Polym. Bull. (2010) 65:893–903
DOI 10.1007/s00289-010-0300-3

ORIGINAL PAPER

Sonochemical synthesis of polymethylmethacrylate to be used as biomaterial

C. Albano · G. González · C. Parra

Received: 5 January 2010 / Revised: 15 May 2010 / Accepted: 16 May 2010 /
Published online: 4 June 2010

Abstract In the present study, the synthesis of PMMA was carried out by emulsion polymerization under ultrasonic radiation, varying the concentration of the anionic surfactant and monomer concentration. Redox process was introduced in order to observe if an increment in conversion was obtained. Characterization was performed by FTIR, DSC, SEM, and ^{1}H-NMR of protons. The synthesis with redox initiation produced PMMA with majorly syndiotatic triads. The synthesis carried out under redox initiation resulted in a large increased in conversion, showing that there is an optimum surfactant/monomer ratio. Scanning Electron Microscopy showed that for low concentrations of surfactant (0.5% p/v) the latex particles presented a rough surface but high surfactant concentration showed nanometric spherical particles with a smooth surface. The study of in vitro biocompatibility by adhesion of osteoblasts on the materials resulted in higher cell adhesion in materials synthesized without redox initiation.

C. Albano (✉)
Laboratorio de Polímeros, Centro de Química; IVIC, Caracas, Venezuela
e-mail: carmen.albano@ucv.ve

C. Albano
Escuela de Ingeniería Química, Facultad de Ingeniería, UCV, Caracas, Venezuela

G. González
Laboratorio de Materiales, Centro de Ingeniería de Materiales y Nanotecnologia, IVIC, Caracas, Venezuela

G. González
Escuela de Física, Facultad de Ciencias, UCV, Caracas, Venezuela

C. Parra
Instituto Universitario de Tecnología "Dr. Federico Rivero Palacio", Caracas, Venezuela

Keywords Synthesis of PMMA · Redox initiation and ultrasonic radiation · In vitro biocompatibility · Anionic surfactant · Monomer concentration

Introduction

The synthesis of PMMA has been studied by different methods. One of the most effective method employs redox as initiation processes [1] and ultrasound as energy source [2–4]. An important advantage of this type of initiation lies in the velocity of generation of free radicals in comparison with thermal initiation processes [5]. If additionally, ultrasonic radiation is used as energy source, the reaction can be performed at room temperature, in shorter periods than those required for a normal redox polymerization process.

Emulsion polymerization is produced using a surfactant acting as a tensoactive agent substance with two fundamental properties: the capacity of interface adsorption and its tendency to association to form organized structures by the aggregation of micelles. The surfactant provides stability to the formed polymer and accommodates the hydrophobic monomer during the polymerization process. Additionally, due to the very efficient dispersion produced by sonication, the polymer is formed by nanometric particles with different microstructures [5]. Also, the use of redox initiation with ultrasonic radiation can improve the polymer conversion. Therefore, this method is a very promising route for the synthesis polymers. On the other hand, due to the absence of stabilizing agents or catalysts that could remain as undesirable contaminants, this method could be used for the synthesis of polymers for biomedical applications [6–9]. The objectives of the present study are the synthesis and characterization of PMMA using high frequency ultrasound and the comparison of the processes with and without redox initiation Also, the study of in vitro biocompatibility by adhesion of osteoblasts cells on the materials obtained by both processes.

Experimental

Methylmethacrylate (MMA) analytical grade was used with concentrations of 10, 8, and 6% v/v and an anionic surfactant, Sodium Lauryl Sulfate (SLS), was used, in concentrations of 0.5; 1.0; 1.5, and 2.0% p/v. The redox system was 5 mL of a solution of ferrous sulfate heptahydrate [$FeSO_4 \cdot 7H_2O$], 1 g of ammonium peroxydisulfate [$(NH_4)_2S_2O_8$], added to the solution of monomer and surfactant. This mixture was placed for 60 min under ultrasonic radiation at frequency of 20 kHz. The polymer was precipitated in cold methanol, carefully washed to eliminate the remaining reactants and dried in vacuum for 24 h.

