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CALCIUM CARBONATE MINERALIZATION. PART II: EFFECT OF POLY(ETHYLENE GLYCOL) AND BLOCK COPOLYMERS MOLECULAR WEIGHT ON FORMATION OF PRECIPITATE

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Abstract: In this study the role of PEG and PEO-PPO-PEO block copolymers molecular weight in precipitation of calcium carbonate was examined. The CaCO₃ particles were characterized by FTIR spectroscopy, X-ray, SEM and particle size distribution analysis. In absence and presence of modifiers, mixing of the reagents led to the formation of calcite crystals. The calcium carbonate obtained with poly(ethylene glycol) and block copolymers was characterized by smaller diameter in comparison with the one without modifiers. It was observed that using compounds with different molecular weights has no obvious effect on the form and properties of precipitated calcium carbonate particles.

Keywords: mineralization, block copolymers, PEG, calcite

Introduction

It is widespread in biological systems that living organisms synthesize inorganic minerals with complex shapes, hierarchical structures and fascinating properties (Meldrum and Colfen, 2008; Zhu et al., 2013). Biomaterials are particularly promising materials, which can be environmentally friendly synthesized and possess high biocompatibility (Xu et al., 2007). These biological structures are a source of inspiration for approaching a variety of technical challenges in materials science (Ehrlich et al., 2010). The design of novel biomaterials relies on an understanding of the organic matrix proteins and templating structures in nature (Ichikawa et al., 2003; Ehrlich et al., 2010).

One of the most common biomaterial in nature is calcium carbonate. In nature, calcium carbonate is present in marine invertebrate animals such as mollusk, coral and forminifera, as well as fish otolith and animals shells (Ichikawa et al., 2003; Meldrum and Colfen, 2008; Zhu et al., 2013). This material has found abundant applications in the cosmetics, paper, paint, rubber and adhesive industries, and in biomedical application like drug delivery (Chibowski et al., 2005, Kurapati and Raichur, 2013). These applications of calcium carbonate mainly depend on parameters, such as average particle size, particle size distribution, morphology, polymorphism and chemical purity (El-Sheikh et al., 2013). Literature data revealed that to obtain the desired properties of CaCO_3 particles it is necessary to control pH, temperature, concentration of CO_3^{2-} and Ca^{2+} ions, the type and the concentration of additives (Kitamura, 2002; El-Sheikh et al., 2013). During the last decade most investigations have been performed by using different additives such as polymers, biopolymers, proteins, surfactants and their mixtures to guide CaCO_3 crystallization, (Wang et al., 2009a; Wang et al., 2009b; Shestak et al., 2011; Zhao et al., 2012; Deng et al., 2013; El-Sheikh et al., 2013; Polowczyk et al., 2013; Szczes, 2013). Addition of these compounds to precipitation system led to calcium carbonate with different morphology, size and crystalline form. The most of these studies were performed using proteins, especially that present in the avian eggs shells (Hernandez-Hernandez et al., 2008; Wang et al., 2009a; Wang et al., 2009b). In literature it can be seen that not only the natural biopolymer can be used to control the properties of CaCO_3 but also the synthetic compounds (Xie et al., 2006; Xu et al., 2008; Ehrlich et al., 2010; Sadowski et al., 2010; Su et al., 2010; Xu et al., 2011; Deng et al., 2013, Polowczyk et al., 2013; Zhu et al., 2013). For example El-Sheikh and co-workers (2013) have done research on precipitation of CaCO_3 in the presence of cationic surfactant, cetyltrimethylammonium bromide, using the reaction system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O-CO}_2$. They observed that precipitate morphology was significantly changed from rhombohedral to scalenohedral calcite with concentration of surfactant. Additionally, the presence of CTAB molecules influenced the properties of calcium carbonate, such as size or zeta potential. The properties of precipitate can also be influenced by the oxyethylene groups. Su and co-workers (2010) have investigated the influence of poly(ethylene glycol)-block-poly(acrylic acid)-block-poly(styrene)) polymers on the crystallization, morphology and size of CaCO_3 . They observed that the formation of vaterite depends on the number of carboxyl groups in the copolymer and its concentration. Vaterite is the other anhydrous polymorph of calcium carbonate, and is the least stable phase since it slowly recrystallizes to become calcite in contact with water (Kim and Park, 2010). It is characterized by large specific surface and high surface activity, which can be used to improve mechanical properties of product in industry (Kim and Park, 2010). Zhao and co-workers (2012) observed that increasing the concentration of block copolymer F68, made up of symmetrical poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PP-PEO), affected the morphology of CaCO_3 but has no influence on the crystalline form. The groups of EO

