeneity were also observed in non-imprinted polymer material. Moreover, there was a lack of the presence of large cavities on the surface of non-imprinted polymer material. Due to this fact, there is a very low possibility that studied PBDE compounds will be adsorbed on the surface of this polymer material.

3.4. The binding/sorption capabilities and imprinting efficiency studies

The results of performed static adsorption studies associated with the developed DMIP sorption materials and their equivalent NIPs were presented on Fig. 6. The error bars shown on the mentioned Fig. 6 are defined by the standard deviation (SD) of obtained results (n = 4). Taking into account previously shown particles surface characteristics of developed DMIPs materials and non-imprinted materials (the presence of significant differences between surface particles parameters), it might be assumed that further studies linked to the sorption capabilities might be omitted. However, to receive the reliably information about imprinting efficiency and sorption capabilities and to show the potential field of application, it is obliged to compare the properties of developed DMIPs to their directed corresponding NIPs. Investigating the information presented on Fig. 4, it might be observed that in every case of DMIP sorption material the values of adsorption capabilities (defined by the amount of adsorbed analyte) were increased proportionally to the initial PBDE-47 and PBDE-99 concentration. The higher values of adsorption capacity were related to the high concentration of defined analyte solution. Moreover, the obtained results indicated that developed DMIP_2 sorption material, was characterized by the lowest adsorption capacity (2.40 ng mg^{-1} for PBDE-47 and 2.34 ng mg^{-1} for PBDE-99, at the concentration equal 0.15 ng mL^{-1}). For the other developed sorption materials (DMIPs) the calculated values of adsorption capacities at the selected analytes concentration equal 0.15 ng mL^{-1}, were at the range from 2.40 ng mg^{-1} to 2.67 ng mg^{-1} for PBDE-47 and from 2.34 ng mg^{-1} to 2.60 ng mg^{-1} for PBDE-99. Mentioned results might let to the conclusion that the slightly better affinity of developed DMIP sorption materials for PBDE-47, then PBDE-99. Analyzing the information presented on Fig. 6 associated with non-imprinted polymers it was observed that also in this case the adsorption capabilities were increased proportionally to the initial PBDE-47 and PBDE-99 concentration. However, static adsorption studies on the NIP materials showed clear differences between imprinted and non-imprinted materials. In each case, the calculated values of adsorption capabilities for developed DMIPs were higher, than for their equivalent NIPs. It was noticed that for the prepared NIPs the calculated values of adsorption capacities at the selected analytes concentration equal 0.15 ng mL^{-1}, were at the range from 0.78 ng mg^{-1} to 1.78 ng mg^{-1} for PBDE-47 and from 0.65 ng mg^{-1} to 1.96 ng mg^{-1} for PBDE-99. Taking into account the adsorption capabilities of synthesized non-imprinted materials it was observed that NIP_1 (prepared on THF as a porogen agent and MMA as a functional monomer) was characterized by the lowest adsorption capacity. The highest adsorption capacity of non-imprinted materials was calculated for NIP_4 (prepared on ACN as a porogen agent and MAA as a functional monomer). Moreover, it should be highlighted that non-imprinted polymers from NIP_1 to NIP_3 were characterized by similar dynamic of low mass PBDEs sorption process – the average value of adsorption capacities for the PBDE-47 and PBDE-99 at the content level equal 0.15 ng mL^{-1} were 0.77 and 0.96 ng mg^{-1}, respectively. As for the NIP_4 static sorption characteristic, in each case the measured values of adoption capacity were much higher, in comparison to the other non-imprinted polymers (1.78 and 1.96 ng mg^{-1}). Gathering mentioned information it

