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Structure and properties of poly(benzyl acrylate) synthesized under microwave energy

Tamara G. Oberti[a,b], M. Mercedes Schiavoni[b], M. Susana Cortizo[a,*]

[a]*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata-CONICET Casilla de Correo 16, Sucursal 4, 1900 La Plata, Argentina*
[b]*Laboratorio de Estudio de Compuestos Orgánicos (LADECOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina*

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Abstract

Benzyl acrylate was polymerized under microwave irradiation using radical initiation (benzoyl peroxide, BP). The effect of the concentration of BP and power irradiation on the conversion, average molecular weights and the polydispersity index (M_w/M_n) were investigated. The ^{1}H NMR and ^{13}C NMR spectra analysis showed tendency to syndiotacticity and branched polymers were obtained at high conversion of reactions. A significant enhancement of the rates of polymerization and similar thermodynamic behavior, as compared with those obtained under thermal conditions was found.

Keywords: Benzyl acrylate; Radical polymerization; Microwave; Chain transfer; Viscosity

1. Introduction

Acrylic polymers are considered as one of the most versatile materials because their chemical, physical and mechanical properties, which can be modulated by an appropriate selection of its ester constituent and comonomer (Zhu et al., 2004; Guo et al., 1994; Angelovici and Kohn, 1991). These kinds of polymers have properties that make them suitable for a variety of industrial applications, among the most interesting are those related to varnishes, adhesives and biomaterials (Gower and Shanks, 2006; Soundararajan et al., 1987; Langer and Peppas, 2003).

The application of microwave energy to organic synthesis is known for a long time (Strauss and Trainor, 1995; Lidström et al., 2001) and in the last decade was successfully applied to radical and condensation polymerization reactions (Bogdal et al., 2003; Wiesbrock et al., 2004). It has been demonstrated that it is possible to obtain polymers with good yields at short times of reaction under irradiation with microwaves (Jacob et al., 1995a; Cortizo, 2007). Although many monomers have been polymerized in these conditions, the effect of microwave irradiation on the rate of chemical reactions is still under debate and many investigators had mentioned the existence of a so-called non-thermal or specific microwave effect, responsible of the acceleration of the reaction rate and for which some theories have been proposed (Perreux and Loupy, 2001; Jacob et al., 1995b).

Systematic studies of acrylic esters radical polymerization using microwave energy are scarce. Methyl acrylate and methacrylate were investigated, showing an important acceleration of the reaction rate under microwave conditions in comparison to thermal conditions (Jacob et al., 1995a, 1997). Poly(benzyl acrylate) has particular interest due to its very high thermal and photochemical stability (Cameron and Kane, 1968; Itoh et al., 2001).

The aim of the present study was to analyze the effect of the different experimental variables (power, time and initiator concentration) on the structure, kinetics of polymerization, average molecular weight, molecular weight distribution and solution properties of poly(benzyl acrylate) obtained under microwave conditions.

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*Corresponding author. Fax: +54 221 425 4642.
E-mail address: gcortizo@inifta.unlp.edu.ar (M.S. Cortizo).

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2. Experimental part

2.1. Materials and instruments

Methyl acrylate and benzyl alcohol (Merck, PA), were used as received. Benzoyl peroxide (BP) was recrystallized from methanol. Other solvents were purchased from Merck and Sintorgan (PA).

A Shimadzu IR-435 spectrometer was used to record the infrared spectra of the monomer as a capillary film onto a sodium chloride (NaCl) window.

^{1}H NMR and ^{13}C NMR spectra of monomer and polymers were recorded on a Variam-200 MHz (Mercury 200) at 35 °C in $CDCl_3$. Two-dimensional gradient heteronuclear single quantum coherence (gHSQC) spectrum was obtained.

The molecular weight distribution and the average molecular weights were determined by size exclusion chromatography (SEC) with an LKB-2249 instrument at 25 °C and differential refractive index detector (Waters). A series of four μ-Styragel columns, ranging in pore size 10^5, 10^4, 10^3, 100 Å was used with tetrahydrofuran as eluent. The sample concentration was 4–5 mg ml^{-1} and the flow rate was 0.5 ml min^{-1}. The calibration was done with polystyrene standards supplied by Polymer Laboratories and Polysciences, Inc.

