PMMA-b-PMAA Diblock Copolymer as a Reactive Polymeric Surfactant for the Functionalization of ZnO Nanoparticles

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Dedicated to the memory of Prof. Dr. Marija Kosec.

Abstract

We investigated the efficiency of poly(methyl methacrylate)-*b*-poly(methacrylic acid) (PMMA-*b*-PMAA) diblock copolymers as reactive polymeric surfactants for the functionalization of ZnO nanoparticles (NPs) of diameters ranging from 20 to 80 nm. PMMA-*b*-PMAA with molar masses in the range of 20.000 and 30.000 g/mol and PMAA content between 3 and 30 mol % were prepared by reversible addition-fragmentation chain transfer (RAFT) radical polymerization. Scanning transmission electron microscopy (STEM) showed efficient coverage of the particle surface with a polymer layer and infrared (IR) spectroscopy provided evidence of interaction of the PMAA segment (anchoring chains) with the NP surface. As demonstrated by dynamic light scattering (DLS) and UV-vis spectroscopy, the amphiphilic PMMA-*b*-PMAA block copolymers prevented agglomeration of ZnO NPs to great extent and thus increased transparency of ZnO suspensions in tetrahydrofuran (THF) and PMMA/ZnO nanocomposites in the visible light region. We also demonstrated the importance of the length of PMAA segment for ZnO surface functionalization. Optimal UV-vis performance of suspensions of functionalized NPs in THF as well as of PMMA/ZnO nanocomposites was achieved with PMMA-*b*-PMAA block copolymers containing 3 and 15 mol % of anchoring PMAA segment.

Keywords: Block copolymers, PMMA-*b*-PMAA, ZnO, polymeric surfactant, functionalization, PMMA/ZnO nanocomposite

1. Introduction

Polymeric nanocomposites with inorganic nanoparticles as nanofillers are used in a wide range of applications in various fields, such as medicine, textiles, cosmetics, agriculture, optics, food packaging, optoelectronic devices, semiconductor devices, aerospace, construction and catalysis. One of the main issues with polymer nanocomposites is to achieve homogeneous dispersion of nanoparticles (NPs) in the polymer matrices. It is known, namely, that NPs tend to agglomerate due to their large specific surface area and volume effects.[1] This problem can be overcome by functionalization of the surface of the inorganic NPs with small molecules, such as silanes and phosphonates, or polymers, to become more compatible with polymer matrix.[1–3] The dispersion stability of nanoparticles in organic solvents or monomers is known to be remarkably improved when polymers are grafted on their surfaces. From the thermodynamic point of view, the most favorable structures for polymeric surfactants are block and graft copolymers.[4] In general, one or more segments of such macromolecules, referred to as the "anchoring" chains, are chosen because of their high affinity for the NP surface. Other parts of the polymer molecule have very low affinity for the NP surface but are strongly solvated by the medium.

In our previous work we synthesized polyol modified ZnO NPs *in situ* and ZnO NPs modified by polymer as well as block copolymer.[5–7] In the present work we evaluate a poly(methyl methacrylate)-*block*-poly(methacrylic acid) (PMMA-*b*-PMAA) diblock copolymer as a reactive polymeric surfactant for the postmodification of nanosized ZnO. Many di- and triblock copolymers such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA),[8] poly(ethylene oxide)-*b*-poly(propylene oxide) (PEO-*b*-PPO),[9] poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO),[10] poly(ethylene oxide)-*b*-poly(methacrylic acid) (PEO-*b*-PMAA),[11] poly(ethylene oxide)-*b*-poly(styrene sulfonic acid) (PEO-*b*-PSSH)[12] and polystyrene-*b*-poly(2-vinyl-pyridine) (PS-*b*-P2VP)[13] have been employed for preparation and stabilization of ZnO NPs and thin films. The use of PMMA-*b*-PMAA for these purposes has not been described in the literature yet, although the solution and association behavior of PMMA-*b*-PMAA in water[14,15] as well as its use as a polymeric dispersant in microemulsion polymerization[16] were already reported. However, there are two reports on using block copolymers with hydrophilic PMAA segments as nanoreactors for the synthesis of ZnO NPs.[6,17]

Pizarro *et al.*[17] synthesized PS-*b*-P(MMA-*co*-MAA) by atom transfer radical polymerization (ATRP). After the introduction of ZnCl₂ and association of Zn²⁺ ions with the second block, the self-organized block copolymer served as a nanoreactor for the synthesis of nanosized ZnO. Kos *et al.*[6] synthesized poly(methyl methacrylate)-*b*-poly(methyl methacrylate-*co*-(zinc methacrylate acetate)), PMMA-*b*-P(MMA-*co*-ZnMAAc) as a polymeric precursor for the ZnO synthesis, *via* the reversible addition-fragmentation chain transfer (RAFT) radical polymerization. The block copolymer self-organized in solvent and acted as a nanoreactor during the synthesis of ZnO by hydrolysis with hydroxide. In both cases the copolymer remains (as a polymeric surfactant) on the surface of ZnO. No detailed information regarding the dispersing action of the copolymer are given.

