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Different composition poly(methyl methacrylate-co-butyl methacrylate) copolymers through seeded semi-batch emulsion polymerization

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Abstract In the present work the synthesis and the chemical and thermal characterization of poly(methyl methacrylate-co-butyl methacrylate) copolymer, in three different macromolecular compositions, are reported. The aim of the present work was the identification of a standard method to obtain copolymers with controlled macromolecular composition, molecular weights and particle size distribution, together with the identification of the effect of the macromolecular composition on the material properties. A monomer-starved seeded semi-batch emulsion reaction was carried out and optimized, monitoring the kinetic of the copolymerization through the evaluation of residual monomer amounts. Then, an evaluation of the macromolecular composition was performed by Fourier transform infrared spectroscopy analysis. Molecular weight, molecular weight distribution, latex characteristics and thermal behaviour were also investigated.

Keywords Monomer-seeded semi-batch emulsion polymerization · Radical polymerization · Poly(methyl methacrylate-co-butyl methacrylate)

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Introduction

Copolymers are widely employed in industrial processes because their physicochemical properties, like strength, elasticity or thermal behaviour, can be modified by varying their macromolecular composition. The final functional versatility of these materials takes also origin from the possibility to carry out the synthesis by chemical reactions involving different monomers with different reactivity ratios and properties.

Industrial copolymerizations are based on systems implicating the presence of two or more monomers generally with high water solubility [1, 2] as carboxylic monomers, used in the production of particles with reactive groups on their surface [3, 4]. These monomers have a specific role in imparting a colloidal stability of dispersions used in the production of adhesives and binding agents and films and membranes with specific mechanical properties. In this contest, emulsion polymerization is a widely used technique employed in industrial production of latexes, paints, coatings, adhesives and bindings [5]. Acrylic polymers are a group of materials obtained by emulsion polymerization, where *n*-butyl acrylate (*n*-BA), *n*-butyl methacrylate (*n*-BMA) and methyl methacrylate (MMA) are the most commonly used monomers.

Final systems are widely versatile and many latexes, showing several applications as coatings and adhesives, can be produced by varying the molar ratio between comonomers. Final properties of these latexes highly depend on the micro-structural properties of the polymer and, for this reason, it is essential to understand the physicochemical phenomena involved in the emulsion copolymerizations.

Previous studies [6–8], focused on the *n*-BA/MMA semi-batch emulsion copolymerization, evaluated the effects of various reaction parameters on the particle nucleation and growth, also through mathematical models to describe the particle growth and the mechanism of particle formation. In this work, in order to control the effective final macromolecular composition of synthesized materials, copolymerization was carried out via a semi-batch emulsion polymerization under monomer-starved conditions [9–13] that allows controlling also the temperature of the reactor [14] and the particle size distribution [15].

From literature [16–20], copolymers composed of methyl methacrylate and *n*-butyl methacrylate are very interesting. Monomers chemical structures resemble each other and a similar behaviour can be expected. In practice, homopolymers obtained from these monomers are very different in chemical, mechanical and thermal properties.

In the present work an optimized method suitable to control the composition during the synthesis, the effects of the comonomers ratio on the monomer consumption and effects due to the macromolecular composition on the thermal properties were studied. The copolymer poly(methyl methacrylate-co-butyl methacrylate) in three different molar compositions was synthesized and characterized in order to evaluate the instantaneous composition of the reactive mass, the molecular weight, the molecular weight distribution, the latex properties and the thermal behaviour.

Experimental section

In the present work, three different composition materials were synthesized by varying the feed used for the reaction. Starting percentage molecular feed compositions of MMA/BMA used were: 87.5/12.5, 75/25 and 50/50, polymer nomenclature was referred to the feed reactor molar composition. Also, homopolymers PMMA and PBMA were synthesized with the same scheme used for copolymer synthesis with the aim of comparing copolymers properties with reference homopolymers and evaluating effects of composition on the properties of newly synthesized materials.

Copolymer synthesis

Materials

Materials were synthesized in a seeded semi-batch emulsion copolymerization under a monomer-starved condition and the same scheme was used for the synthesis of homopolymers.

Methyl methacrylate and *n*-butyl methacrylate, both obtained from Sigma Aldrich, were purified to remove the hydroquinone inhibitor before the use. The monomers were afterwards stored in the dark at −20 °C and used within 2 weeks. Potassium persulphate (KPS, Lancaster®, purity grade: 99.99%) was used as initiator and sodium dodecyl sulphate (SDS, Sigma Aldrich®) as emulsifier agent. Bidistilled and deionised water was used as emulsion medium for all reactions. KPS amount introduced within the reactor was 0.027% (mol/mol) with respect of the total monomer moles amount, SDS introduced was 0.25% (w/v) with respect of the total liquid amount in the reactor, constituted of water and monomers. The reactions were carried out with constant number of monomer moles (0.25 mol) and total liquid volume (500 ml), then SDS amount was 1.25 g and KPS amount was 0.018 g for all reactions. Amounts of MMA, BMA and water employed for reactions were reported in Table 1.