A domestic oven (DiplomaticGR-19R), which produced microwaves at a frequency of 2450 MHz and a maximal power of 800 W, was used.

2.2. Monomers synthesis

Benzylacrylate was synthesized by transesterification method starting from methyl acrylate and benzyl alcohol together with a catalytic amount of *p*-toluensulfonic acid (Rehberg, 1946). The product was purified by distillation under vacuum and the yield of the reaction was 70% ($n_D = 1.5168^{20}$). Monomer characterization and identification was carried out by infrared (IR) and ^{13}C NMR spectra. IR (ν cm^{-1}): 1720 (C=O), 1635 ($H_2C = CHR$), 1585 (C=C aromatic), 1260 and 1160 (acyl-O–R), 740 (C–H aromatic); ^{13}C NMR, δ (ppm): 174.43 ($\underline{C}$=O), 136.07 (Ar, α-methylene), 128.73, 128.53, 128.38 (Ar), 129.30 ($\underline{C}$H=), 68.77 (COO$\underline{C}H_2$), 130.05 ($\underline{C}H_2$ =).

2.3. Microwave polymerization

The general procedure to carry out the polymerization under microwave conditions has been described (Cortizo, 2007). Briefly, the reaction was carried out in bulk in a conical Pyrex flask of 25 cm^3 closed by a septum. One gram of monomer was added to a previously weighted amount of initiator (BP). The initiator concentration was changed between 20 and 40 mM. The flask was purged with N_2 during 30 min and then was placed in the center of turntable of the oven and irradiated with microwaves at different power (136, 256, 352 W) and times (between 1 and 6 min). After reaching room temperature, the polymer was isolated and purified by toluene solubilization and precipitation on methanol, dried at constant weight and the conversion determined gravimetrically. The polymer was identified by nuclear magnetic resonance spectroscopy. The weight average molecular weight and polydispersity index were determined by SEC. The measurement of the sample temperature was carried out with an accurate mercury thermometer on benzyl acetate and registered in less than 30 s at different conditions of power and time (Hogan and Mori, 1990).

2.4. Viscometry

The determination of the intrinsic viscosity ($[\eta]$) was carried out by dissolving the polymer in butanone under mechanical agitation during 24 h at room temperature. After that, dilutions were prepared from a stock solution such that $0.3 < \eta_{sp} < 0.8$ (η_{sp} being the specific viscosity). Dilutions viscosities were measured with Ostwald capillary viscometer ($t_0 > 120$ s) at 35 °C. The viscometric average molecular weight (M_v) was estimated according to the following Mark-Houwink equation (Patra and Mangaraj, 1968):

$$[\eta]\,(\text{ml g}^{-1}) = 0.58 \times 10^{-3} M_v^{0.883} \quad (1)$$

Besides, measurements were carried out in nitromethane at 46.6 °C as a theta solvent (Mathakiya et al., 2003). In that case the stock solution was maintained at 50 °C until total dissolution and dilutions were prepared in a similar way as described above.

3. Results and discussion

3.1. Structural analysis

Fig. 1(a) shows the ^{1}H NMR spectrum of the poly(benzyl acrylate) and its structure. The corresponding H assignations are as following (δ, ppm): 7.336; 7.259; 7.246 ($\underline{H}$–Ar), 5.090; 5.032; 4.971 ($\underline{H}_2$C–Ar), 2.379 (>C$\underline{H}$–C=O), 1.927; 1.640; 1.481 (–C$\underline{H}_2$–). The spectrum shows the splitting due to the signals of hydrogen –CH_2– of the main chain resonances between 1.927 and 1.481 ppm. These signals correspond to the different configurational possibility of the polymers. The analysis, by means of the signals integrations, allowed us to obtain the following percent of tacticity (Porter et al., 1992): 68% of syndiotatic and 32% of isotactic configuration of the polymer. This result seems to indicate certain stereoespecificity of the polymerization reaction under microwave conditions, which was not observed under thermal conditions.