Another indication that poly(methacrylic acid) (PMAA) can act as a suitable anchoring site for ZnO NPs comes from work of Tang *et al.*[18] They modified the surface of ZnO nanoparticles by grafting or anchoring PMAA chains on the NPs' surfaces to create better dispersion in an aqueous system. The -OH groups on a ZnO surface reacted with carboxyl groups (-COOH) in the PMAA segments to form a poly(zinc methacrylate) complex on the surface. The modification with PMAA did not alter the crystalline structure of ZnO nanoparticles according to the X-ray diffraction patterns.

The aim of our work was to synthesize PMMA-*b*-PMAA diblock copolymers with different lengths of anchoring PMAA segment by RAFT radical polymerization and to apply them as reactive polymeric surfactants for the functionalization of ZnO NPs. Morphology of the functionalized ZnO, the interaction of the polymer with

the NPs and dispersibility of the modified ZnO in organic solvent (THF) were studied by scanning transmission electron microscopy (STEM), IR spectroscopy and dynamic light scattering (DLS). Secondly, the relation of length of anchoring PMAA block in PMMA-*b*-PMAA diblock copolymer and the efficiency of the ZnO surface coverage was evaluated by measuring the optical properties of functionalized ZnO NPs by UV-vis spectroscopy in THF suspensions as well as in PMMA/ZnO nanocomposites.

2. Experimental

2. 1. Materials

Methyl methacrylate (MMA), methacrylic acid (MAA), azobis(isobutyronitrile) (AIBN), 1,1'-azobis(cyclohexanecarbonitrile) (AICN), RAFT agent 2-cyano-2-propyl benzodithioate (CPDB), NaOH, THF, methanol, *N,N*-dimethylformamide (DMF), and ether were of analytical grade, purchased from Sigma Aldrich, and, unless otherwise mentioned, used as received without any further purification. MAA and MMA were distilled under reduced pressure; MMA was distilled after removal of the inhibitor with a 5% aqueous NaOH solution. AIBN was recrystallized from methanol. Nanosized ZnO (av. part. size = 32 nm, part. size distribution = 20–80 nm, diol content = 1.8 wt %) was synthesized by the polyol method according to the already published procedure.[5,19,20]

2. 2. Synthesis of the PMMA Block (PMMA Macro-RAFT Agent A₁–A₃)

The synthesis of the first block (PMMA macro-RAFT agent) was performed by RAFT polymerization. A round bottom flask was charged with 28 g (280 mmol) MMA, 10 mL toluene, 40 mg (0.24 mmol) AIBN for A₂ and A₃ and 20 mg (0.12 mmol) for A₁, and 121 mg (0.55 mmol) CPDB for A₁ and A₂ and 256 mg (1.16 mmol) CPDB for A₃. The reaction mixture was degassed through three freeze-pump-thaw cycles. Polymerization was carried out by immersing the reaction flask into an oil bath at 70 °C for 8 hours (A₁ and A₃) or 60 °C for 6 hours (A₂). The polymer was isolated and purified by precipitation from methanol. The polymer was dried at reduced pressure to a constant mass at room temperature. The monomer conversion was determined gravimetrically (30% for A₁, 28% for A₂, 60% for A₃).

2. 3. Synthesis of PMMA-*b*-PMAA Diblock Copolymers (B₁–B₄)

PMMA macro-RAFT agent was dissolved in DMF and then MAA and AIBN were added. The reaction mixture was degassed through three freeze-pump-thaw and heated to the polymerization temperature (Table 1). The

Table 1. Experimental parameters for the synthesis of the PMMA-*b*-PMAA diblock copolymers **B₁**–**B₄** in DMF (m(PMMA macro-RAFT agent).= 1g).

Block copolymer	PMMA block	n(MAA) (mmol)	n(AIBN) (mmol)	n(DMF) (mmol)	Polymerization temperature (°C)	Polymerization time (h)
B₁	A₂	4	0.40	416*	60	3
B₂	A₁	30	0.022	89	70	0,5
B₃	A₃	8.7	0.0064	26	70	2
B₄	A₁	30	0,022	89	70	1

**THF was used instead of DMF as a solvent

resulting diblock copolymer PMMA-*b*-PMAA was isolated by precipitation from ether and dried under vacuum to a constant mass at room temperature (RT).

2. 4. ZnO Functionalization (ZnO/B₁–ZnO/B₄)

In a typical procedure, 200 mg (1 μmol) of diblock copolymer (**B₂**) was dissolved in 10 g THF and the solution mixed with 100 mg nanosized ZnO. The dispersion was homogenized in ultrasound bath for 30 minutes and then mixed at RT for 48 hours. Isolation of the product (**ZnO/B₂**) was performed by centrifugation at 8000 rpm for 30 minutes. Product was dried under vacuum to a constant mass at RT. Yield of the functionalization reaction refers to the mass ratio of ZnO in functionalized ZnO (determined by TGA) and unmodified ZnO (Table 3).

2. 5. Preparation of PMMA/ZnO Nanocomposites

In a typical procedure, 5 mg of functionalized ZnO NPs (**ZnO/B₂**) and 20 mg (0.08 mmol) AICN were dispersed in 5 g (50 mmol) MMA. After sonication for 20 minutes, the suspension was filtered through the polytetrafluoroethylene (PTFE) filter (0.45 μm), transferred into a glass reactor (dimensions 10 × 10 × 0.15 cm), and polymerized for 16 h at 70 °C. The reference PMMA plate was prepared in the same way omitting the addition of modified ZnO.