Polymerization apparatus

Reactions were carried out in a three-neck round-bottom flask immersed in a thermostatic oil-bath. An Allihn reflux condenser, refrigerated with water at room temperature, was used to avoid the loss of monomers. A paddle equipped with a

Table 1 Recipes of the monomer-seeded semibatch emulsion copolymerizations

Material	MMA (mol)	BMA (mol)	H_2O (ml)
PMMA	0.25	–	473.27
P(MMA-co-BMA) 87.5/12.5	0.219	0.031	471.63
P(MMA-co-BMA) 75/25	0.188	0.062	470
P(MMA-co-BMA) 50/50	0.125	0.125	466.75
PBMA	–	0.25	460.24

Teflon® impeller was used, connected to a Heidolf RZR 2020 engine set to 260 rpm. Reaction was carried out under continuous N_2 flux. Temperature was uniformly maintained at 75 °C and controlled by a thermocouple trough all reaction period. The reaction was divided in three parts: during the first, both monomers MMA and BMA were fed, in the second only MMA monomer was fed and in the third the reaction was allowed to proceed without any feed. Each part of the reaction lasted 1 h and then total reaction time was 3 h.

Polymerization method

The SDS emulsifier was dissolved in 400 ml of water and, after the complete dissolution, was introduced in the reactor and heated at 70 °C. The KPS initiator was dissolved in the rest of the water with respect of the Table 1. A seed of 32% (w/w) of monomers was added to the initial reactor charge and purged with nitrogen for 10 min then the temperature was increased to 75 °C. When the temperature reached 75 °C, KPS solution was introduced in the reaction mixture. From this point, the feed was added in spot every 15 min for eight times (see Table 2). Four additions of both MMA and BMA monomers were carried out in the first hour, while four additions of only MMA monomer were carried out in the second hour of reaction. This parcelling was selected in order to avoid having a great amount of MMA in the reactor during the first period of reaction of copolymers 87.5/12.5 and 75/25. For analogy, the same scheme was adopted for copolymer 50/50.

Polymerization was stopped by rapidly reducing the temperature at 25 °C using an ice bath.

Study of the monomer consumption

During the polymerization, samples were withdrawn for off-line analyses from the polymerization mass at regular intervals of time. Samples were withdrawn immediately after the feed and then after 1, 2, 5 and 10 min. 5 μl were withdrawn and diluted in 5 ml of bidistilled and deionised water. Reaction was sharply blocked by decreasing the temperature using ice and then putting the sample at −20 °C.

Samples were analysed by High Performance Liquid Chromatography (HPLC) to evaluate the effective amount of residual unreacted monomers present in the reactor.

Table 2 MMA feeds were introduced within the reactor for eight times every 15 min after the initial charge during the first and the second part of the reaction (2 h), BMA feeds were introduced for four times every 15 min after the initial charge

Material	Initial charge (mol)	MMA step-by-step feeds (mol)	BMA step-by-step feeds (mol)
PMMA	0.080/–	0.021	–
P(MMA-co-BMA) 87.5/12.5	0.070/0.010	0.019	0.005
P(MMA-co-BMA) 75/25	0.060/0.020	0.016	0.011
P(MMA-co-BMA) 50/50	0.040/0.040	0.011	0.021
PBMA	–/0.170	–	0.043

Withdrawn samples contained MMA and BMA monomers, SDS, KPS and water, therefore a chromatographic method was necessary to separate all components. A chromatographic method was developed expressly for this aim, inspiring to the work proposed by Sofou et al. [21]. HPLC apparatus consisted in a 410 LC pump, an ALLTECH C18 3U column with a non-polar phase (dimensions 100 mm × 4.6 mm) and a UV detector (Perkin-Elmer). Reagents used were specific HPLC grade acetonitrile (ACN, Carlo Erba Reagenti®) and double deionised water. The mobile phase was constituted by 80% ACN and 20% water, test time was 10 min, internal flux rate was 0.8 ml/min, injected volume was 50 μl and wavelength was 210 nm at room temperature.

Characterization

After synthesis, materials were analyzed in order to evaluate the chemical and morphological characteristics, the molecular weight, the effective macromolecular composition and the thermal behaviour.

The polymeric powder was isolated from the latex structure drying the latex in a vented oven at 40 °C for 24 h. The dried powder was washed with hot water (70 °C) to eliminate the SDS; the solid content was recovered from the water and then dried again. Copolymers were also washed with methylene chloride to eliminate the PMMA homopolymer and then with isopropanol to eliminate the PBMA homopolymer eventually produced in the copolymerization reactions. After these purifications, the solid content was recovered and dried in a vented oven at 40 °C for 24 h before the use.

Morphological analysis and latex characterization

A morphological analysis was performed onto the dried latex and the washed polymeric powders to evaluate the particle size and the particle size distribution. Analyses were carried out through Scanning Electron Microscopy (SEM) JEOL JSM 5600.