The characterization of all the samples was carried out by Fourier Transformed infrared spectroscopy, in a NICOLET 500 FTIR spectrometer. The microstructure was evaluated by proton nuclear magnetic resonance spectroscopy (^{1}H-RMN) in a BRUKER ADVANCED 300 spectrometer, operating at 300, 13 kHz.

Thermal analysis was carried out in a differential scanning calorimeter METTLER TOLEDO DSC 821, from 25 to 250 °C with a heating rate of 20 °C/min.

The morphology and particle size were determined by scanning electron microscopy (SEM) using a Hitachi Field Emission S-4500 electron microscope operating at 8 kV. The samples were prepared by suspension in an ethanol–water mixture (75/25) and Pt-C coated in a Balzers BAE 300 evaporator.

The determination of the average molecular weight was determined by the Mark Houwink equation [10]:

$$[n] = KM_v$$

where $[n]$ is the intrinsic viscosity, "K" and "a" depend of the polymer and solvent used and M_v is the molecular viscosimetric weight. The molecular weight were determined following the ASTM D2857 standard, 1,2 dicloroethane was used as solvent.

For the determination of cell adhesion, the materials were treated with 70% ethanol to remove the superficial grease. Then they were washed extensively with deionized water and finally sterilized with a 25 kGy gamma radiation dose. Spot samples of 6 mm diameter were tested using a 96 well-plate (for tissue culture, NUNC). The cell number on the materials and controls were determined using a commercial kit (CyQuant) following the instructions of the manufacturer. A 3×10^3 cells/mL suspension was seeded with the different materials and control (which corresponds to an empty well). After 16 h of incubation in optimal culture conditions (37 °C, in a fully humidified atmosphere at 5% CO_2 in air), adhered cells were quantified using the CyQuant kit.

Results and discussion

Figure 1 shows the FTIR spectra of PMMA synthesized under different reaction conditions with and without redox initiation. In both spectra the vibration bands at 3,000 and 800 cm^{-1} are observed, corresponding to the characteristic principal absorption bands of PMMA. Therefore, both processes (with and without redox initiation) resulted in successful PMMA production.

Table 1 shows the conversion of polymerization for different surfactant and monomer concentrations, for processes with and without redox initiation. For processes carried out with redox initiation, maximum conversion was observed in the range 1.0–1.5% (w/v), for all monomer concentrations. The process carried out without redox initiation also showed a dependence on the surfactant and monomer concentrations.

The surfactant plays an important role in the polymerization process, encapsulating the polymer as the polymerization proceeds. The stability of the reaction media depends on the number of micelles formed; therefore, a critical surfactant/monomer concentration and the free radicals generated during the ultrasonic irradiation process seem to fulfill the conditions for optimum polymerization yield

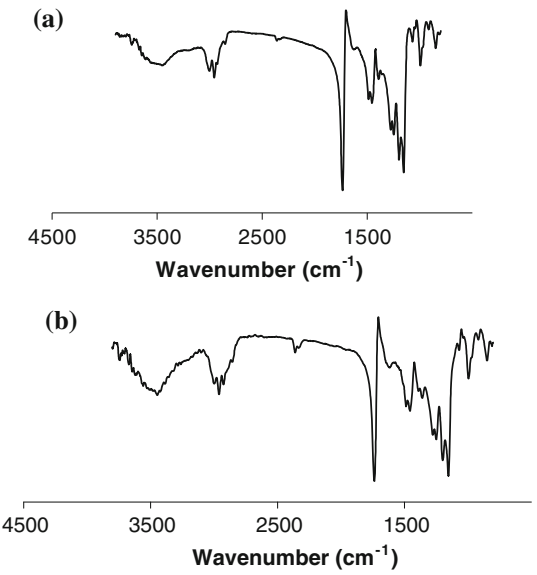

Fig. 1 FTIR spectra of PMMA **a** synthesized with 10% (v/v) MMA and 2.0% (w/v) SLS without redox initiation, **b** synthesized with 10% (v/v) MMA and 2.0% (w/v) SLS with redox initiation

Table 1 Conversion of polymerization reactions using ultrasonic irradiation with and without redox initiation