2. 6. Characterization

SEC: The molar mass characteristics (number-average molar mass, M_n, mass-average molar mass, M_w, molar-mass dispersity, $Đ_M$, where $Đ_M = M_w/M_n$) of the homopolymers were determined by size exclusion chromatography (SEC) on a modular system composed of an isocratic pump – Hewlett Packard 1100 Series, column and a precolumn MIXED-E, 3 μm (Polymer Laboratories), refractive index (RI) and UV detector in series (RI Agilent Series 1100, DAD Agilent Series 1260 at 310 nm). The solvent was 0.05 M LiBr/ *N,N*-dimethylacetamide (DMAc) with a flow rate of 0.7 mL/min and system pressure of 80

bar. PMMA standards were used for calibration. Concentration of the specimens was 1 mg/mL, injection volume 100 μL.

NMR: The ¹H nuclear magnetic resonance (¹H NMR) spectra were collected on an Agilent DD2 300 MHz NMR spectrometer in deuterated dimethylsulfoxide (DMSO-d_6) as a solvent and tetramethylsilane (TMS) as the internal standard. The M_n of PMMA macro-RAFT agents, as determined by NMR, were calculated as a ratio of the integral of RAFT fragments at 7.7 ppm and that of the methoxy groups of PMMA at 3.6 ppm multiplied by the molar mass of MMA taking into account the ratio of protons of both groups. The length of the PMAA block in the block copolymer, as determined by NMR, was calculated as a ratio of the integral of carboxylic proton of PMAA at 12.4 ppm (while subtracting the unreacted MAA monomer, calculated from integral of vinyl groups at 5.6 and 6 ppm) and that of the methoxy groups of PMMA at 3.6 ppm taking into account the ratio of protons of both groups.

TGA: Thermogravimetric (TGA) curves of functionalized ZnO were measured on a Mettler Toledo TGA/DSC 1 Star System in the temperature range between 50 °C and 700 °C with a heating rate of 10 K/min and in an air flux of 20 mL/min. The sample quantity was approximately 10 mg. From TGA curves block copolymer content was calculated from a difference to a ZnO content, which was determined as a residue at 600 °C.

IR: The chemical composition of the block copolymers and PMMA/ZnO nanocomposites was studied by IR spectroscopy using an FTIR spectrometer Spectrum One (Perkin Elmer) in the spectral range between 4000 and 400 cm⁻¹ with a spectral resolution of 4 cm⁻¹ in transmittance mode using the KBr pellets technique.

UV-vis: UV-vis spectra of suspensions of functionalized ZnO NPs in THF and PMMA/ZnO nanocomposites were measured on a Perkin Elmer Lambda 25 UV-vis spectrometer in the spectral range between 300 and 600 nm in a transmittance mode. Suspensions in THF were filtered through the 0.45 μm PTFE syringe filter directly before the measurement. PMMA/ZnO nanocomposites were prepared from suspensions of modified ZnO in MMA, which were filtered through the 0.45 μm PTFE

syringe filter before the bulk polymerization of MMA. UV-vis spectra were measured on PMMA plates with thickness of 1.4 mm.

Concentration of ZnO in THF suspensions containing functionalized ZnO NPs was calculated from UV data according to Beer–Lambert law (Equation 1a):

$$c(\text{ZnO}) = \frac{A(350)}{\varepsilon \cdot l} \qquad (1a)$$

$$A(350) = -\log_{10}\left(\frac{I(350)}{I_0(350)}\right) = -\log_{10}(T(350)) \qquad (1b)$$

where *A(350)* is absorbance of ZnO at 350 nm, calculated according to Equation 1b from transmittance T at 350 nm, *l* is path length (1 cm) and ε is the molar absorption coefficient (971 L·mol^{-1}cm^{-1} from literature[21]).

STEM: The ZnO particle size and morphology of PMMA/ZnO nanocomposite materials were studied by STEM. STEM micrographs of the nanocomposites were taken on an electron microscope Zeiss Supra 35 VP at an acceleration voltage of 20.0 kV and working distance of 4.5–5 mm using a STEM electron detector. Samples for the STEM measurements were prepared by drop-casting of the diluted suspension of functionalized nanosized ZnO in THF on the copper grid.

DLS: Size and agglomeration behavior of unmodified nanosized ZnO NPs and ZnO NPs, functionalized by block copolymers, were determined for suspensions in THF (c = 0.5 mg/g THF) by DLS at 25 °C using a Malvern Zetasizer Nano-ZS at an angle of 173°. The particle/aggregate size (average hydrodynamic diameter, D_z) and the size distribution of the sample (given by the dispersity factor, σ) were evaluated using the fully automatic mode of the Nano-ZS system. Measurements of the unmodified ZnO in THF was accomplished immediately (10 minutes) after sonication in order to prevent further agglomeration and sedimentation of particles.