Also, a characterization was performed on the latex. In particular, the experimental and the theoretical solid contents were evaluated. Theoretical (Eq. 1) and experimental (Eq. 2) solid contents of the latex were evaluated as [22]:

$$\mathrm{SC_{th}}\ \% = \frac{\text{weight of introduced solid (g)}}{\text{sample weight (g)}} \times 100 \tag{1}$$

$$\mathrm{SC_{exp}}\ \% = \frac{\text{weight of dried latex (g)}}{\text{sample weight (g)}} \times 100 \tag{2}$$

These values were calculated taking the presence of the SDS amount into account.

Molecular weight and molecular weight distribution

Mean molecular weights (number, viscosity, weight and z) and dispersion indexes were determined by gel permeation chromatography (GPC) using a Perkin Elmer apparatus, equipped with a LC 90 UV spectrophotometric detector, a Series 200 refractive index and one ResiPore column (dimensions 300 × 7.5 mm, particle size 3 μm). Tetrahydrofuran (THF, Lab Scan®, HPLC purity degree) was used as solvent at a flow rate of 1 ml/min. Standard calibration curve was obtained analyzing narrow polystyrene standards with known molecular weights using appropriate Mark-Houwink-Sakurada constants [23] and TurboSEC software. For synthesized homopolymers, the Mark-Houwink-Sakurada constants were obtained from literature [24] and, supposing that copolymer macromolecules were linear, a linear interpolation of literature data was performed in order to obtain k and α values of copolymers.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) analyses were carried out by a Perkin Elmer Mod Spectrum GX. FT-IR analysis allowed evaluating the effective macromolecular composition of copolymers, identifying characteristic bands for homopolymers within the copolymers spectra.

Chemical analysis

To chemically characterize synthesized copolymers, ^{1}H NMR analysis was carried out.

^{1}H NMR spectra of PMMA, PBMA and P(MMA-co-BMA) copolymers were measured at room temperature and 200 MHz, with NMR Varian-Gemini 200 Spectrophotometer, starting from 2% solutions of copolymer in deuterated chloroform, using 5 mm diameter tubes and the solvent as standard.

Thermal analysis

The glass transition is considered one of the most relevant characteristics to appreciate the practical use of amorphous polymers [25]. Glass transition temperatures (T_g) for synthesized copolymers were evaluated by Differential Scanning Calorimetry (DSC). Calorimetric analyses were obtained using a Perkin Elmer DSC 7 instrument. Samples (4 ± 0.2 mg of polymeric powder) were sealed in aluminium pans. The thermal behaviour of the materials was followed from 0 to 200 °C (heating and cooling) at a rate of 10 °C /min. The results of the second heating scan were considered. Nitrogen, with a flow rate of 10 mL/min, was used as a purge gas during the scans.

Results and discussion

Synthesis and monomer consumption

In order to describe the progress of the reactions, the standard assumption of well-mixed reactor was considered. When the reaction started, the reactive mass within the reactor was completely transparent, during the reaction it came firstly bluish and then white. The presence of the surfactant and the high-stirred conditions ensured the formation of very small polymeric particles that gave rise to the formation of a stable latex.

For a semi-batch reaction, monomer conversion is defined as the number of moles of monomer reacted into the reactor divided by the total number of moles of monomer loaded and fed to the reactor [14, 15, 26–28]. According to this definition, monomer conversions were evaluated and in Table 3 the final conversions is reported.

Also, the overall (Eq. 3) and the instantaneous (Eq. 4) conversions, indicated respectively as x_{ov} and x_{in}, were evaluated as [27]:

$$x_{\mathrm{ov}} = \frac{\text{moles fed at time } t - \text{unreactedmoles}}{\text{total added moles}} \tag{3}$$

$$x_{\mathrm{in}} = \frac{\text{moles fed at time } t - \text{unreactedmoles}}{\text{moles fed at time } t} \tag{4}$$

In Fig. 1, x_{ov} and x_{in} for the P(MMA-co-BMA) 75/25 copolymer, are reported. From Fig. 1 it is possible to observe that the most important condition in a semi-batch reaction, that is the reaching of a high conversion before the addition of fresh monomers, was respected.

Monomer-starved conditions proposed for the synthesis of these materials imply that the monomers are added in the reacting mass with a rate similar to the polymerization rate [29]. For this reason, is important to have a fast reaction and the time elapsed between feeds has to be enough to permit the almost complete consumption of the monomers. Monitoring the monomer disappearance is possible to establish these parameters. A trial-and-error procedure was executed before to reach the scheme proposed in this paper that was able to inflect the macromolecular

Table 3 Conversion values of monomers

Material	Fed moles	Residual moles	Final conversion
PMMA			
MMA	0.25	1.27×10^{-4}	0.990
BMA	–	–	–
P(MMA-co-BMA) 87.5/12.5			
MMA	0.219	1.17×10^{-4}	0.999
BMA	0.031	2.07×10^{-4}	0.993
P(MMA-co-BMA) 75/25			
MMA	0.188	1.72×10^{-4}	0.999
BMA	0.063	6.63×10^{-5}	0.999
P(MMA-co-BMA) 50/50			
MMA	0.125	4.82×10^{-4}	0.996
BMA	0.125	8.02×10^{-5}	0.999
PBMA			
MMA	–	–	–
BMA	0.25	1.93×10^{-5}	0.999