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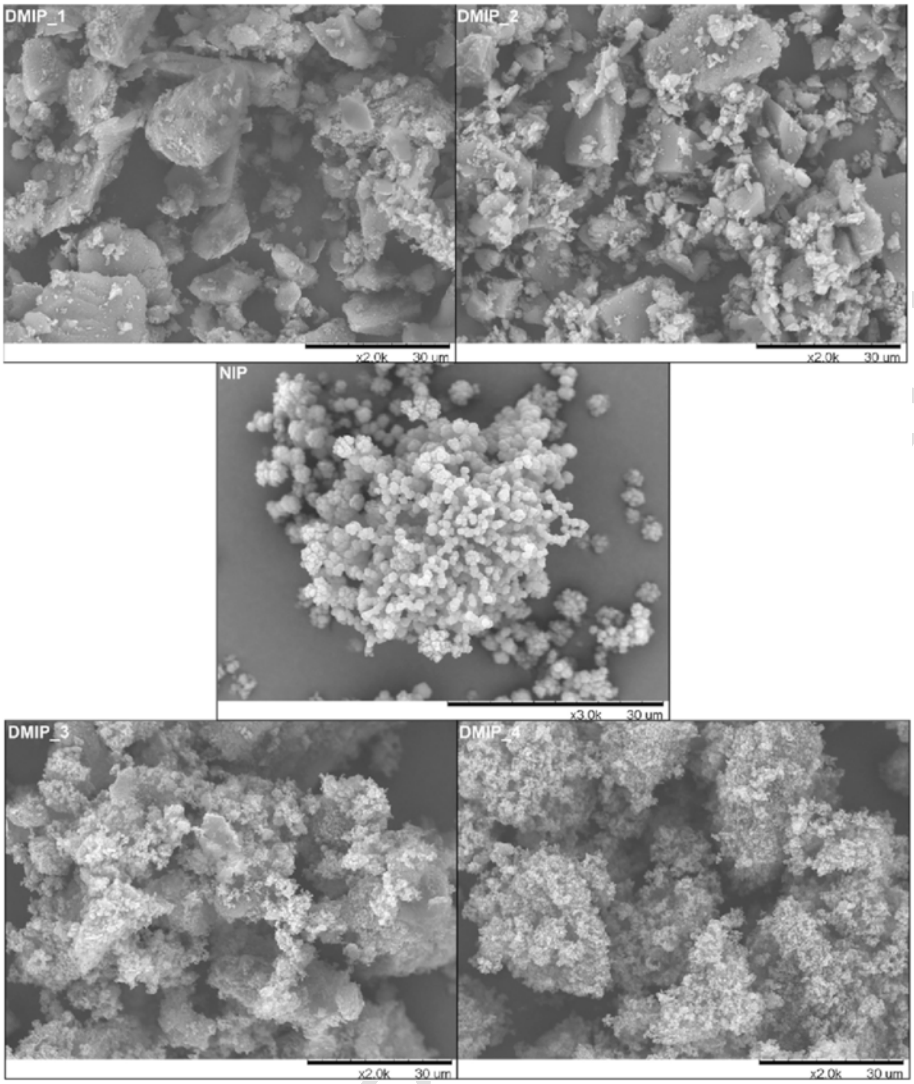

Fig. 5. The images obtained by SEM of particles morphological structure of prepared DMIPs and particles morphological structure of selected non-imprinted material (NIP_4).

could be concluded, that prepared DMIPs based on a proposed structural analogue are characterized by good affinity to the low mass PBDEs and might be considered as potential sorbents in SPE techniques for specific recognition of selected PBDEs.

The presence of this phenomenon corresponds to the results associated with the DMIPs particle surface characteristic. In mentioned studies, The DMIP_1 was characterized by the largest particles surface area ($352\,m^2\,g^{-1}$) and the DMIP_3 was characterized by the largest cumulative pore volumes ($0.46\,cm^3\,g^{-1}$) and average pore diameter (14.1 nm). As for the DMIP_2 sorption material it was characterized by the smallest particles surface area ($118\,m^2\,g^{-1}$) and the samples values of cumulative pore volumes ($0.12\,cm^3\,g^{-1}$). This lead to the conclusion that, in a case of prepared DMIP sorbents, the particles surface morphology and the availability of binding sites have a significant impact on the final results of static adsorption characteristic.