3. Results and Discussion

The aim of this work was to synthesize PMMA-*b*-PMAA diblock copolymer and use it as a reactive polymeric surfactant for the functionalization of nano ZnO (Scheme 1). PMMA was selected for the first block as it assures solubility in organic solvents and provides inherent compatibility with the PMMA matrix. PMAA block was selected as anchoring chain since it was already proven[18] that it successfully binds to the nanosized ZnO surface. As polymer type and length (among other factors) determine whether the dispersion of functionalized NPs in a polymer matrix will be favored[22], we synthesized block copolymers with different lengths of PMAA block
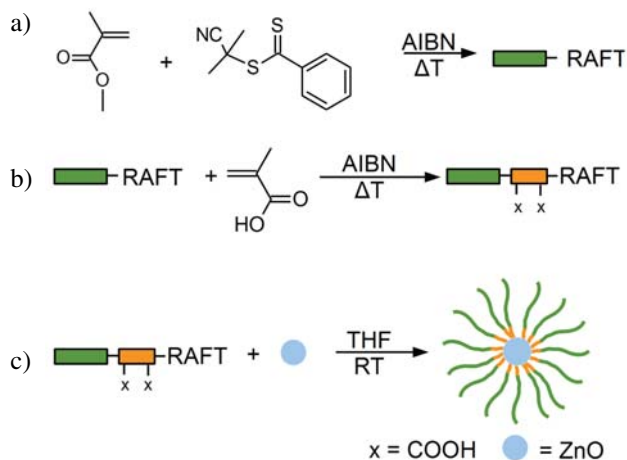
Scheme 1. Synthetic approach to nano ZnO functionalized by PMMA-b-PMAA diblock copolymer: a) preparation of PMMA with RAFT (dithiobenzoate) end group, b) preparation of PMMA-b-PMAA diblock copolymer, c) surface functionalization of ZnO nanoparticles by PMMA-b-PMAA diblock copolymer.

(PMAA content between 3 and 30 mol %) in order to evaluate their efficiency as dispersants for ZnO NPs. Optical properties of THF suspensions of functionalized ZnO and of PMMA/ZnO nanocomposites were used for the evaluation of efficiency of the synthesized PMMA-*b*-PMAA block copolymers acting as dispersants for ZnO nanoparticles.[23]
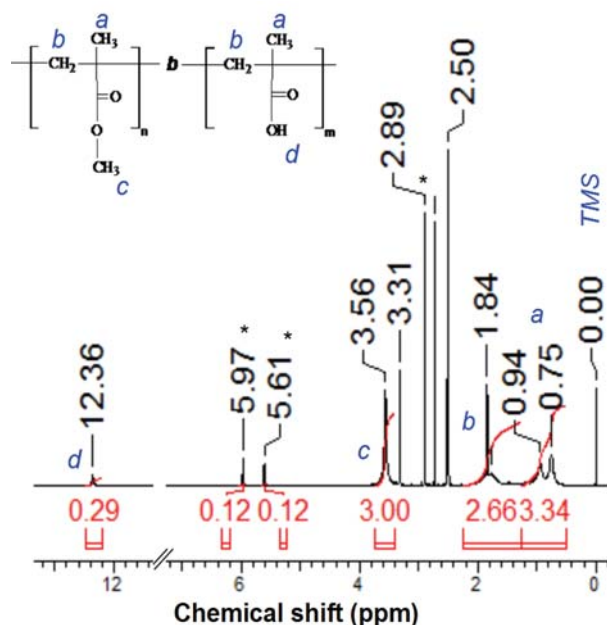
3. 1. Synthesis of PMMA-*b*-PMAA Diblock Copolymer

The RAFT polymerization method, one of the reversible-deactivation radical polymerizations[24] (also called "controlled" or "living" radical polymerizations), was chosen for the preparation of block copolymers as it allows good control over the molar mass, molar mass dispersity, and polymer end groups, and is suitable for the synthesis of block copolymers.[25] Additional advantage of RAFT polymerization is the possibility to polymerize acidic monomers like methacrylic acid directly without the need of using protected monomers,[27] although some side reactions were observed.[28] 2–Cyano-2-propyl benzoditioate (CPDB) was selected as a RAFT agent, as it allows good control over methacrylate polymerization.[26,29]

In the first step, PMMA macro-RAFT agents **A₁** – **A₃** were synthesized. As can be seen in Table 2, the molar masses of the PMMA macro-RAFT agents (as determined by SEC) were in the range of 16600 and 25100 g/mol, with dispersities between 1.2 and 1.4. The PMMA dithiobenzoate end groups of CPDB fragments were used for M_n determination by NMR spectroscopy. The results correlated well with the M_n determined by SEC.

PMMA-*b*-PMAA diblock copolymers (**B₁**–**B₄**) were prepared from macro-RAFT agents **A₁**–**A₃** by extension

Table 2. Properties of PMMA macro-RAFT agents (**A₁**–**A₃**) and PMMA-*b*-PMAA diblock copolymers (**B₁**–**B₄**).