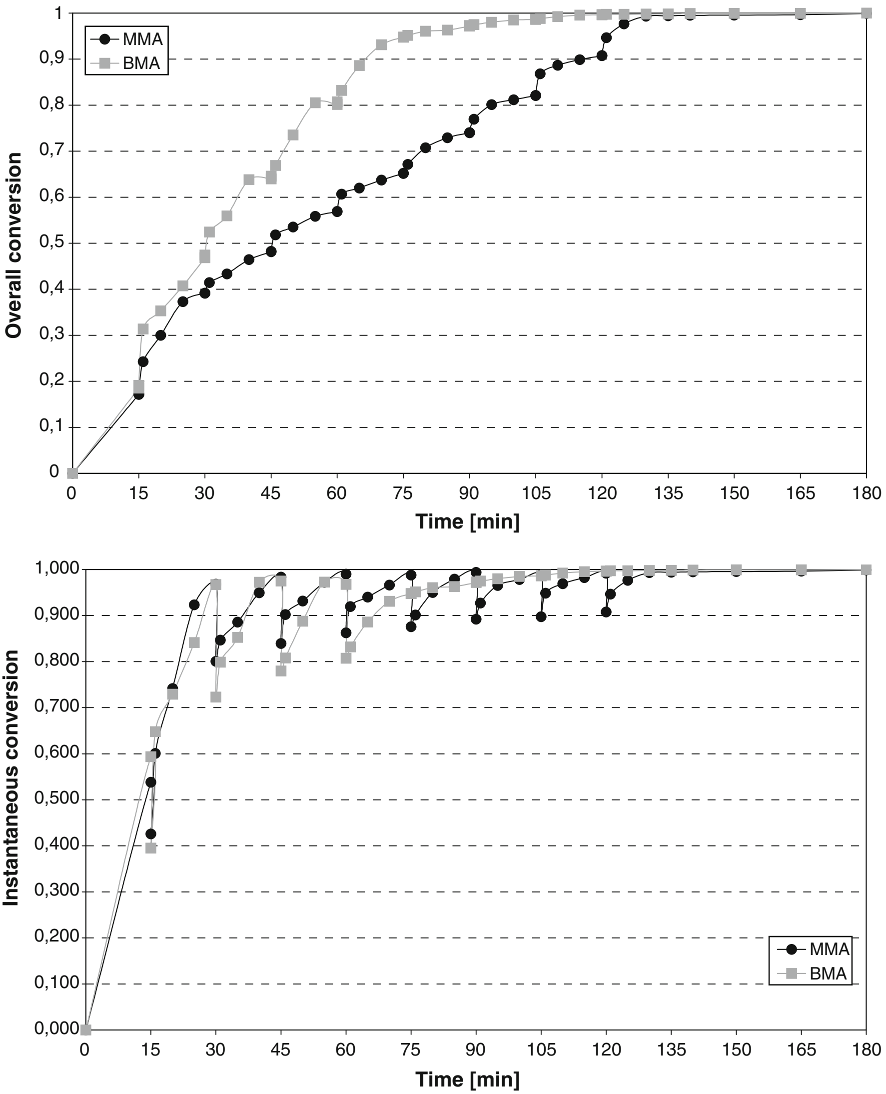

Fig. 1 Overall (*top*) and instantaneous (*bottom*) monomer conversions evaluated by HPLC analysis. In this figure results obtained for the copolymer P(MMA-co-BMA) 75/25 are reported

composition. The amount of monomers present in the reactor was monitored off-line by HPLC, using the chromatographic method previously reported. In order to save space, only results relative to P(MMA-co-BMA) 50/50 copolymerization are showed in this paper (Fig. 2). For all reactions results are similar.

The amount of monomer added in each feed polymerized almost immediately after the introduction in the reactor. This remark was of paramount importance to ensure the monomer-starved condition and in consequence to control the composition of the copolymers obtained in the semi-batch reaction.