and EG are of particular interests because its molecules contain hydrophilic groups, which can act as a donor to metal ions to form metal complexes with diverse conformations (Xu et al., 2003; Bastrzyk et al., 2012). The effect of these type of functional groups on the properties of calcium carbonate precipitated is not well understood. This paper is a continuation of our research on this topic. In our earlier studies on precipitation of calcium carbonate it was observed that PEG 5000000 can affect the morphology of CaCO_3 crystals as well as a size distribution of precipitate. At a higher polymer concentration, 0.05, 0.1 and 0.5%, spherical forms of carbonates appeared in the system (Polowczyk et al., 2013). The aim of this paper is to investigate the effect of molecular weight of PEG and block copolymer (PEO-PPO-PEO) on the crystal growth of calcium carbonate.

Materials and Methods

Calcium chloride dihydrate (purity > 99%) and disodium carbonate were purchased from Sigma Aldrich. PEG 1000, PEG 6000, PEG 20000, PEG 300000 were purchased from BDH Chemicals. The following Pluronic[®] block copolymers: PE 3500, PE 6400, PE 6800, PE 10500 were purchased from BASF. F68 and F127 were purchased from Sigma Aldrich. All chemicals used in these syntheses were applied without further purification. The structure of all molecules of block copolymers[®] used in experiments are shown in Table 1.

Table 1. Structure of block copolymers

Name of copolymer	The structure of copolymer
PE 3500	$\text{EO}_{11}\text{PO}_{16}\text{EO}_{11}$
PE 6400	$\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$
PE 6800	$\text{EO}_{73}\text{PO}_{28}\text{EO}_{73}$
PE 10500	$\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$
F 68	$\text{EO}_{80}\text{PO}_{30}\text{EO}_{80}$
F 127	$\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$

The preparation of calcium carbonate was performed according to the method reported in our earlier paper (Sadowski et al., 2010). The solutions of sodium carbonate (0.1 M) and calcium chloride (0.1 M) with PEG or block copolymer (0.1%) were prepared one day before the calcium carbonate synthesis and have been stirred overnight. The PEG and block copolymers with different molecular weight were used. The precipitation experiments were carried out in the Erlenmeyer flasks by mixing of a sodium carbonate solution with calcium chloride one at the speed of the magnetic stirrer of 300 rpm. After 5 min or 24 h the precipitated calcium carbonate was removed from solution by centrifugation. The deposit was collected and washed twice with 100 cm^3 of deionized water and dried at $30 \text{ }^\circ\text{C}$. The experiments were conducted at ambient temperature.

The microstructure of precipitate was observed using a JSM 5800 LV scanning electron microscope (JEOL). The crystallographic structure of calcium carbonates was determined by using an D8 Advance (Bruker) X-ray powder diffractometer with CuK α radiation. Fourier transform infrared spectroscopy (FTIR) was carried out using PE 1600 FTIR spectrometer (Perkin Elmer). The samples were mixed with KBr powder. The spectra were recorded in a reflection mode from 4000 to 400 cm⁻¹ at a resolution of 2 cm⁻¹. Particle size analysis was realized using a Mastersizer 2000 laser diffractometer, equipped with HydroMu dispersion unit (Malvern). In the process, about 3 cm³ of calcium carbonates suspension were poured into 700 cm³ of water cross-flowing through the measuring cell. The particle size measurements were carried out without and afterwards under operation of ultrasounds in the dispersion unit, so the possible agglomerates of calcium carbonate could have been broken. The surface area of the samples were measured by the BET method with helium/nitrogen mixture using a FlowSorbII apparatus (Micromeritics).