Diblock copolymer	M_n of PMMA block (SEC) (g/mol) ($Đ_M$)	M_n of PMMA block (NMR) (g/mol)	MMA to MAA mole ratio	M_n of PMAA block (NMR) (g/mol)
B₁	**A₂:** 21000 (1.2)	21800	97:3	500
B₂	**A₁:** 16600 (1.4)	18000	75:15	4300
B₃	**A₃:** 25100 (1.2)	27200	78:22	5800
B₄	**A₁:** 16600 (1.4)	18000	69:31	8100

Figure 1. ¹H NMR spectrum of PMMA-b-PMAA diblock copolymer **B₂**. Mark * denotes signals of unreacted MAA and residual solvent.

with methacrylic acid (MAA). The length of the PMAA block was adjusted through the molar ratio of MAA monomer and initiator as well as through the time of polymerization, while the temperature of polymerization was kept constant (Table 1). The M_n of the PMAA blocks were determined by NMR (Figure 1, Table 2) and are in the range of 500 and 8100 g/mol.

3. 2. Functionalization of ZnO with PMMA-*b*-PMAA

Functionalization of nanosized ZnO was performed in THF as it is a good solvent for the PMMA block. First ZnO was dispersed in THF and then the block copolymer was added. The suspension was homogenized by sonication. After stirring the suspension at room temperature for 48 hours the product was isolated by centrifugation (Table 3). The polymer content in the product was in the range from 6 to 8 wt % as determined by TGA measurements (Table 3). Calculating the grafting density σ_{TGA}[30] from TGA gives σ_{TGA} between 0.1 and 0.2 molecules/nm². Comparing these results to literature data it can be seen that Tang *et al.*[18] observed coverage of 5 wt % for the PMAA functionalized nanosized ZnO and Chevigny *et al.*[31] observed a good dispersion of silica nanoparticles grafted with polystyrene (M_n = 24000 g/mol) in a PS matrix having grafting densities of 0.2 molecules/nm².

In order to check anchoring of the block copolymer on the surface of ZnO nanoparticle, the functionalized ZnO were characterized by STEM. The STEM images of unmodified and functionalized ZnO NPs are shown in Figures 2a and 2b. ZnO NPs show round morphology and good monodispersity with sizes between 20 and 80 nm. As is shown in Figure 2b, the black and translucent parts in the micrographs represent nano ZnO and PMMA-*b*-PMAA diblock copolymer, respectively. It is clearly seen, that the surface of ZnO nanoparticles is covered with a thin layer of the block copolymer.

Table 3. Functionalization of nano ZnO with PMMA-*b*-PMAA diblock copolymers and its dimensions in THF suspensions as measured by DLS.

Sample	Yield (%)	Polymer content* (wt %)	Dimensions			
			non-filtered sample		filtered sample	
			D_z (nm)	Dispersity factor σ	D_z (nm)	Dispersity factor σ
ZnO/B₁	98	8	152	0.14	130	0.08
ZnO/B₂	76	6	138	0.09	129	0.07
ZnO/B₃	88	6	184	0.08	163	0.04
ZnO/B₄	73	7	323	0.33	162	0.10

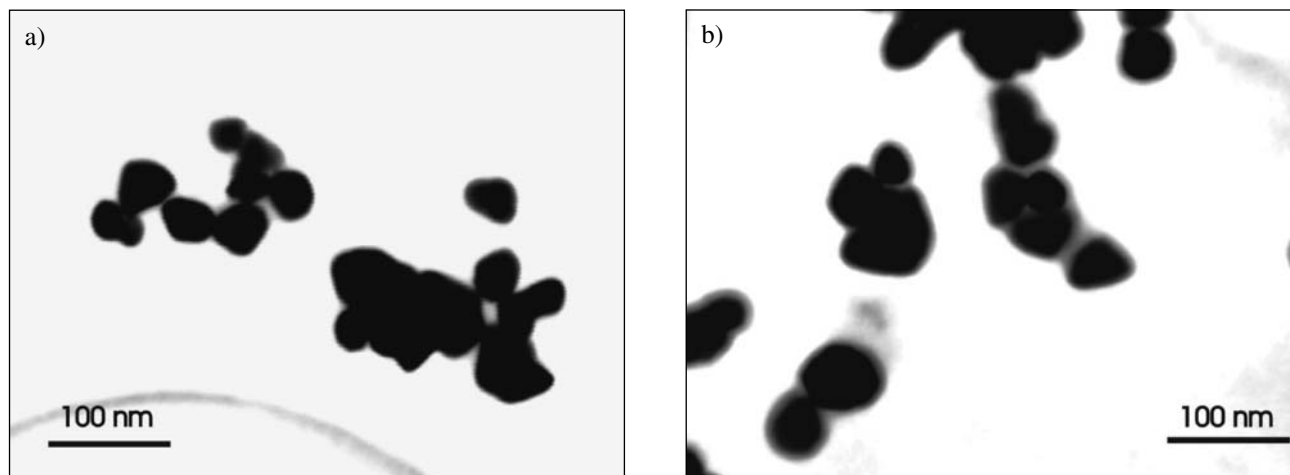* Polymer content of functionalized ZnO nanoparticles as determined by TGA

Figure 2. STEM micrographs of unmodified ZnO (a) and of ZnO functionalized with PMMA-b-PMAA (**ZnO/B₃**) (b).

The nature of the interaction between the block copolymer and the surface of the nanosized ZnO was explored using FTIR spectroscopy (Figure 3).