From the ^{13}C NMR spectrum (Fig. 1(b)), the following C assignations are obtained: 174.56–174.27 ($\underline{C}$=O), 136.07 ($\underline{C}$Ar, α-CH_2), 128.73–127.83 (Ar), 66.64 (O–$\underline{C}H_2$–Ar), 41.65 (>$\underline{C}$H–CO), 35.41 (–$\underline{C}H_2$–), confirming the corresponding structure. Others relevant signals that appears in this spectrum will be explained below.

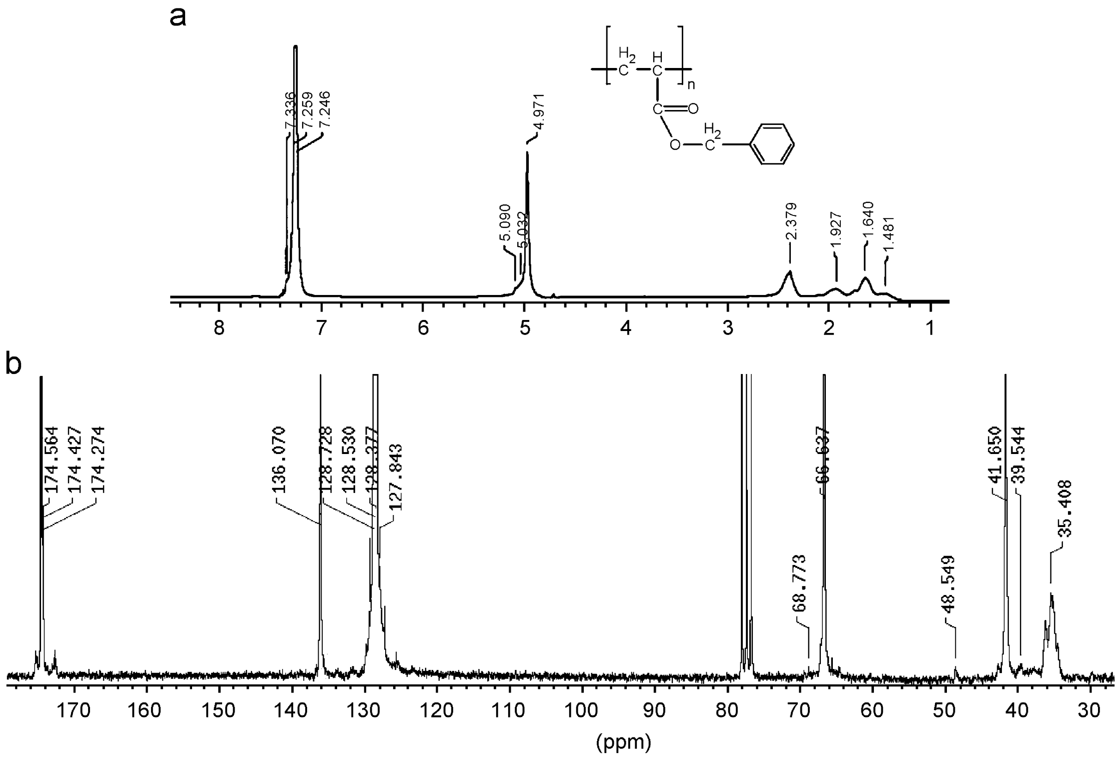


Fig. 1. NMR spectra of poly(benzyl acrylate) obtained under microwave conditions: (a) ^{1}H and (b) ^{13}C.

3.2. *Effect of the irradiation power*

During the course of our studies of radical polymerization of diisopropyl fumarate under microwave irradiation (Cortizo, 2007), we evaluated the decomposition kinetics of benzoyl peroxide and 2,2′-azobisisobutyronitrile (AIBN) according the Ng methodology (Ng and Chee, 1982). In that study we found that BP was more efficient that AIBN for to initiate the radical reaction. In the present case, working with benzyl acrylate, we verified the same behavior of both initiators (data not shown) and so we decided continues the study with BP.