The general results of preformed kinetic/dynamic adsorption studies regarding the developed types of DMIP sorption materials and their equivalent NIPs were presented schematically on Fig. 7. Analyzing the information gathered in Fig. 7 it was noticed that in a case of developed DMIPs and their equivalent NIPs, the amount of selected low mass PBDEs up to 240 min was characterized by binding/sorption fluctuations and it was not increased constantly. In both cases, the presence of this phenomenon might be caused by the unavailability of all binding sites (selective cavities) in defined mixing time. Furthermore, the binding/sorption fluctuations in the period from the incubation start up to 240 min might be associated with the fact that the selected layout (DMIP or NIP) does not reach the clear equilibrium state in the mentioned short range of incubation time. Moreover, the low mass PBDEs sorption capacities fluctuations might be generated by the differences in the sorption materials structure morphology, mainly related to the size and distribution of particle pores. After 240 min the values of adsorption capacities reached equilibrium state. However, the equilibrium state after 240 min of incubation is much more clear in the case of DMIPs sorbents, then for their corresponding NIPs. For the developed DMIPs sorbents, the calculated values of adsorption capabilities did not differ in a statistically significant way after the 240 min of incubation. Moreover, it might be observed that taking into account the calculated values of standard deviations (showed as an error bars on Fig. 7) there were no clear differences between the developed DMIPs. This led to the conclusion that for every type of developed DMIP sorption material the

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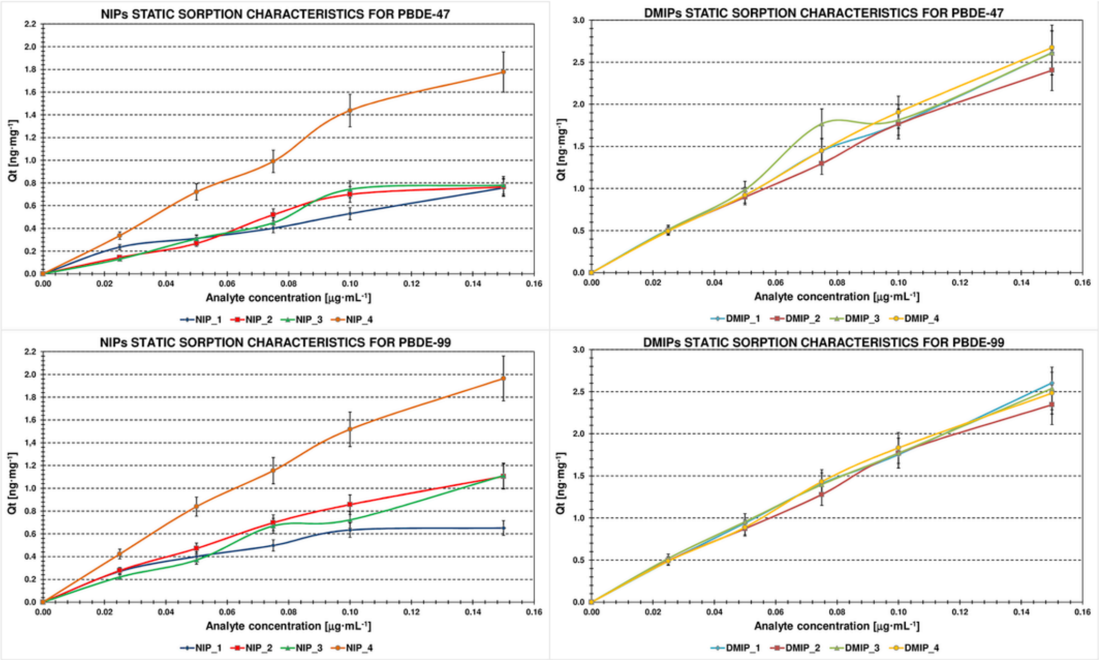

Fig. 6. Binding affinity studies of developed DMIPs and equivalent NIPs – static adsorption characteristic.