IR spectrum of the functionalized ZnO is dominated by broad Zn-O stretching vibrations at 472 cm^{-1}. The second strongest peak at 1731 cm^{-1} is characteristic of the C=O stretching vibrations of PMMA,[32] and bands at 1483, 1448, 1436 and 1388 cm^{-1} correspond to the copolymer backbone. In the IR spectrum of functionalized ZnO there is a new broad band at 1586 cm^{-1}, not present in the spectrum of the block copolymer, which was designated by Tang *et al.*[18] as a newly formed poly(zinc methacrylate) complex due to the interaction of –OH groups on the surface of ZnO and -COO⁻ groups of PMAA chain.
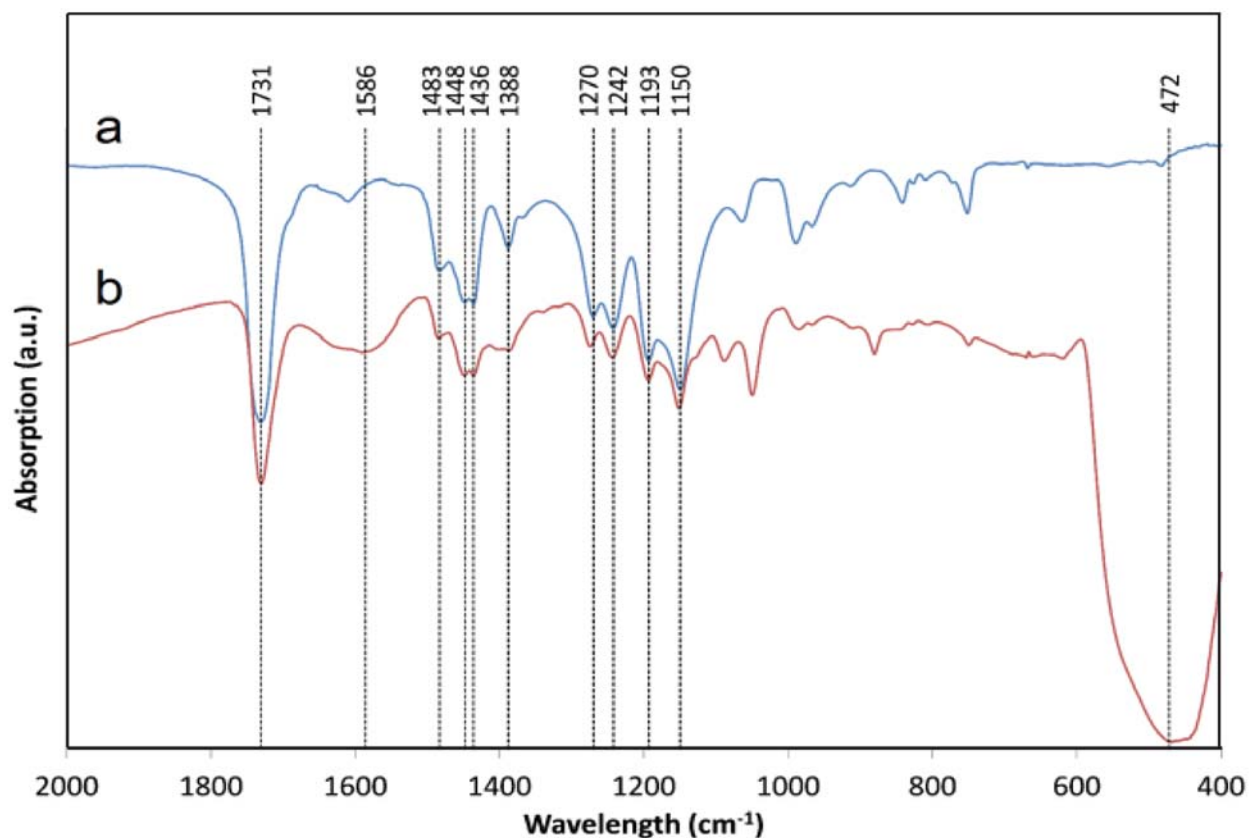

Figure 3. IR spectra of block copolymer **B₁** (a) and functionalized ZnO (**ZnO/B₁**) (b).

3. 3. Dispersibility of Functionalized ZnO Nanoparticles

The dispersibility of the functionalized ZnO nanoparticles in THF was analyzed by DLS. Dispersions were prepared by sonication of functionalized ZnO and THF in ultrasonic bath for 10 minutes (0.05 wt % of modified ZnO in THF). DLS results of non-filtered samples (Table 3) show Z-average diameters of agglomerates in the range between 168 and 323 nm and dispersity factors σ between 0.08 and 0.33. NPs diameters of filtered samples are between 130 nm and 160 nm indicating the removal of bigger agglomerates during filtration, which is supported also by substantially lower σ values. Measurement of the unmodified ZnO in THF was performed immediately after the sonication in order to avoid additional agglomeration[5] and gave Z-average diameter of 215 nm and σ of 0.10. Taking into consideration that the size of unmodified ZnO is below 80 nm, as determined by STEM, we can see, that ZnO NPs agglomerate in THF, however, agglomeration can be prevented to a certain extent by functionalization with PMMA-*b*-PMAA block copolymer. Suspensions remain stable for days. This can be an indication that the grafting density in this system is close to the optimum graft density σ_c between 0.15 and 0.19 molecules/nm[2] (for our block copolymer lengths) as calculated according to Hasegawa *et al.*[33] We can also see that the smallest agglomerates and smallest change of size after filtration are observed in the case of sample **ZnO/B₂** with PMMA-*b*-PMAA block copolymer containing 15 mol % PMAA meaning that it is efficient polymeric surfactant in the system used. We rationalize these results in a sense that longer PMAA segments in the block copolymer **B₃** and specially **B₄** may not only bind to the ZnO surface but can interact with free PMAA segments of other polymer chains leading to larger NPs agglomerates/aggregates. Larger agglomerates are removed by filtration, however, at the same time also part of ZnO is removed.