Result and discussion

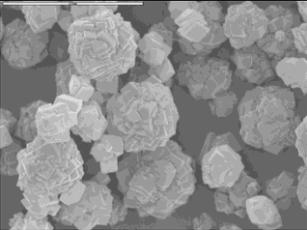
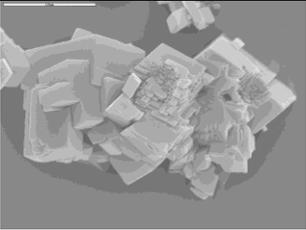
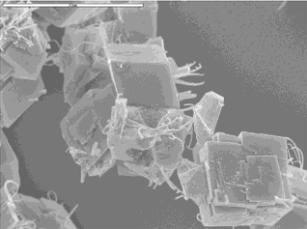
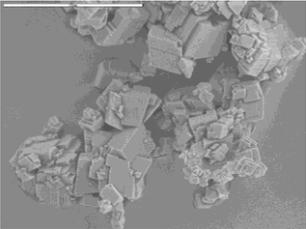
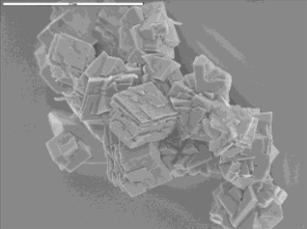
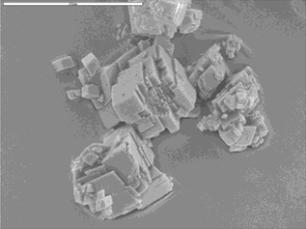
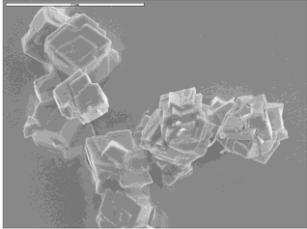
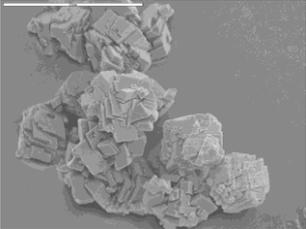
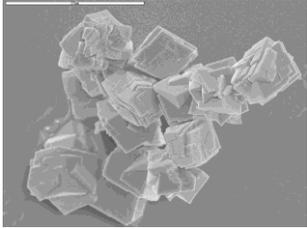
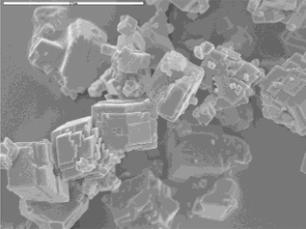
Effect of molecular weight of PEG

Table 2 shows the morphology of calcium carbonate obtained in the presence of PEG with different molecular weight at room temperature, when the concentration of Ca²⁺ and CO₃²⁻ was 50 mmol/dm³, and the samples were collected after 5 min and 24 h of crystallization. The concentration of PEG in all investigated samples was 0.1%.

From Table 2 we can see that without any additives, calcium carbonates formed rhombohedral calcite crystals, aggregated in spherical formations after 5 min of crystallization which recrystallized in bigger non-spherical aggregates after 24 h of incubation. Addition of PEG resulted in the formation of stacked rhombohedral particles, with the ladder-like surface edges (Zhao et al., 2012). In case of low molecular weight PEG 1000 and PEG 6000 in a short time of crystallization process, whiskers-like structures are visible.

These forms were observed by Zhao and co-workers (2012) and reported as calcite. Within one day of the process, needle-like structures disappeared and the morphology of precipitate slightly differ from that without PEG and aggregates are formed of smaller crystals. From literature data, it is known that in course of crystallization the amorphous phase (ACC) is initially formed (Xu et al., 2007). Then, within very short time this phase rapidly transforms to calcite, vaterite or aragonite. The stable ACC of calcium carbonate can only be present in living organism in a form of complex matrices with macromolecules (Xu et al., 2007). Addition of soluble compounds such as polymers or surfactants led to changes in the morphology and size of crystal or various crystalline form (vaterite, aragonite or calcite) (Xu et al., 2007).

Table 2. SEM images of calcium carbonate particles precipitated in the presence of poly(ethylene glycol) with different molecular weights. The polymer concentration was 0.1%