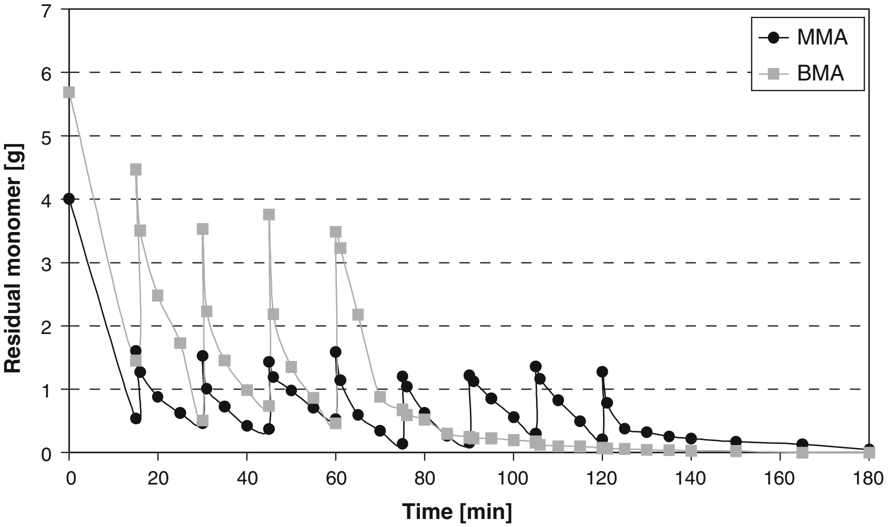

Fig. 2 Amount of residual monomers (g) in the reactor versus time for the copolymerization of P(MMA-co-BMA) 50/50

In effect, to take full advantages of semi-batch emulsion polymerization, it is necessary to have a monomer-starved condition to prevent accumulation of monomers in the reactor. For this reason, a continuous monitoring of the residual monomers concentration was important to ensure the mentioned starved condition.

Characterization

Latex structure

Conventionally, emulsion polymerizations are used when monomers are hardly soluble in water. However, this procedure is also used in many industrial polymerizations involving the use of highly soluble monomers, as carboxylic monomers. In this work to obtain an emulsion polymerization and a latex structure a great amount of emulsifier agent SDS was introduced in the reactor (0.25% w/v with respect of the total liquid amount). The presence of the surfactant and the high-stirred condition within the reactor ensure the formation of a time-stable latex, constituted of non-settle particles. Dimension of particles was evaluated by SEM. In Fig. 3 a SEM image of particles obtained during the P(MMA-co-BMA) 50/50 copolymerization is reported as example. By the SEM analysis, a mean value of the particle dimension was evaluated together with the polydispersity index, defined as:

$$\mathrm{PDI} = \sum \frac{\text{number of particles with diameter } i}{\text{total number of particles}} \times \text{ diameter } i \qquad (5)$$

Dimensions of particles are included between 200 and 500 nm for all synthesized materials. Results are summarized in Table 4. It was not notice a trend of these values in function of the feed compositions.

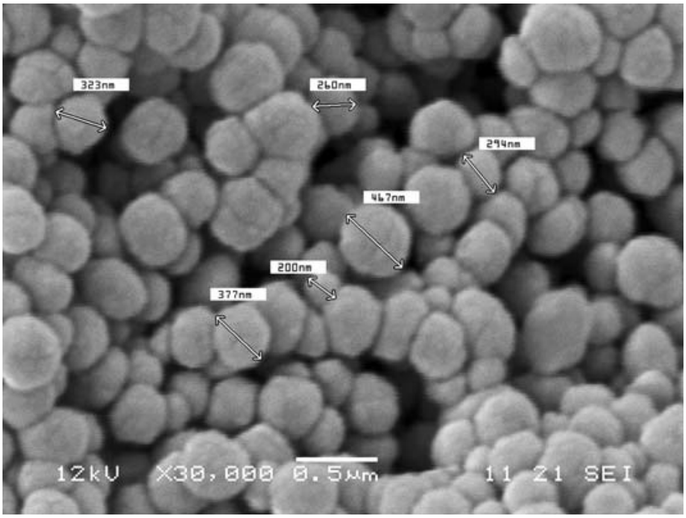

Fig. 3 SEM picture of the particles obtained during the copolymerization of P(MMA-co-BMA) 50/50

Latex can be characterized determining the solid content present in the reacted mass after the stripping of the unreacted monomers.

Experimental values for the solid contents are very similar to theoretical. From the latex characterization was possible to evaluate the gravimetrical conversion of monomers. Gravimetrical conversion was evaluated on the total amount of monomers in the formulations and then represents only a global conversion. Gravimetrical conversion was evaluated from Eq. 6 and obtained results are summarized in Table 5.

$$\text{Gravimetrical conversion} = \frac{SC_{\text{exp}}\%}{SC_{\text{th}}\%} \tag{6}$$

Molecular weights

Emulsion polymerizations generally lead to obtain products with high molecular weight and high dispersion index [22]. In the reaction system applied, the composition of the monomer mixture is equal to the desired copolymer composition. In this work molecular weights were evaluated through chromatographic analyses by GPC. Using the calibration curve, constructed as previously described, polymeric solutions (5% w/v) in THF were prepared and analyzed.

Mark–Houwink–Sakurada (MHS) constants for polystyrene and for tested materials are reported in Table 6.

A copolymer with a given composition and a maximum polymerization rate was the main target of the present work and to maintain the desired copolymer composition we needed to keep the corresponding composition of the reacting mass under control by adding the monomers at an appropriate rate, maintaining at any rate a final high molecular weight of polymeric materials.