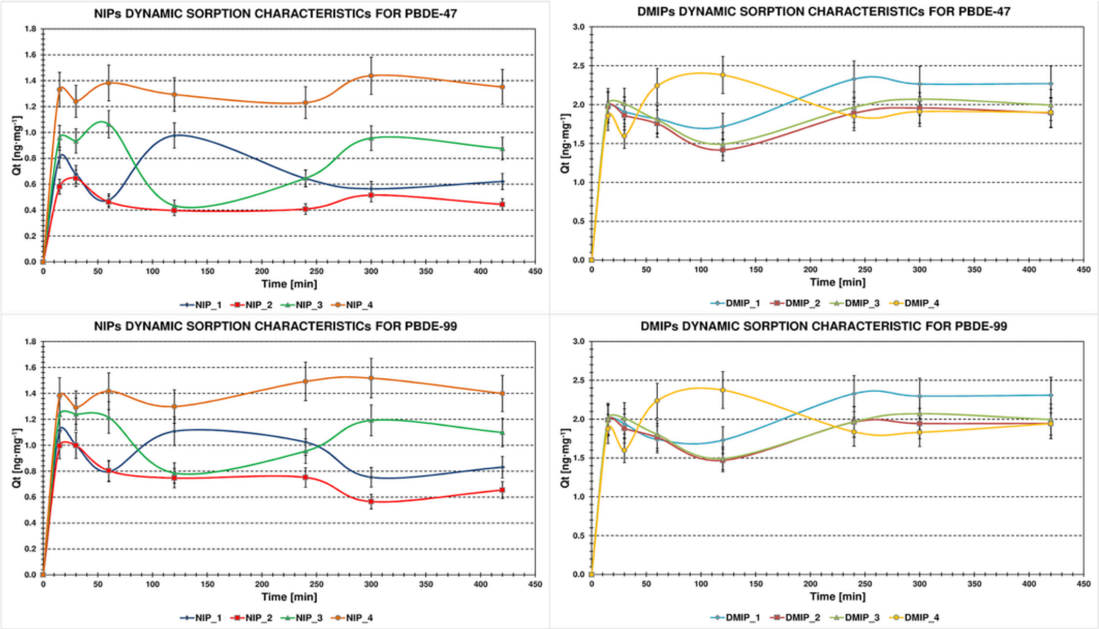

Fig. 7. Binding affinity studies of developed DMIPs and for corresponding NIPs – dynamic adsorption characteristic.

period of 240 min might be sufficient to obtain the equilibrium state. As for the appropriate non-imprinted materials it might be noticed that the clear equilibrium state might be considered after 300 min from the beginning of incubation time. Making an allowance for the values of standard deviation for the prepared NIPs, the calculated values of adsorption capabilities did not differ in a statistically significant way after 300 min of mixing time. It was observed the clear difference between final values of kinetic adsorption capabilities measured after 420 min of incubation for developed DMIPs and their equivalent NIPs. In each case the adsorption capacity of non-imprinted polymers were lower in comparison to DMIPs sorbents. Considering the adsorption capacity of prepared NIPs, the lowest values were measured for NIP_2 (0.41 ng mg^{-1} for PBDE-47 and 0.67 ng mg^{-1} for PBDE-99). The highest values of adsorption capacities were noticed for NIP_4 (1.35 ng mg^{-1} for PBDE-47 and 1.40 ng mg^{-1} for PBDE-99). Moreover, it might be seen that the non-imprinted polymers in which the ACN was used as a porogen agent were characterized by higher adsorption capabilities to low mass PBDEs, then those NIPs in which THF was used as a porogen agent.

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Taking into account the data presented on Fig. 7 it was observed that, after 420 min, the DMIP_1 was characterized by the highest values of adsorption capacity for PBDE-47 and PBDE-99 (2.26 and 2.31 ng mg^{-1}, respectively). The lowest values of adsorption capacities for PBDE-47 and PBDE-99 were noticed for DMIP_2 (1.89 and 1.94 ng mg^{-1}, respectively). For both, the DMIP_3 and DMIP_4, the adsorption capacities values were similar and oscillated around 2.00 ng mg^{-1}. The differences in adsorption capacities values for selected PBDE compounds between DMIP_1 and DMIP_2 probably are initiated by the application of different functional monomers and their interactions with THF porogen agent. In a case of developed sorption materials based on the ACN as a porogen solvent, mentioned relation was not observed. The presence of a clear difference in kinetic adsorption capacities between developed DMIPs and their corresponding NIPs might be a proof to the presence of specific binding sites which are able to identify and selectively adsorb defined chemical compounds. In a case of non-imprinted polymers, it might be conclude that there is a lack of specific binding sites and interactions between the sorbent surface and the defined chemical compounds. The binding abilities of prepared NIP materials to defined low mass PBDE compounds mainly might arise from intermolecular interactions such as the van der Waals forces.