	5 min	24 h
without PEG		
PEG 1000		
PEG 6000		
PEG 20000		
PEG 300000		

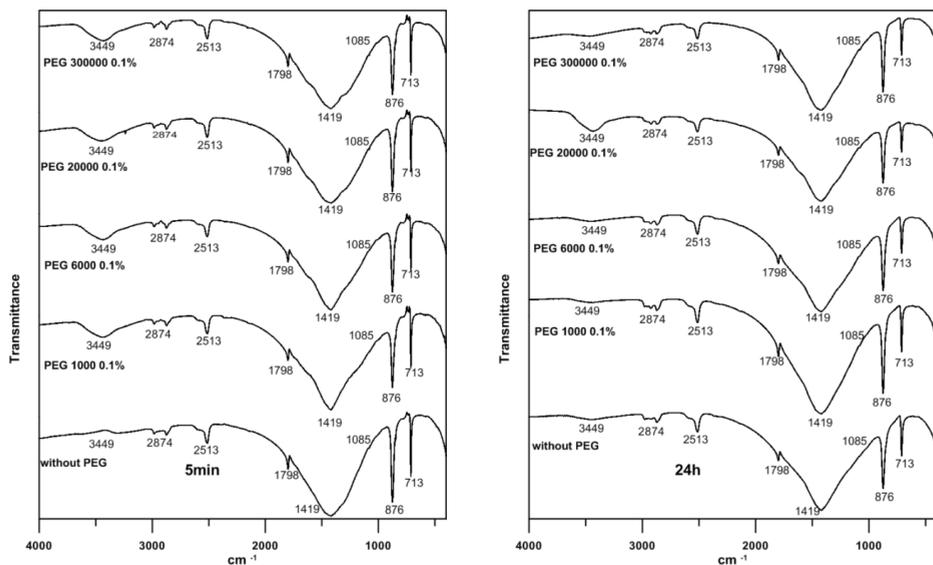


Fig. 1. FTIR spectra of calcium carbonate precipitated after 5 min and 24 h in the presence of PEG having various molecular weight

The FTIR analysis of powders obtained in the presence of PEG 1000, PEG 6000, PEG 20000 and PEG 300000 after 5 min and 24 h (Fig. 1) revealed characteristic spectra of calcite crystals based on the in-plane band and on the out-plane band at ~ 712 and ~ 875 cm^{-1} respectively, and anti-symmetry stretch at ~ 1420 cm^{-1} characteristic of calcite (Addadi et al., 2003; Kim and Park, 2010; Polowczyk et al., 2013). The X-ray powder diffraction patterns presented in Fig. 2 also evidenced the calcite phase creation.

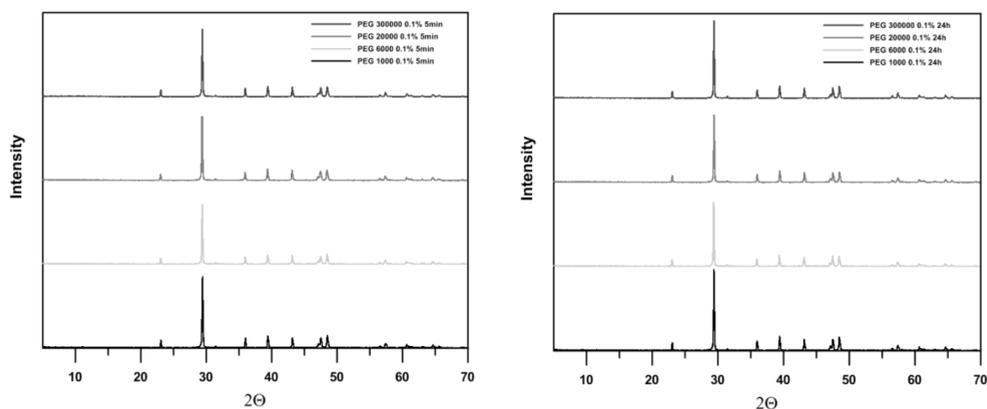


Fig. 2. XRD patterns of calcium carbonate crystals obtained in the presence of PEG, with various molecular weight after 5 minutes and 24 hours of precipitation

Presented above data revealed that particles obtained in the presence of PEG with different molecular weight are quite similar to those obtained in aqueous solution without poly(ethylene glycol), indicating that presence of this type of molecules in such concentration has no obvious influence on the crystalline form of CaCO_3 . In the investigated systems after 5 min and 24 h only calcite crystals were formed. These data are in good agreement with data published in literature (Xie et al., 2006; Polowczyk et al., 2013). Xie and co-workers (2006) observed that PEG 6000 at concentration of 0.1% favored the precipitation of CaCO_3 as calcite. In our earlier studies it was observed that using PEG 5000000 at concentration of 0.1 % lead to formation of calcite after 24 h of precipitation. However, after 5 min of precipitation the spherical morphologies of calcium carbonates (vaterite, 10.6 wt.%) and calcite (89.4 wt.%) mixture was found (Polowczyk et al., 2013). On a base of this it can be supposed that poly(ethylene glycol) mostly favored the precipitation of calcite. The presence of small amount of vaterite using high molecular weight PEG polymer after short time of precipitation can result from inhibiting effect of this polymer on growth of calcite in system. Comparing the pictures of particles in Table 2 it can be said that after 24 h of crystallization the edges of crystals are more irregular in the presence of polymer than without PEG. It means that PEG has an effect on the course of calcium carbonate precipitation. The mean diameters as well as BET specific surface areas of calcite obtained with or without the polymer are presented in Table 3.