% SLS (w/v)	% Conversion without redox initiation			% Conversion with redox initiation		
	6% (v/v) MMA	8% (v/v) MMA	10% (v/v) MMA	6% (v/v) MMA	8% (v/v) MMA	10% (v/v) MMA
0.5	18.61	18.34	36.37	20.55	29.36	18.25
1.0	26.39	18.80	23.65	28.40	41.07	52.50
1.5	39.80	22.47	39.72	50.55	37.66	58.26
2.0	23.95	16.54	24.43	22.04	18.80	28.45

[11], a mechanistic explanation can be given to justify the increment in conversion when redox initiation was employed.

The surfactant in aqueous solution can be dissociated easily under ultrasonic irradiation; the decomposition process proposed is as follows [12]:

$$C_{11}H_{23}-CH_2-O-SO_3^-Na^+ \xrightarrow{\text{ultrasound}} C_{12}H_{25}^{\cdot} + {}^{\cdot}O-SO_3^-Na^+ \quad (1)$$

The free radicals generated during ultrasonic radiation initiate growth of the polymer chain, this process occurs at a reasonable velocity and a high polymer yield is obtained.

The redox system provides additional formation of free radicals according to reaction (2), contributing to the polymerization process, this can justify the increase in conversion observed during this process.

$$S_2O_8^{2-} + Fe \xrightarrow{\text{ultrasound}} 2SO_4^{2-\cdot} + Fe^{+3} \quad (2)$$

Tables 2 and 3, summarize the glass transition temperatures of the most representative tested samples of PMMA synthesized with different surfactant concentrations and 10% v/v of MMA concentration without and with redox initiation, respectively.

These results have a good agreement with the glass transition temperatures reported in the literature for atactic and syndiotactic PMMA configurations [13–15]. The different synthesis conditions used do not affect the glass transition temperature significantly.

The microstructural characteristics of the synthesized PMMA were carried out by ^{1}H-NMR. Figures 2 and 3 show the PMMA spectra synthesized with 1.5% w/v SLS and 10% MMA with and without redox initiation, respectively.

Both spectra are very similar showing three characteristic signals for PMMA, one broad peak in 0.8914 ppm and a narrow peak in 0.9084, both assigned to the protons of the methyl group, corresponding to triads of syndiatactic (rr) configuration of PMMA. A less intense peak in 1.0633 ppm corresponding to protons of the CH_3 group distributed atactically (rm, mr). Additionally, peaks associated to CH_2 groups in the range 1.5–2.3 ppm and to $COOCH_3$ groups in the range 2.920–3.62 ppm. Similar results were reported by Yeong et al [16] in the synthesis of PMMA using redox initiation.

Tables 4 and 5 show the general microstructure obtained from the ^{1}H-NMR spectra, for a group of PMMA samples prepared under different surfactant/monomer concentrations ratio), without and with redox initiation, under 60 min of ultrasonic irradiation.

The configurations obtained for two surfactant concentrations and two different monomer concentrations synthesized without redox initiation (Table 4) are similar for all the cases, resulting in triads with syndiotactic and atactic configurations. It is observed that the degree of syndiotacticity is considerable high. Similar results were

Table 2 Glass transition temperatures of PMMA obtained without redox initiation using 10% v/v of MMA

Surfactant	Surfactant concentration(%w/v)	T_g (°C) ± 2
SLS	0.5	122
	1.0	120
	1.5	125
	2.0	124

Table 3 Glass transition temperatures of PMMA obtained using redox initiation with 10% v/v of MMA

Surfactant	Surfactant concentration(% w/v)	T_g (°C) ± 2
SLS	0.5	122
	1.0	120
	1.5	121
	2.0	124