Table 4 Mean diameter of the particles obtained and polydispersity index, evaluated using Eq. 5

Material	Mean diameter (nm)	Polydispersity index
PMMA	315	0.76
P(MMA-co-BMA) 87.5/12.5	321	0.83
P(MMA-co-BMA) 75/25	329	0.74
P(MMA-co-BMA) 50/50	312	0.82
PBMA	346	0.79

Table 5 Theoretical and experimental solid contents of the latex and gravimetrical conversions

Material	SC_{th} %	SC_{exp} %	Gravimetrical conversion
PMMA	5.02	5.02	1.000
P(MMA-co-BMA) 87.5/12.5	5.29	5.28	0.999
P(MMA-co-BMA) 75/25	5.58	5.57	0.999
P(MMA-co-BMA) 50/50	6.09	6.09	1.000
PBMA	7.17	7.13	0.995

Table 6 Molecular weights: number (M_n), viscosity (M_v), weight (M_w) and z (M_z), dispersion indexes (DI = M_n/M_w), Mark-Houwink-Sakurada (MHS) constants and intrinsic viscosities (η) evaluated by GPC

Material	M_n (Da)	M_v (Da)	M_w (Da)	M_z (Da)	DI (M_n/M_w)
Molecular weights and DI					
PMMA	433,000	784,000	840,000	1,243,089	1.94
P(MMA-co-BMA) 87.5/12.5	383,000	802,000	866,000	1,296,158	2.26
P(MMA-co-BMA) 75/25	430,000	840,000	907,000	1,343,791	2.10
P(MMA-co-BMA) 50/50	518,000	1,030,000	1,110,000	1,564,185	2.15
PBMA	394,000	1,050,000	1,160,000	1,762,706	2.95

Material	k (dl/g)	α	η (dl/g)
MHS constants and intrinsic viscosity			
PMMA	9.44×10^{-5}	0.719	1.633
P(MMA-co-BMA) 87.5/12.5	1.05×10^{-4}	0.711	1.657
P(MMA-co-BMA) 75/25	1.12×10^{-4}	0.704	1.658
P(MMA-co-BMA) 50/50	1.24×10^{-4}	0.691	1.770
PBMA	1.48×10^{-4}	0.664	1.476

Molecular weight resulted to be not affected by the macromolecular composition because a trend with the macromolecular composition was not highlighted. Molecular weights obtained are high and it can be explained by the great radical concentration within the formed particles with respect of the rest of the mass, constituted substantially of water. When the step-by-step monomeric feed was introduced, radicals were active in the particles and a greater possibility of a chain growth, with respect of the formation of a new chain, occurred.

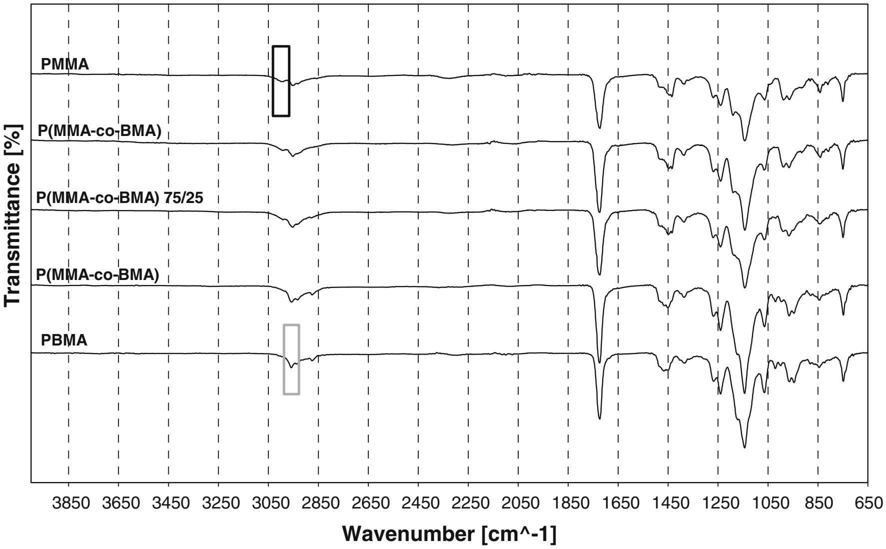

Fig. 4 Spectra of the synthesized materials. In the spectra of the homopolymers are highlighted the characteristic bands used to quantify the copolymer compositions

Fourier transform infrared analysis

FT-IR analysis allowed evaluating experimentally the actual macromolecular composition from the spectra of the tested materials. Within the spectra of the homopolymers, a characteristic band for PMMA was identified at 2,994 cm^{-1} (corresponding to the asymmetric stretching of the CH_3 bond) and for PBMA at 2,951 cm^{-1} (corresponding to the symmetric stretching of the CH_2 bond). In Fig. 4 spectra of tested materials are reported. Using the spectral calculator, three theoretical spectra were numerically evaluated and the peak intensities, corresponding to the characteristic bands of the homopolymers, were calculated. From these values the ratios (*R*) was calculated and a work line was constructed. From its expression and the evaluation of the ratios for real synthesized copolymers, final macromolecular compositions were obtained.

Obtained results from FT-IR analyses are reported in Table 7.