Table 3. Specific surface BET areas and diameters of calcium carbonate particles precipitated in the presence of poly(ethylene glycol) with various molecular weight.
Concentration of the polymer was 0.1 %

Sample name	Time	BET S.A. (m^2/g)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
			no-ultrasound/ ultrasound	no-ultrasound/ ultrasound	no-ultrasound/ ultrasound
Without PEG	5 min	0.99	9.8/6.6	22.7/12.5	47.2/23.2
	24h	0.74	16.4/7.9	32.6/21.5	59.3/40.44
PEG 1000	5 min	0.46	12.9/10.5	23.8/17.3	43.7/28.5
	24h	0.72	9.3/6.9	19.5/14.1	44.0/24.8
PEG 6000	5 min	0.55	10.0/7.9	19.5/14.1	37.4/23.5
	24h	0.75	10.3/7.7	20.0/14.9	35.9/25.9
PEG 20000	5 min	0.65	8.5/6.9	18.4/13.4	39.7/23.7
	24h	0.81	8.9/6.7	18.9/13.1	36.1/23.9
PEG 300000	5 min	0.58	8.3/6.5	16.4/11.7	35.7/19.7
	24h	0.84	8.6/6.6	18.1/13.1	36.8/23.6

From data presented in Table 3 we can see that the specific surface area of calcium carbonate particles did not exceed one square meter per gram. Values of BET surface areas increased in the presence of PEG for the samples after 24 h of crystallization. It can be explained by the size of precipitates. Calcite obtained without polymer possesses volume median diameters, d_{50} , of 12.5 and 21.5 μm after 5 min and 24 h, respectively. The value of BET surface area of CaCO_3 particles was 0.99 and 0.74