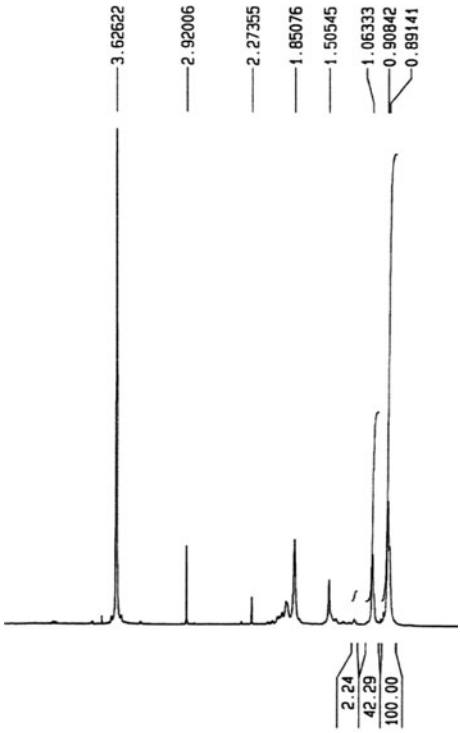

Fig. 2 ^{1}H-NMR spectrum of PMMA obtained from 1.5% SLS and 10% MMA, under ultrasonic irradiation without redox initiation

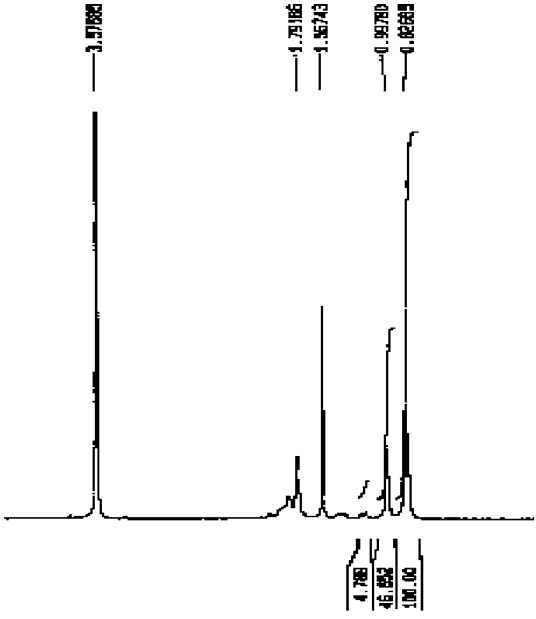

Fig. 3 ^{1}H-NMR del PMMA obtained from 1.5% SLS 10% MMA under ultrasonic irradiation and using redox initiation

Table 4 Tacticity of PMMA synthesized with different SLS and monomer concentrations after 60 min of ultrasonic radiation (without redox initiation)

Surfactant	% (w/v) SLS	% (v/v) MMA	Microstructure		
			Isotactic (mm)	Atactic (rm)	Syndiotactic (rr)
SLS	0.5	6	3	27	70
	2.0	6	2	28	70
	0.5	10	2	30	38
	2.0	10	2	29	69

Table 5 Tacticity of PMMA synthesized with different SLS and monomer concentrations under redox initiation and 60 min of ultrasonic radiation

Surfactant	% (w/v) SLS	% (v/v) MMA	Microstructure		
			Isotactic (mm)	Atactic (rm)	Syndiotactic (rr)
SLS	0.5	6	4	6	90
	2.0	6	5	3	92
	0.5	10	4	3	93
	2.0	10	4	5	91

obtained for all the other samples synthesized with different concentrations of SLS and MMA. These results are in good agreement with the glass transition temperature observed. Similar results have been reported by Isobe et al [17] and Price et al [18].

Redox initiation remarkably increases the proportion of syndiotatic triads in the polymer chains (90%) (Table 5). This is attributed to the relaxation processes that show some amorphous polymers during their formation [19]. However, the values of syndiotacticity of PMMA obtained without redox initiation are very similar to those obtained by conventional thermally initiated methods [20] and by photoinitiated methods [21].

Figure 4 shows the morphology of the PMMA synthesized with and without redox initiation varying the surfactant concentration for a fix monomer concentration of 10% v/v MMA and 60 min of ultrasonic irradiation. The latex particles of PMMA obtained without redox initiation (Fig. 4a, b) have a smaller particle size in the range of 65 to 100 nm, showing agglomerates of spherical morphology. Similar results are observed for the other surfactant concentrations studied.