Experimental results showed that the real macromolecular composition evaluated from FT-IR spectra of materials can be controlled adopting the seeded semi-batch emulsion copolymerization scheme, because all synthesized materials showed a final molar composition very similar to the global recipe composition.

Chemical analysis

^{1}H NMR analysis was performed on polymeric solutions in CDCl3. Because of only one difference occurred between the monomeric units (the alcoholic group bonded to the carboxylic group), from obtained spectra was not possible to detect chemical shifts due to this difference.

Table 7 Ratios between peak intensities of characteristic bands of PMMA and PBMA in copolymers spectra, and percentage macromolecular weight and molar compositions of synthesized materials

Material	R	% weight composition MMA/BMA	% molar composition MMA/BMA
P(MMA-co-BMA) 87.5/12.5	0.538	82.4/17.6	85.9/14.4
P(MMA-co-BMA) 75/25	0.487	67.1/32.9	73.5/26.5
P(MMA-co-BMA) 50/50	0.405	42.1/57.9	50.7/49.3

Table 8 Glass transition temperatures evaluated for tested materials

Materials	T_g (°C)
PMMA	118
P(MMA-co-BMA) 87.5/12.5	95
P(MMA-co-BMA) 75/25	80
P(MMA-co-BMA) 50/50	55
PBMA	24

From this analysis was in any case possible to deduce the stereochemical configuration of the macromolecules that resulted atactic for all synthesized materials.

Thermal analysis

Glass transition temperatures were evaluated for all synthesized materials. Obtained results for copolymers were compared to homopolymer results. Samples underwent two scans and T_g values were evaluated using the second scan thermograms.

For PMMA, the T_g was 118 °C while for PBMA was 24 °C. Introduction of PBMA units within the copolymer macromolecule increased the chain flexibility and the T_g for copolymers showed intermediate values. Results obtained were reported in Table 8.

Experimental behaviour can be compared to theoretical approaches proposed by Fox (Eq. 7) [30] and Gordon–Taylor (Eq. 8) [31] equations:

$$\frac{1}{T_{g,\text{copolymer}}} = \frac{w_{\text{MMA}}}{T_{g,\text{MMA}}} + \frac{w_{\text{BMA}}}{T_{g,\text{BMA}}} \tag{7}$$

$$T_{g,\text{copolymer}} = \frac{w_{\text{BMA}} \cdot T_{g,\text{BMA}} + k \cdot (1 - w_{\text{BMA}}) \cdot T_{g,\text{MMA}}}{w_{\text{BMA}} + k \cdot (1 - w_{\text{BMA}})} \tag{8}$$

where w_{MMA} and w_{BMA} are the weight fractions of the functional units present in the copolymer chain, $T_{g,\text{MMA}}$ and $T_{g,\text{BMA}}$ are the glass transition temperatures of the homopolymers and k is a characteristic coefficient of the material [32], defined as $\frac{\rho_1}{\rho_2} \cdot \frac{\Delta\alpha_2}{\Delta\alpha_1}$, where ρ_i is the density and $\Delta\alpha_i = \alpha_{\text{melt}} - \alpha_{\text{glass}}$ is the increment at T_g of the expansion coefficient of the component i; k is generally replaced by the fitting parameter C obtained from experimental data. Depending from C value, the curves representing T_g versus the macromolecular composition deviate from the linear behaviour, defined by $C = 1$.

For the fitting of the experimental data it is convenient to linearize the Gordon–Taylor equation as follows:

$$T_g - T_{g,A} = C \cdot \left(T_{g,B} - T_g\right) \cdot \frac{w_B}{w_A} \tag{9}$$

where the components A and B are assigned such $T_{g,A} < T_{g,B}$.

From experimental results a plot of ($T_{g,\text{copolymer}} - T_{g,\text{PBMA}}$) versus ($T_{g,\text{PMMA}} - T_{g,\text{copolymer}}$)·$w_{\text{MMA}}/w_{\text{BMA}}$ yields C from a linear interpolation, as reported in Fig. 5. Slope of the linear interpolation represents C parameter.

The C value obtained (0.6453) was employed to determine the Gordon–Taylor curve following reported. In Fig. 6, glass transition temperatures, evaluated experimentally and using both Fox and Gordon–Taylor equations, are reported. From these results is possible to observe a negative deviation of the experimental data with respect of the linear behaviour; also, a well description of experimental data with Gordon–Taylor equation, that describes the dependence of the glass transition temperature from the composition of random copolymers, can be highlighted.

The Fox equation represents a rough evaluation of the T_g for the copolymers, based on the assumption that the glass transition temperature of a copolymer is only an additive combination of the T_g of the corresponding homopolymers but it is not verified for many copolymers. The Gordon–Taylor equation takes also the C parameter into account. This parameter is related to the densities and the coefficients of expansion of the materials, and it represents a more accurate model to describe the thermal behaviour of random copolymers. The correspondence of experimental T_g with the Gordon–Taylor model could be attributed to the greater accuracy of the Gordon–Taylor equation with respect of the Fox model. The Fox equation in general could be used to evaluate positive or negative deviations in thermal behaviour with respect to the linear trend, instead, the Gordon–Taylor can be used to carefully predict the T_g, when the C parameter is known, as in this work.