The general information about the values of imprinting factor (IF) calculated for developed DMIP sorption materials based on the static adsorption capacity studies was presented on Fig. 8. The error bars shown on the mentioned Figure are defined by the standard deviation

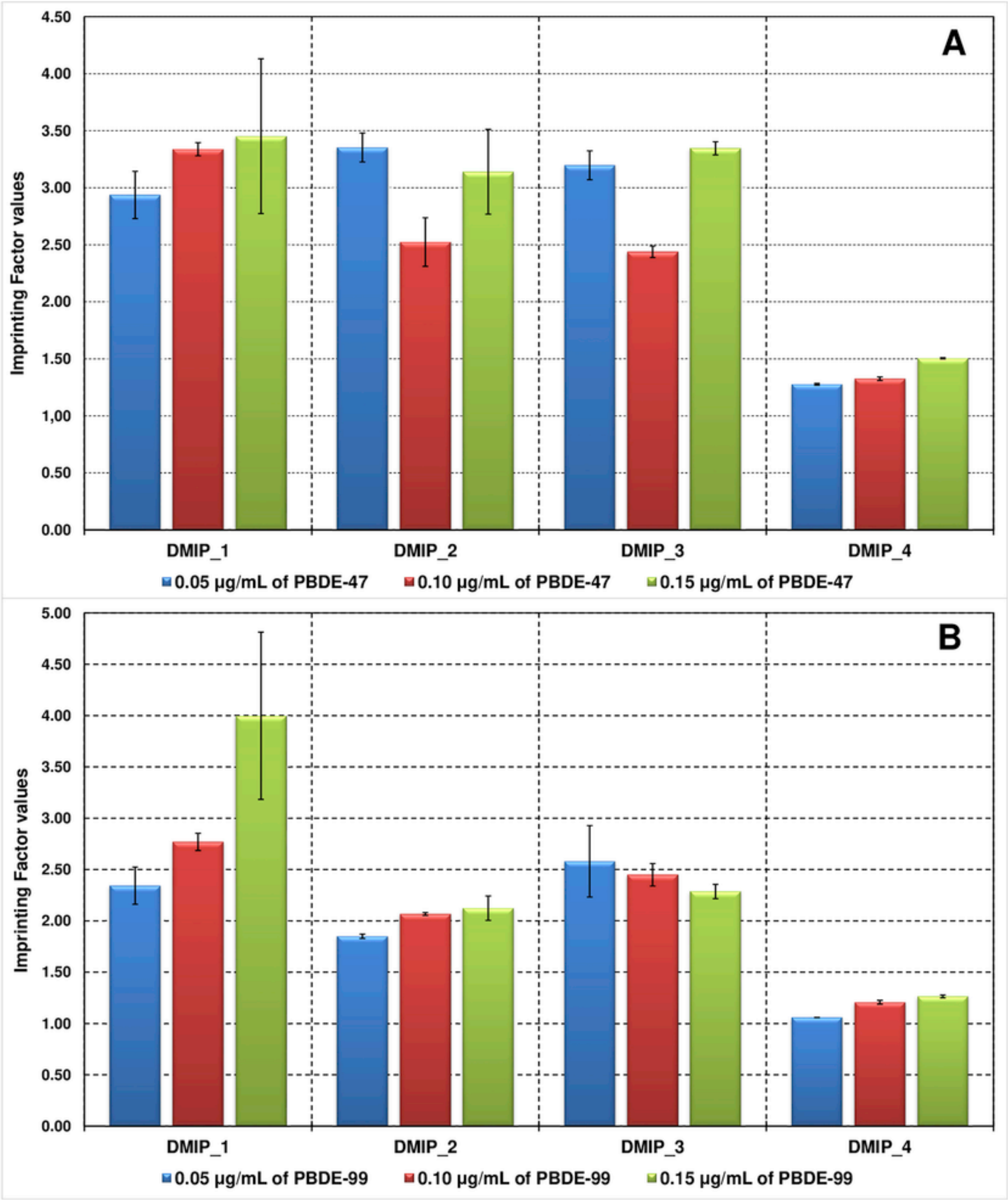

Fig. 8. The general results of calculated values of imprinting factors (IF) for developed imprinted polymer materials: A – calculated IF values of PBDE-47; B – calculated IF values of PBDE-99.