The PMMA particles obtained using redox initiation (Fig. 4c, d) showed a rough external surface for low surfactant concentration and a smooth surface for high concentrations. The particle size for both surfactant concentrations is in the range of 2–4 μm, this is around an order of magnitude larger than those particles obtained without redox initiation. This could be due to the higher generation of free radicals during redox initiation and therefore a large amount of short polymer chains are formed and more polymer chains within the polymer particles are present implying larger particle sizes.

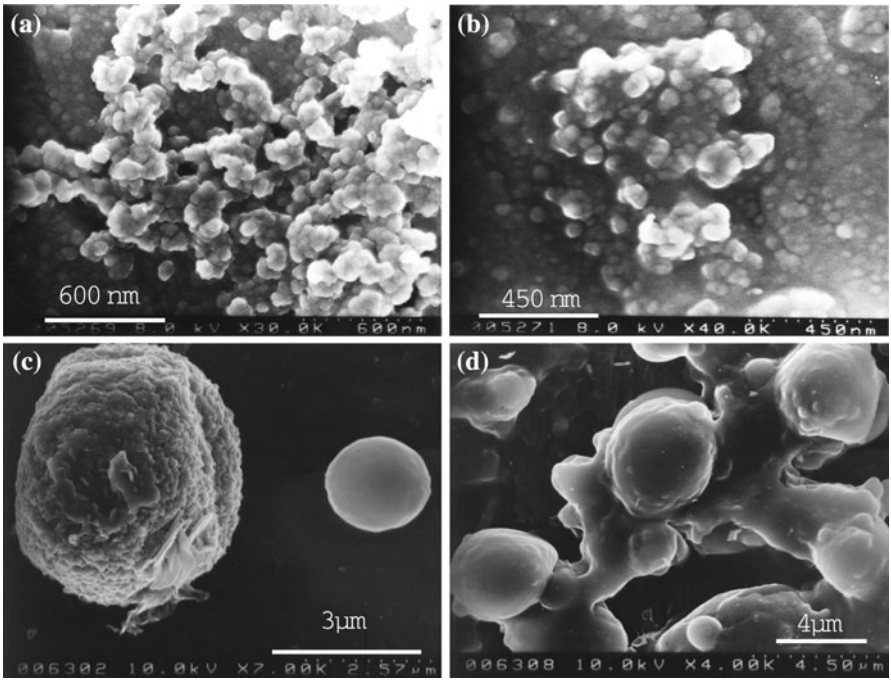

Fig. 4 SEM micrographs of PMMA synthesized with 10% v/v MMA and different SLS concentrations after 60 min of ultrasonic irradiation. **a** 0.5 p/v, **b** 2.0% p/v (without redox initiation); **c** 0.5% p/v, **d** 2.0% p/v (with redox initiation)

Piltcher and Ford [22] reported the dependence of particle size with surfactant/monomer ratio (S). They found that for $S < 1$ the particle size decreases with increasing S and for $S > 1$ the particle size does not change. In our case, S values were all <1, and it was observed that the particle size increased as S increased (Fig. 4), in good agreement with these authors, for both synthesis processes (with and without redox initiation).

It is important to point out that the morphology is controlled by thermodynamic and kinetic factors [23]. The thermodynamic factors depend on the rate of polymerization (directly related to the conversion) and on the diffusion rate of the polymeric chains. The kinetic factors depend on the chain mobility. Therefore, under redox conditions the polymerization rate is faster than the diffusion of polymer chains and this seems to be controlling the particle morphology.

The viscosimetric molecular weight (M_v) was determined to a group of samples prepared under different synthesis conditions.