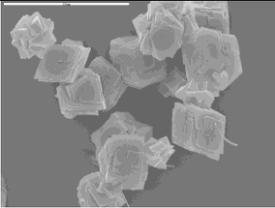
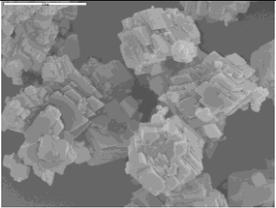
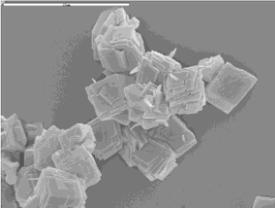
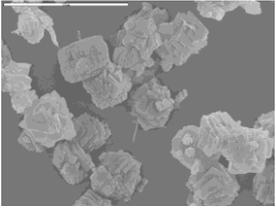
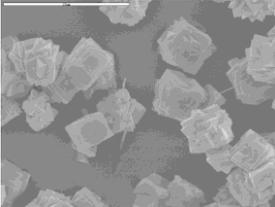
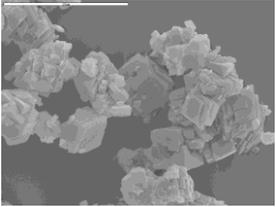
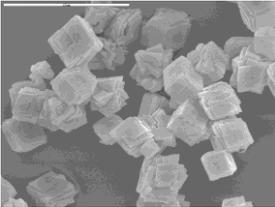
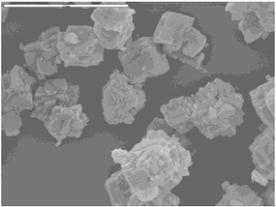
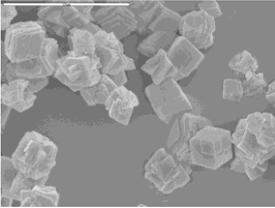
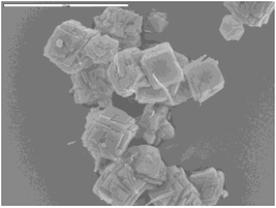
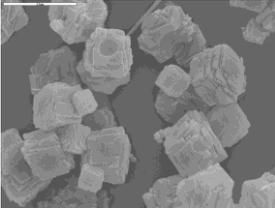
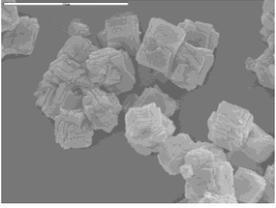
m²/g after 5 min and 24 h of precipitation. Comparing the morphology of the samples obtained after 5 min and 24 h (Table 2) it can be seen that shape of precipitate differs significantly. The crystals obtained after 5 min had irregular sphere-like structure resulting in bigger surface BET area. Addition of poly(ethylene glycol) to system resulted in a slight changes in diameter of particles precipitated after 5 min. Furthermore, decrease of the BET surface area of crystal obtained with polymer addition after 5 min of crystallization was observed. The lower value of BET surface area in the presence of polymer for these samples can be explained by different shape of particles. More irregular shape of crystals gives a large number of edges with high surface energy (Xu et al., 2007). In contrast, the particles obtained after 24 h were characterized by smaller diameter in the presence of polymer during crystallization process. Addition of PEG 1000, PEG 6000, PEG 20000 and PEG 300000 led to production of particles with d_{50} equal 14.1, 14.9, 13.1 and 13.1 μm , respectively. Also the upper-decile, d_{90} , is much lower with PEG addition, especially after treatment of ultrasounds the aggregates were easily broken. The SEM images evidenced these results. In earlier studies it was observed that diameter of particles obtained in the presence of PEG 5000000 polymer at concentration of 0.1 wt.% was 15.7 and 15.6 μm after 5 min and 24 h of incubation, respectively (Polowczyk et al., 2013). Slight increase in a mean diameter of calcite was explained by flocculation effect (Polowczyk et al., 2013). This behavior can be explained by specific adsorption of these molecules onto calcium carbonate surface during crystallization process (Xie et al., 2006; Polowczyk et al., 2013). The poly(ethylene glycol) possesses functional groups which have ability to bind Ca^{2+} on the special face of formed CaCO_3 , and inhibits the growth of crystals in suspension. Also, these polymers probably change the viscosity of suspension, and slow down the diffusion of ions in a system.

Effect of poly(ethylene)-poly(propylene)-poly(ethylene) block copolymers

In Table 4 the SEM images of calcium carbonates synthesized in the presence of block copolymers with different molecular weights are presented. These copolymers contain various number of EO and PO block in their structure (Table1).

It was observed that in all cases the main components of precipitate was rhombohedral calcite. The obtained forms are similar to those obtained without and with PEG polymers. For block copolymers such as PE 3500, PE 6400, PE 6800 and F 68 the needle-like structure appeared. According to data shown in Fig. 5, it can be said that addition of PEO-PPO-PEO copolymers results in calcite formation. The characteristic peaks of calcite are 712, 875 and 1420 cm^{-1} . There were no peaks of aragonite and vaterite in the obtained samples. The needle-like structure, according to literature, can occur both for aragonite and also calcite (Chen et al., 2011; Zhao et al., 2012). Zhao and co-workers (2012) observed that in the presence of F68, aggregated rod-like calcites can appear.

Table 4. SEM images of calcium carbonate particles precipitated in the presence of block copolymers with different molecular weight. The polymer concentration was 0.1 %