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(SD) of obtained results (n=4). At this point it should be highlighted that selectivity coefficient (α) was not calculated, due to the fact that this kind of data might be considered only as screening information. It results from the fact, that during the DMIPs preparation process the typical PBDE compound as a template was not used. The performed synthesis was based on the proposed structural analogue of PBDE compounds - 4,4′-Dihydroxydiphenyl Ether. Only in a case, in which during the polymer sorption material preparation process the applied template is a direct representative of defined group of chemical compounds, the information about the α coefficient has the reliable meaning. For this reason, showing the information about the calculated values of α coefficient might not be an appropriate parameter to compare the developed polymer sorption materials. Referring to the data related to the calculated values of IF, it was noticed that the highest values for both PBDE-47 and PBDE-99 were determined for DMIP_1 and DMIP_3. In a case of DMIP_1, the calculated values of IF for each of low mass PBDEs content level were ranged from 2.94 to 3.45 for PBDE-47 and from 2.32 to 4.00 for PBDE-99. As for the DMIP_3, the assessed values of IF were oscillated from 2.44 to 3.35 for PBDE-47 and from 2.29 to 2.58 for PBDE-99. The lowest IF values for each of low mass PBDEs content level were determined for DMIP_4, and were ranged from 1.28 to 1.50 for PBDE-47 and from 1.06 to 1.26 for PBDE-99. Taking into account the data about the assessed values of IF for developed sorption materials it was observed that in almost every case the IF values were higher for PBDE-47, then for PBDE-99. The presence of this phenomenon might be caused by smoothly differences in a chemical structures of studied low mass PBDEs. PBDE-47 (2,2′,4,4′-tetrabromodiphenyl ether) has in its structure 4 bromine atoms, two at each of the aromatic rings (in a symmetrical way). In contrast, PBDE-99 has in its structure 5 bromine atoms - 2 with one aromatic ring and 3 at the other. Therefore, it could be concluded that PBDE-47 might be more bound by developed sorption materials due to its more symmetrical and more similar chemical structure to the applied structural analogue (dummy template) applied in DMIPs preparation process. In addition, considering the information presented on Fig. 8 in might be observed that calculated values of imprinting factors for each of prepared DMIP sorption materials in selected concentration levels of low mass PBDEs were above one (IF > 1). According to the information listed in the literature [58], the presence of this phenomenon might be associated with the inordinate affinity of DMIPs for selected low mass PBDEs. It was also noticed, that in a case of DMIP_1 and DMIP_4, the estimated values of IF were correlated to the concentration of determined low mas PBDEs - IF values increased with the increment of both PBDE-47 and PBDE-99 content level.

Analyzing this information it might be concluded that the type of applied functional monomer and porogen agent in the polymer synthesis have a significant impact on the sorption abilities of developed sorbents. The calculated values of IF for DMIP sorbents corresponds to the obtained results associated with the particle surface characteristic – the DMIP_1 was characterized by the largest particles surface area (352 $m^2 g^{-1}$) and the DMIP_3 was characterized by the largest cumulative pore volumes (0.46 $cm^2 g^{-1}$) and average pore diameter (14.1 nm).

3.5. Molecularly imprinted solid phase extraction recovery studies

The solid-phase extraction basic studies were performed in accordance to the protocol described in the 2.6. section based on the appropriate prepared reference solutions of hexane: DCM (50: 50). The general information about the obtained rates of recovery of selected PBDE compounds for each of developed DMIP sorption materials and for suitable non-imprinted polymers (NIPs) was presented on Fig. 9. The error bars shown on the mentioned Figure are defined by the standard deviation (SD) of obtained results (n=4).