The values obtained are between 590,000 and 1,700,000 g/mol. The M_v increases when the surfactant concentration increases (from 0.5 to 2% w/v), for both initiation conditions (with and without redox initiation). This is attributed to the increase in the polymerization rate with increasing surfactant concentration and it is presumably due to the increase in the free radical generation rate resulting from an increase in the number of surfactant molecules acting as initiators. The dependence of the

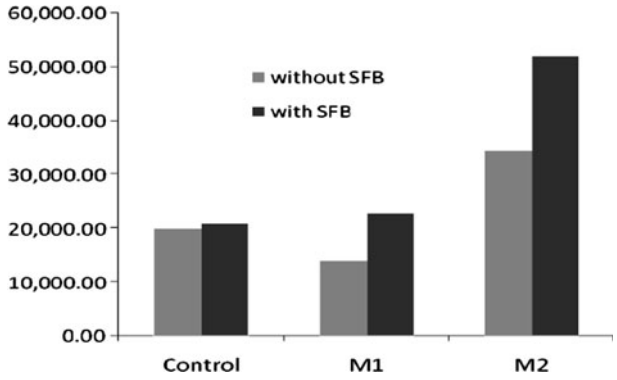

Fig. 5 Cell adhesion of PMMA synthesized under different conditions. *M1* PMMA synthesized using redox, *M2* PMMA synthesized without redox

polymerization rate and the polymer molecular weight on the surfactant concentration follows the prediction of the Smith–Ewart theory [24]. On the other hand, for a fix surfactant concentration, the increase in monomer concentration results in an increase of the molecular weight from 1,600,000 to 2,400,000, for monomer concentration of 6 and 10% v/v, respectively [25].

Figure 5 shows the cellular adhesion behavior after 16 h in the culture media, with and without fetal bovine serum (FBS). It can be observed that when the synthesis of PMMA was carried out in absence of redox initiators, the cellular adhesion increased, compared to the control sample and to PMMA with redox initiation. Additionally, when the culture media contains FBS the adhesion behavior is enhanced.

The differences in cellular adhesion observed in PMMA, synthesized under redox initiation could be attributed to the toxic nature of redox initiators (ferrous sulfate heptahydrate and ammonium peroxydisulfate) that could remain in traces, influencing the cell adhesion and proliferation. Other methods of initiation of methylmethacrylate carried out with benzoyl peroxide and acceleration by *N*, *N* dimethylaniline has also been proved to be cytotoxic for osteoblast adhesion [26, 27]. Studies of ferrous sulfate toxicity have reported that small traces of this compound presented necrosis and poisoning [28]. Therefore, the results obtained in this study are not surprising, since it is possible that small traces of the initiators remain after the synthesis of PMMA.

It is remarkable that in both synthesis conditions, the presence of FBS increases cell adhesion and promoting the interaction of proteins present in FBS with the material.

Conclusions

The polymerization process under the complex reaction taking place is affected by the reactivity of the radical species present (surfactant, monomer, and redox system)

and ultrasonic radiation. This process results in the formation of polymer triads chains with different configurations (atactic or syndiotactic).

The conversion increases for a critical surfactant concentration (1.5% w/v), using redox initiation, and favouring syndiotactic configuration. Also an optimum surfactant/monomer ratio is necessary for maximum conversion.

The latex particles of PMMA obtained using redox initiation have a larger size and rougher external surface than when the process is carried out without redox initiation.

The cellular adhesion behavior was favored in PMMA samples obtained without redox initiation.

Acknowledgments The authors want to thank the IVIC, FONACIT and CDCH (UCV) for their financial support.