3. 4. Optical Properties of Functionalized ZnO Nanoparticles

Optical properties of functionalized ZnO NPs in THF suspensions and PMMA/ZnO nanocomposites were measured by UV-vis spectroscopy in order to evaluate the correlation of length of anchoring PMAA block in PMMA-*b*-PMAA and the efficiency of the ZnO surface coverage. We first prepared suspensions of functionalized ZnO in THF (same procedure as for DLS measurement) and evaluated their UV-vis spectra (Table 4 and Figure 4a) according to Demir et al.[21] We chose the transmittance at 550 nm as a reference value for absorption in visible range, and transmittance at 350 nm as a reference value for absorption in ultraviolet range due to the presence of ZnO nanoparticles. The best result (in a sense of highest transmittance at 550 nm and lowest transmittance at 350 nm)

was obtained for the sample **ZnO/B₂**. The samples **ZnO/B₁** and **ZnO/B₄** actually showed higher transmittance at 550 nm, but also lower absorption at 350 nm due to elimination of larger agglomerates by filtration. The UV-vis spectra show higher transmittance in the visible range (lower content of larger particles with higher dissipative power) and higher transmittance at 350 nm (since also part of ZnO was removed by filtration). From the absorption at 350 nm and the Beer–Lambert law (Equation 1a), it is possible to calculate the concentration of ZnO in THF suspensions (Table 4), where the molar absorption coefficient, ε, of 971 Lmol⁻¹cm⁻¹ is calculated from literature data for nano ZnO.[21] This calculation shows in case of **ZnO/B₂**, that more than 96 wt % of ZnO was still present after filtration and only 19 wt % in case of **ZnO/B₄**.

Table 4. UV-vis results of THF suspensions of modified ZnO (filtered samples) of nominal concentration c(ZnO modified) = 0.25 mg/g and of PMMA plates containing modified ZnO of nominal concentration of 1 mg/g.

Sample	Suspensions of functionalized ZnO in THF		c(ZnO) (mg/g)[#]	PMMA/ZnO nanocomposites with functionalized ZnO	
	T(550)[*]	T(350)[**]		T(550)[*]	T(350)[**]
ZnO/B₁	88	1.0	0.20	80	1.1
ZnO/B₂	85	0.4	0.24	81	0.6
ZnO/B₃	77	0.4	0.24	81	4
ZnO/B₄	96	33.5	0.05	84	13

[*]Transmittance at 550 nm in % [**]Transmittance at 350 nm in % [#]Concentration of functionalized ZnO in THF suspensions calculated from UV absorption at 350 nm (see experimental part 2.6) and polymer content (Table 3)

Nanocomposites of functionalized nanosized ZnO and PMMA were prepared by radical bulk polymerization of suspensions of functionalized ZnO in MMA. MMA suspensions were filtered prior to the polymerization in order to eliminate larger agglomerates. UV-vis results of PMMA/ZnO nanocomposites are qualitatively similar to the results of suspensions in THF (Table 4 and Figure 4b), demonstrating similar behavior of functionalized ZnO in THF and MMA. It has to be stressed, that the stability of functionalized ZnO in MMA facilitates homogeneous dispersion of ZnO during the polymerization of MMA taking several hours. PMMA/ZnO nanocomposite with **ZnO/B₂,** like THF suspension of **ZnO/B₂**, exhibited the best results showing transmittance of 81% at 550 nm as compared to 91% for reference PMMA plate and transmittance of less than 1% of UV light at 350 nm, closely followed by **ZnO/B₁** showing similar properties.