The recovery results were also compared to the obtained rates of recovery for two types of commercially available sorption materials. Analyzing the information presented on Fig. 9, in each of the cases the significant differences between developed DMIP sorption materials and appropriate non-imprinted polymers were observed. The occurrence of this phenomenon might be caused by the presence of selective binding sites in the surface structure of developed DMIP ma-

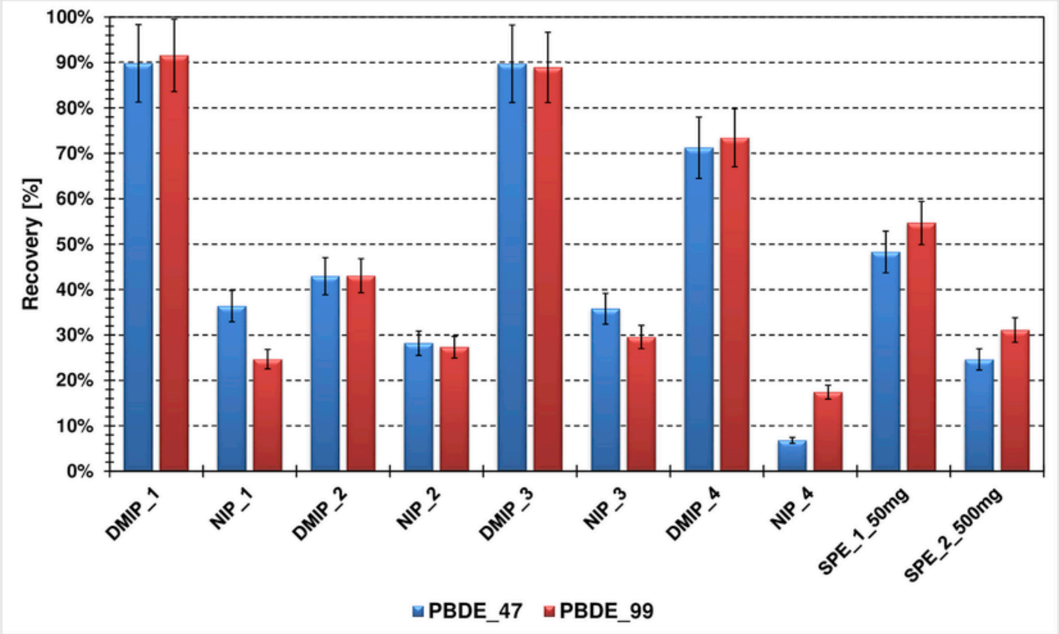

Fig. 9. The general results of recovery comparison studies of PBDE-47 and PBDE-99 compounds in reference solution for developed DMIPs and corresponds NIPs.

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terials. Due to this, the use of prepared DMIP materials (especially DMIP_1 and DMIP_3) gives a possibility to recognize and to collect the selected PBDE compound from the prepared reference solution in an effective way. This results corresponds to the calculated imprinting factor, which reached the highest numerical values in a case of DMIP_1 and DMIP_3. Considering the information presented on Fig. 9, it might be noticed that the highest values of recovery of PBDE-47 and PBDE-99 were observed for DMIP_1 (89.9% and 91.6%, respectively) and DMIP_3 (89.7% and 88.9%, respectively). As for the equivalent non-imprinted materials, the average values of recovery for selected PBDEs were 36.4% and 24.7% for NIP_1 and 35.8% and 29.6 for NIP_3. The average recovery value above 70% was also noticed for DMIP_4 sorption material (71.2% and 73.4%, respectively). The lowest recovery values in a case of developed DMIP sorbents were noticed for DMIP_2 (42.9% and 43.1%, respectively). At this point it should be mentioned, that in the case of a comparison of recovery values for DMIP_2 and NIP_2, the difference between the estimated values was the smallest. The lack of clear difference between recovery values of DMIP_2 and NIP_2 might lead to the conclusion that developed DMIP_2 material is not an appropriate sorbent in SPE technique to selective recognition of low mass PBDE compounds. By making a comparison between DMIP_4 and its direct non-imprinted counterpart (all NIPs were synthesized based on the same type and amount of functional monomer, porogen agent and cross-linker as equivalent DMIP sorption materials), it might be seen a clear difference in estimated recovery values. For the DMIP_4 the recovery values of PBDE-47 and PBDE-99 were, respectively, ca. 10 times and ca. 4 times higher, than for equivalent non-imprinted material – NIP_4. The obtained results associated with the recovery values of selected PBDE compounds for developed DMIP sorption materials also corresponds to the results concerning the morphology of particles structure. Taking into account the following relation it might be concluded that the main impact on the recovery values have such morphological factors as pore surface area, cumulative pore volumes and average pore diameter. In a case, where the studied sorption material is characterized by better particles morphology, it is possible to obtain better and more satisfying values of analytes recovery. Additionally, at this point should be mentioned that analyzing the data presented on Fig. 9, it was noticed a clear difference between developed DMIP (especially DMIP_1, DMIP_3 and DMIP_4) sorption materials and selected commercially available sorption mediums in SPE tubes. Due to the imprinting effect and the presence of selective binding sites the developed DMIP sorbents were characterized by the much better recovery values than selected commercially available SPE sorbents. However, making this kind of comparison it should be kept in mind that this is only screening, preliminary comparing information. It is caused by the fact, that selected commercially available SPE sorbents are characterized by the different particles surface morphology, are dedicated not to a selected chemical compound, but for a specific group of chemical compounds (they might be not selective enough for studied PBDE compounds). Furthermore, there is a possibility that a in a case of commercially sorbents the conditioning process might be different, than in a case of developed DMIP sorbents. Because of this, the efficiency of SPE process using commercially available sorbents and the recovery values of selected PBDE compounds might be understated.