References

1. Sarac AS (1999) Redox polymerization. Prog Polym Sci 24:1149–1204
2. Green B, Saunders F (1970) In situ polymerization surface-active agents on latex particles: III. The electrolyte stability of styrene/butadiene latexes. J Colloid Interface Sci 33:393–404
3. Price G, Norris D, West P (1992) Polymerization of methyl methacrylate initiated by ultrasound. Macromolecules 25:6447–6454
4. Liao Y, Wang Q, Xia H, Xu X, Baxter S, Slone R, Wu S, Swift G, Westmoreland D (2001) Ultrasonically initiated emulsion polymerization of methyl methacrylate. J Polym Sci 39:3356–3364
5. Parra C, Albano C, González G (2008) Effect of surfactant type on the synthesis of PMMA using redox initiation and high frequency ultrasound. Polym Eng Sci 48:2066–2073
6. Anagnostou F, Debet A, Pavon-Djavid G, Goudaby Z, Hélary G, Migonney V (2006) Osteoblast functions on functionalized PMMA-based polymers exhibiting *Staphylococcus aereus* adhesion inhibition. Biomaterials 27:3912–3919
7. Pande M, Spalton D, Marshall J (1996) Continuous curvilinear capsutorhexis and intraocular lens biocompatibility. J Cataract Refract Surg 22:89–97
8. Collis DK (1991) Long-term (twelve to eighteen-year) follow-up of cemented total hip replacements in patients who were less than fifty years old. A follow-up note. J Bone Joint Surg 73:593–597
9. Kusy RP (1978) Characterization of self-curing acrylic bone cements. J Biomed Mater Res 12:271–305
10. Billingham NC (1977) Molar mass measurements in polymer science. Wiley, New York
11. Parra C, Gonzalez G, Albano C (2005) Synthesis and characterization of Poly (methyl methacrylate) obtained by ultrasonic irradiation. e-polymers 025
12. He Y, Cao Y, Fan Y (2005) Using anionic polymerizable surfactants in ultrasonically irradiated emulsion polymerization to prepare polymer nanoparticles. J Appl Polym Sci 43:2617–2622
13. Stevens MP (1990) Polymer chemistry: an introduction. Oxford University Press, New York
14. Hatada K, Kitayama T, Ute K (1988) Stereoregular polymerization of α-substituted acrylates. Prog Polym Sci 13:189–276
15. Jiang W, Yang W, Zeng X, Fu S (2004) Structure and properties of poly (methyl methacrylate) particles prepared by a modified microemulsion polymerization. J Polym Sci A 42:733–741
16. Yeong S, Hyeong T, Chung I (2003) Polymer/silicate nanocomposites synthesized with potassium persulfate at room temperature: polymerization mechanism, characterization and mechanical properties of the nanocompostes. Polymer 44:8147–8154
17. Isobe Y, Nakano T, Okamoto Y (2001) Stereocontrol during the free-radicals polymerization of methacrylates with Lewis acid. J Polym Sci A 39:1463–1471
18. Price GJ, West PJ, Smith PF (1994) Control of polymer structure using ultrasound. Ultras Sonochem 1:S51–S57
19. Straka J, Schmidt P, Dybal J, Schneider B, Spevacek J (1995) Blends of poly (ethylene oxide) poly (methyl methacrylate). An i.r. and n.m.r. study. Polymer 36:1147–1155

20. Zhang Z, Zhu X, Zhu J, Cheng Z (2006) Thermal polymerization of methyl (meth) acrylate via reversible addition fragmentation chain transfer (RAFT) process. Polymer 47:6970–6977
21. Allen NS, Edge M, Jasso AR, Corrales T, Tellez-Rosas M (1997) Control of stereoregularity in poly (methyl methacrylate) by photoinitiation polymerization. J Photochem Photobiol A 102:253–258
22. Pilcher SC, Ford WT (1998) Structures and properties of poly (methyl methacrylate). Latex formed in microemulsions. Macromolecules 31:3454–3460
23. Kirsch S, Pfau A, Stubbs J, Sundberg D (2001) Control of particle morphology and film structures of carboxilated poly (n butylacrylate) poly (methyl methacrylate) composite latex particles. Colloids Surf A 183:725–737
24. Smith WV, Ewart RH (1948) Kinetics of emulsion polymerization. J Chem Phys 16:592–599
25. Joe Chou H, Stoffer J (1999) Ultrasonically initiated free radical-catalyzed emulsion polymerization of methyl methacrylate (i). J Appl Polym Sci 72:797–825
26. Ohsawa K, Neo M, Matsuoka H, Akiyama H, Ito H, Nakamura T (2001) Tissue responses around polymethylmethacrylate particles implanted into bone: analysis of expression of bone matrix protein mRNAs by in situ hybridization. J Biomed Mater Res 54:501–508
27. Moreau MF, Chappard D, Lesourd M, Monthéard JP, Baslé MF (1998) Free radicals and side products released during methylmethacrylate polymerization are cytotoxic of osteoblastic cell. J Biomed Mater Res 40:124–131
28. Pestaner JP, Ishak KG, Mullick FG, Centeno JA (1999) Ferrous sulphate toxicity: a review of autopsy finding. Biol Trace Elem Res 69(3):191–198