According to Rozenberg and Tenne[4] the maximum level of adsorption of block or graft copolymers are achieved when approximately 10 mol % of polymer segments
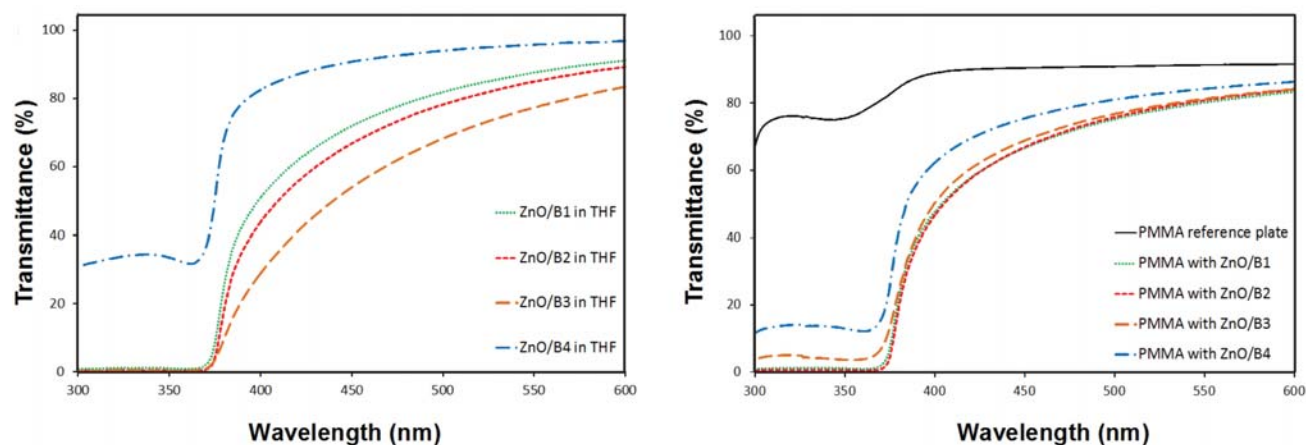
Figure 4. UV-vis spectra of suspensions of modified nanosized ZnO in THF (filtered samples) (a) and UV-vis spectra of PMMA/ZnO nanocomposites with nanosized ZnO functionalized with PMMA-b-PMAA diblock copolymers **ZnO/B₁**, **ZnO/B₂**, **ZnO/B₃**, and **ZnO/B₄** together with reference PMMA plate without ZnO (b).

are anchors. Similar conclusion can be given also in our case. Under the selected experimental conditions (ZnO particle size of 80 nm and PMMA-*b*-PMAA block copolymers with molar masses in the range of 20000 and 30000 g/mol) the optimal optical properties were achieved with relative lengths of anchoring PMAA segment in the range between 3 and 15 mol % (samples **B₁** and **B₂**).

4. Conclusions

We followed two aims in the present work. The first aim was to synthesize PMMA-*b*-PMAA diblock copolymers and use them as reactive polymeric surfactants for the functionalization of nano zinc oxide for the first time. Block copolymers were prepared by RAFT radical polymerization having molar masses in the range of 20000 and 30000 g/mol and PMAA content between 3 and 30 mol %.

By functionalization of ZnO with PMMA-*b*-PMAA block copolymers the surface of ZnO NPs was covered with 6 to 8 wt % of the block copolymer. We showed that even 3 mol % of PMAA segment in block copolymer is sufficient for anchoring of the block copolymer on ZnO. STEM images confirmed the coverage of the particle surface with a polymer layer and IR spectroscopy gave evidence that carboxylic groups of PMAA segment of block copolymer reacted with the surface -OH groups of ZnO by creating zinc methacrylate complex on the surface.

The second aim of this work was to evaluate the efficiency of PMMA-*b*-PMAA block copolymers as polymer dispersants and the optimum length of PMAA anchor block for efficient surface functionalization of ZnO NPs. DLS showed agglomeration of unmodified ZnO nanoparticles in THF, which could be substantially prevented by functionalization of ZnO with PMMA-*b*-PMAA. We found optimal results for PMMA-*b*-PMAA block copolymers having a molar mass of 22000 g/mol and relative lengths of anchoring PMAA segment 3 and 15 mol %. For these block copolymers the best UV-vis performance was observed for suspensions in THF as well as for PMMA/ZnO nanocomposites. Longer PMAA chains most probably not only bind to the ZnO surface but may also bind to free PMAA segments of other polymeric chains leading to larger ZnO NPs agglomerates/aggregates.

5. Acknowledgements

6. References

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Povzetek

Raziskali smo učinkovitost diblokkopolimerov polimetilmetakrilat-*b*-poli(metakrilna kislina), PMMA-*b*-PMAA, kot reaktivnih polimernih površinsko aktivnih snovi za funkcionalizacijo nanodelcev ZnO s premerom 20–80 nm. PMMA-*b*-PMAA z molsko maso med 20.000 in 30.000 g/mol in vsebnostjo PMAA med 3 in 30 mol % smo pripravili z radikalsko polimerizacijo z reverzibilnim prenosom verige z adicijo in fragmentacijo (RAFT polimerizacija). Vrstična presevna elektronska mikroskopija (STEM) je pokazala učinkovito oplaščenje nanodelcev ZnO s plastjo polimera, infrardeča (IR) spektroskopija pa je potrdila interakcijo segmenta PMAA (sidrni blok) s površino nanodelca. Kot je razvidno iz meritev dinamičnega sipanja svetlobe (DLS) in UV-vis spektroskopije, so amfifilni blokkopolimeri PMMA-*b*-PMAA v veliki meri preprečili aglomeracijo nanodelcev ZnO in tako povečali prosojnost suspenzije ZnO v tetrahidrofuranu (THF) in nanokompozitov PMMA/ZnO v območju vidne svetlobe. Prav tako smo dokazali pomembnost dolžine segmenta PMAA za funkcionalizacijo površine ZnO. Optimalne UV-vis lastnosti suspenzije funkcionaliziranih nanodelcev v THF kot tudi nanokompozitov PMMA/ZnO smo dosegli z blokkopolimeri PMMA-*b*-PMAA z vsebnostjo 3 in 15 mol % segmenta PMAA.