4. Conclusions

Gathering all obtained information about the morphological and physicochemical properties of developed DMIP sorption materials, it was concluded that selected chemical compound 4,4′-Dihydroxydiphenyl Ether might be successfully applied, as a structural analogue for the low mass PBDE compounds in new imprinted sorption materials preparation process. It was noticed that the part of developed sorption materials with molecular fingerprint might be used as an effective SPE sorbent for the chemical compounds from PBDE group (not directly selective for the single PBDE compound) in a sample preparation process. However, it was observed the inordinate affinity of prepared DMIP materials for PBDE-47 – probably caused by its symmetrical and much more similar structure to the chemical structure to the applied dummy template. Mainly, it might be caused by the fact, that in the skeleton of the selected dummy template molecule is the same – two aromatic rings combined with ether bond. Due to this, the particles structure of developed imprinted sorption materials are characterized by specific binding sites which are able to identify and selectively adsorb chemical compounds characterized by mentioned earlier molecular structure. Taking into consideration obtained basic laboratory research results it might state that in the near future, selected types of developed DMIPs (considering economic aspects and laboratory safety) could be applied at the enrichment or/and preconcentration stage of low mass PBDE analytes (as a SPE tubes selective sorption medium) from the solid environmental samples such as soil or bottom sediments - the main subject of future research carried out under real conditions.

Theoretical results of the interactions between the selected dummy template molecule and the functional monomers indicated that dummy template molecule forms stable complexes with both functional monomers in the solvents considered. Molecular modeling may be useful for providing information for the choice of suitable functional monomer and proper solvent in the preparation of molecularly imprinted polymers. Computational methods allow faster evaluation of the DMIP pre-polymerization stage reducing the time and cost for developing a DMIP materials.

Analyzing all the information associated with the particles morphology characteristic of the developed DMIP materials, it was observed that particles surface area, average pore diameter and cumulative pore volumes have significant impact on the sorption properties and abilities such as recovery and imprinting factor. Furthermore, it was observed that the selection of the appropriate functional monomer and porogen agent (and their physicochemical properties) have major influence on the sorption abilities and particles surface morphology of the developed DMIP sorption materials. Considering the obtained results about the particles morphology characteristic of the developed DMIPs and their corresponding NIPs, it might be concluded, that probably the material sorption abilities (sorption efficiency) are not only caused by the well-developed pore surface area, but also by the presence of specific binding sites arising from the fingerprint effect. This also might affect the porous structure of sorption material by increasing the amount of mesopores.

Moreover, application of computational molecular modeling methods in basic laboratory studies, especially in a case of synthesis of new type of sorption materials, might significantly reduce the time and costs of whole preparation process. However, it should be keep in mind that theoretical calculations combined with molecular modeling studies requires certain assumptions and are performed at a defined level of probability. Due to this fact, the theoretical studies might indicate the most optimal direction for the real laboratory studies, but they do not give comprehensive assurance that the final synthesis product will be characterized by the best physicochemical properties and the most optimal surface morphological characteristics. The presented characteristics of the conducted basic laboratory studies and the interpretation of the obtained results allow looking optimistically

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in the future in the context of further development of described studies on the application character.

Conflicts of interest

The authors declare that they have no conflict of interest.

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