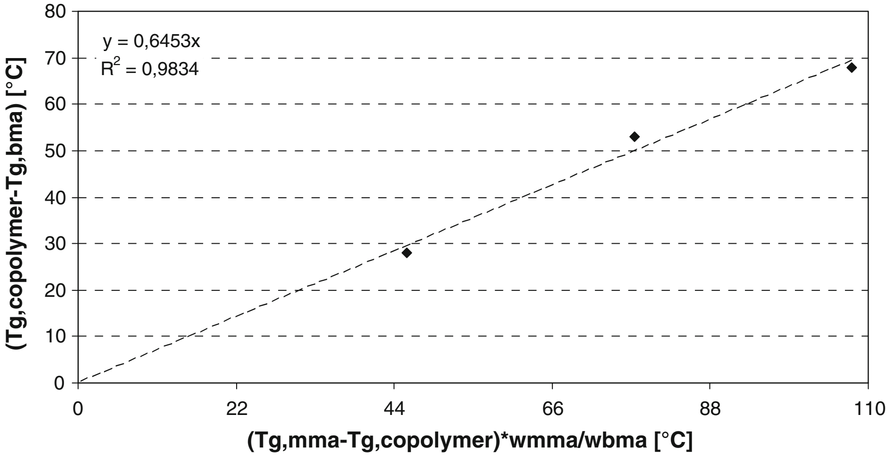

Fig. 5 Evaluation of the C parameter from the linear interpolation of the ($T_{g,\text{copolymer}} - T_{g,\text{PBMA}}$) values versus ($T_{g,\text{PMMA}} - T_{g,\text{copolymer}}$)·$w_{\text{MMA}}/w_{\text{BMA}}$ values

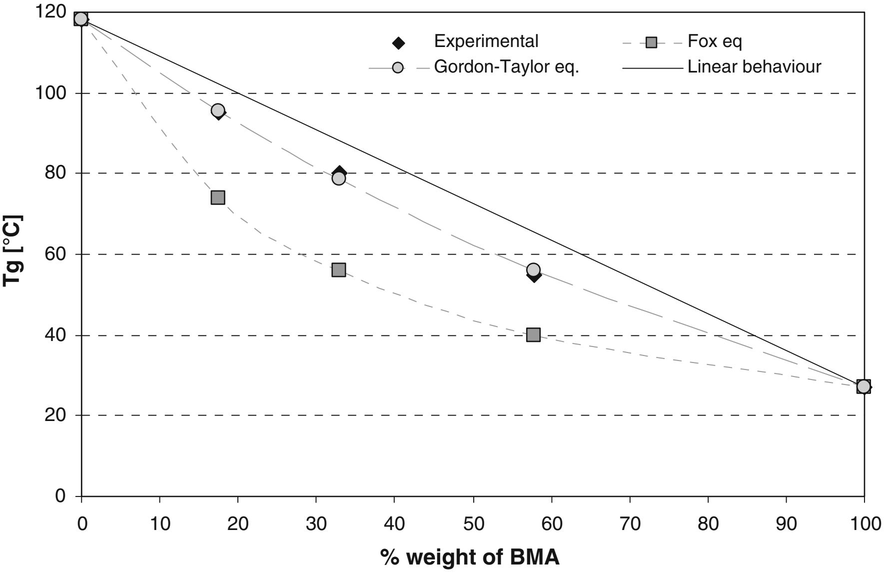

Fig. 6 Glass transition temperatures evaluated experimentally (*black diamond*), via the Fox equation (*black square*) and by the Gordon–Taylor equation (black circle)

Conclusions

In the present work an optimized method to synthesize copolymers with controlled macromolecular composition was proposed. A specific monomer-seeded semi-batch emulsion polymerization was carried out in order to obtain a poly(methyl methacrylate-co-butyl methacrylate) copolymer with three different compositions.

This useful scheme of reaction was developed parcelling the feed in nine parts, paying attention to the elapsing time between the feeds avoiding the drift of residual unreacted monomer. From HPLC results (also confirmed by studies onto the latex) was possible to conclude that monomers consumption was almost complete and the final conversion was very high. The semi-batch reaction allowed controlling the chain growth, kept down the dispersion indexes. FT-IR spectra of the synthesized materials showed that the real macromolecular composition was well controlled through the seeded semi-batch emulsion copolymerization scheme, being the final molar composition very similar to the global recipe composition. Thermal analyses showed that synthesized copolymers are well described by the theoretical Gordon–Taylor model, with a negative deviation from the additivity of the glass transition temperatures.

These controlled composition copolymers present high potentiality in several engineering sectors, such as for example in biomedical engineering field, where a P(MMA-co-BMA) material, having a specific macromolecular composition, could find favourable use in ophthalmic application, orthopaedic sector (bone cement or bone substitute) or in implantable devices as drug delivery platform.

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