	5 min	24 h
PE3500		
PE6400		
PE6800		
PE10500		
F68		
F127		

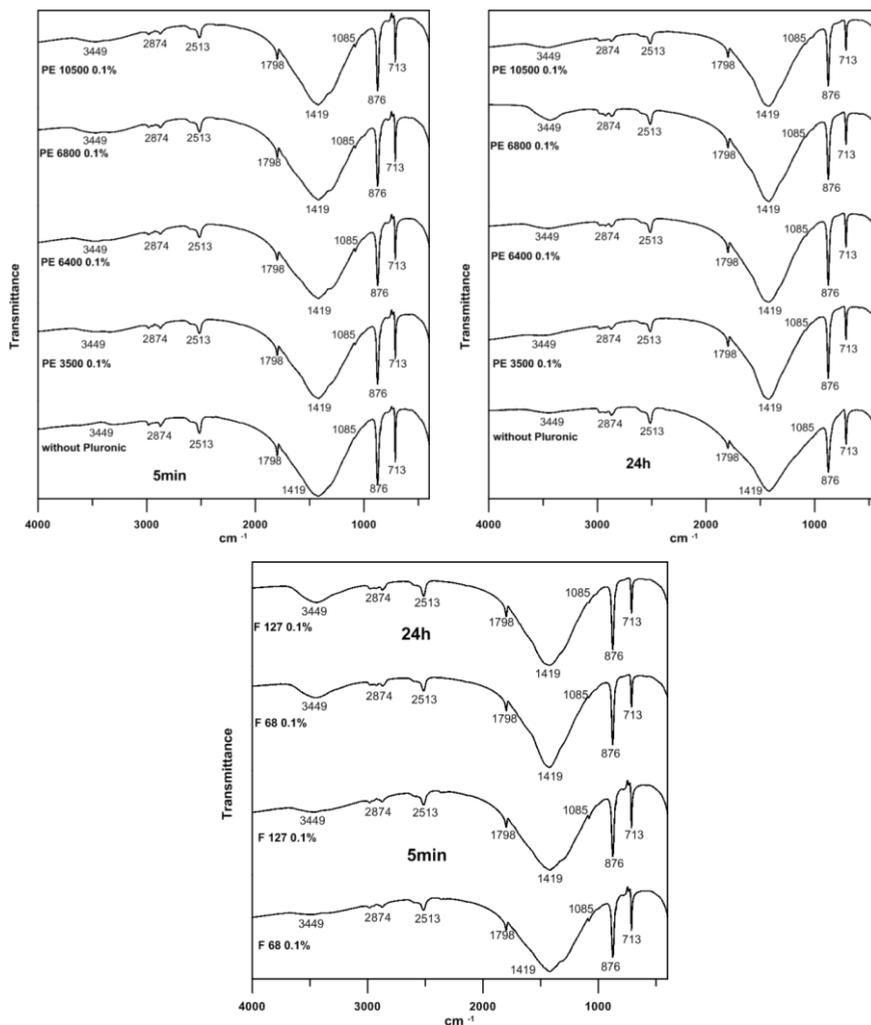


Fig. 5 FTIR spectra of calcium carbonate precipitated after 5 min and 24 h in the presence of block copolymers with various molecular weight

Figure 6 presents XRD analysis of CaCO_3 obtained in the presence of block copolymers after 5 min and 24 h of precipitation. Presented data showed that the only phase of CaCO_3 obtained in the absence and presence of block copolymers was calcite.

The data are in good agreement with literature data. Zhao and co-workers, (2012) observed that at low concentration of F68 copolymer led to precipitation of calcite. They observed that upon increasing the concentration up to 3 g/dm^3 the mixture of calcite and spherical vaterite appeared. In our studies the concentration of block copolymers was 1 g/dm^3 . There was not observed any influence of length of block PEO and PPO on crystalline form of calcite at that concentration. However, it can be

seen in Table 4, that in the presence of block copolymers the surface edges of CaCO_3 are irregular and rather rounded, and this results in complex morphology.

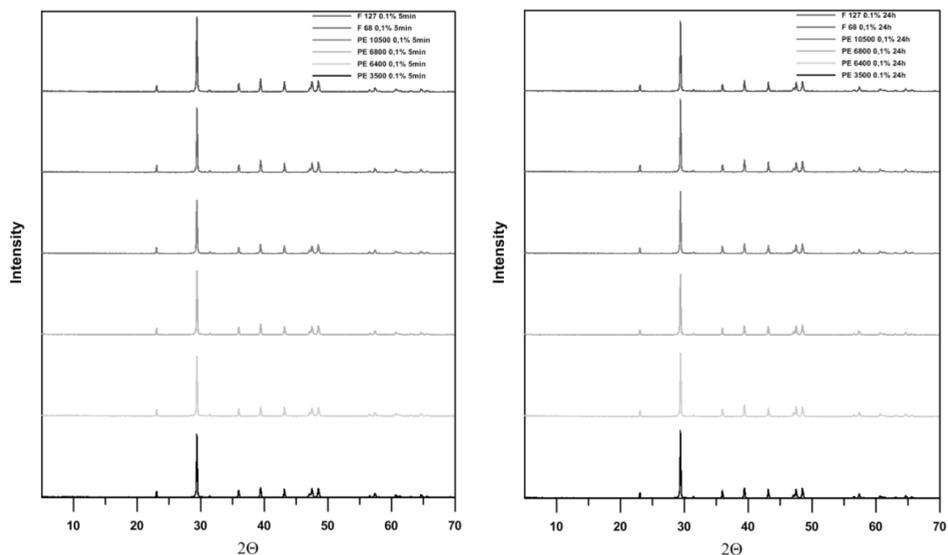


Fig. 6. XRD pattern of calcium carbonate crystals obtained in the presence of PEG with various molecular weights after 5 min and 24 h of precipitation

The BET surface areas and diameters of particles are presented in Table 5. It can be said that the block copolymers significantly influenced the size of obtained CaCO_3 particles as well as a specific surface area. After 24 h of precipitation and in the presence of block copolymers, the specific surface area was higher and the value was 0.95, 1.06, 0.91, 1.06, 0.88 and 0.99 for PE 3500, PE 6400, PE 6800, PE 10500, F 68 and F 127, respectively. It can be explained as a result of a morphology and size of calcite particles. After 5 min of crystallization the mean diameters of obtained precipitate was similar to those obtained without copolymers. However, the diameter d_{90} showed that the precipitate contained 90% of particles smaller than about 20 μm in the presence of copolymers. For the sample without modifiers, 90% of particles had a diameter smaller than 40 μm .

Addition of block copolymers led to a decrease in size of particles after 24 h of precipitation. The mean diameter of particle was 12.9, 12.2, 12.7, 11.9, 14.2 and 12.8 μm in the presence of PE 3500, PE 6400, PE 6800, PE 10500, F 68 and F 127, respectively. These values of diameters are similar to those obtained after 5 min of precipitation. This indicates that presence of block copolymers inhibited the growth of calcium carbonates. The molecules of block copolymers adsorb on the surface of particles. Zhao and co-workers (2012) proposed that one EO block of copolymers can adsorb on the crystal, the other is free in water. The free EO block can interact with another crystal and inhibits the growth of CaCO_3 in system.

Table 5. Surface areas BET and diameters of calcium carbonate particles precipitated in the presence of block copolymers with various molecular weight. Concentration of the polymer was 0.1 %

Sample name	Time	BET surface	d ₁₀ [μm]	d ₅₀ [μm]	d ₉₀ [μm]
		area [m ² /g]	no-ultrasound/ ultrasound	no-ultrasound/ ultrasound	no-ultrasound/ ultrasound
PE 3500	5 min	0.64	8.4/7.2	16.2/12.5	28.4/21.4
	24h	0.95	7.6/6.5	15.4/12.9	29.4/22.9
PE 6400	5 min	0.66	7.5/6.4	14.6/11.6	25.6/20.7
	24h	1.06	7.7/6.0	15.6/12.2	28.3/22.3
PE 6800	5 min	0.69	6.6/5.5	13.9/10.8	26.3/19.3
	24h	0.91	8.1/6.5	16.1/12.7	29.0/22.9
PE 10500	5 min	0.73	7.1/5.4	14.5/10.8	26.0/19.5
	24h	1.06	7.4/6.0	14.6/11.9	26.6/21.9
F 68	5 min	0.65	7.4/5.7	14.6/11.5	25.4/20.2
	24h	0.88	9.0/7.2	17.6/14.2	30.9/25.6
F 127	5 min	0.66	6.8/5.4	13.5/10.8	23.7/19.1
	24h	0.99	7.0/6.2	14.7/12.8	27.1/22.8

Conclusion

Organic additives such as polymers, surfactants or low mass small molecules are known to either promote or inhibit crystal growth (Xu et al., 2007). The calcium carbonate crystals precipitated in the presence of block copolymer and poly(ethylene glycol) are calcite. It was observed that molecular mass of copolymers and PEG did not influence the crystalline form of precipitate. Two types of particles morphology was observed in the presence of block copolymers: stacked-rhombus-shaped and rod-shaped. In the case of PEG, only the rhombohedral calcite was obtained. Addition of modifiers reduced the size of crystals after 24 h and slightly increased the value of specific BET surface area. The mechanism of precipitation of calcium carbonate in the presence of PEG and PEO-PPO-PEO block copolymer are the same, because both modifiers contains in their structure EO blocks that can adsorb on the crystal surface and inhibit its growth.

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