Fig. 2 shows the conversion profiles by using an initiator concentration of 40 mM, under three different power irradiations (136, 256 and 352 W). The time profiles at the three powers exhibited different behavior: at 136 and 256 W at 1 min the conversion is below 5% and then increases fast. At 136 W of power irradiation a sharp increase of the rate of the reaction was observed, indicating a "gel effect" on the kinetic of polymerization. At 352 W of power irradiation and at 1 min of reaction, the conversion is 45% and tends to a constant value near to 60%. The temperatures profiles in Fig. 3 show little differences at the early period: 5 °C below 60 °C for the two first powers and 5 °C above to 60 °C for 352 W.

We attribute the different observed behaviors at short time of reaction at no-thermal microwave effect, which has been evidenced and explained for others system (Perreux and Loupy, 2001; Loupy et al., 2004). Specific microwave effects can be expected when the polarity is increased during a reaction from the ground state (GS) towards the transition state (TS). If the stabilization of TS is more effective than that of GS, this results in an enhancement of reactivity by a decrease in the activation energy due to interactions dipole–dipole with the electric field. According to the mechanism of radical initiation, the rate-determining

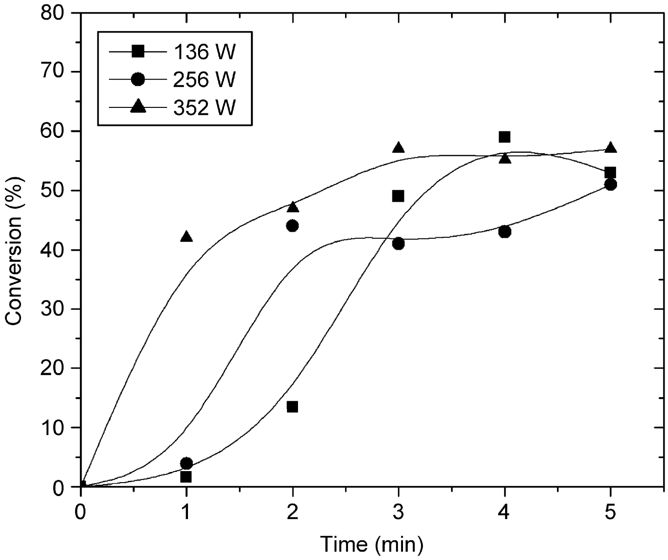


Fig. 2. Conversion versus time plots at three different power irradiation. [BP] = 40 mM.

step is the break of peroxide bond (O–O) of benzoyl peroxide which produces two radical (Scheme 1). During this reaction the TS is more polar than the GS, because to partial localization of radical center on the O atom. So, the dipole–dipole interactions being more development in the TS, which will be more stabilized than GS, decreasing the activation energy. This effect will be more pronounced at highest power irradiation.

On the other hand, the thermal radical polymerization of benzyl acrylate had been study by Patra and Mangaraj (1968). In that study, 5.8% of the conversion after 5 min of reaction time under similar conditions (40 mM, 65 °C) was attained. From these results, an important acceleration of the reaction rate under microwave conditions for the studied monomer is evident, considering that at 352 W at 1 min we obtained 45% of conversion.

Fig. 4 presents the time effect on the weight average molecular weight at different power irradiation. At 136 and 256 W, M_w decreases fast from the beginning of polymerization and then tends to reach a constant value. Two possible explanations have been considered. One of them, the monomer polymerizes and then degrades during the course of reaction, attaining an equilibrium average molecular weight. Similar behavior has been found in methyl methacrylate and some dialkyl fumarate polymerized under microwave conditions (Madras and Karmore, 2001; Cortizo et al., 2007). The other possibility, considering the slow increase of the temperature at early period, is the formation of long chains up to 1 min of reaction and short chains when the temperature overcome 60 °C, which is the optimum decomposition temperature for BP. In order to clarify this aspect we irradiated a sample of PBzA (M_w 134,200) with BP (40 mM respect to polymer) at 256 W during 5 min and then their M_w was analyzed. A decrease of 5% on the M_w and a three-fold increase on the polydispersity index was found by SEC, indicating that the degradation at long time is small. This result suggests that, the main cause that rules the M_w is the thermal effect, due to the increase of temperature during the course of the polymerization.

At 352 W the M_w does not change with the reaction time, which is typical of a radical polymerization. The reactions attained an equilibrium molecular weight distribution with a polydispersity index between 5.2 and 5.6, suggesting that the disproportionation or chain transfer mechanisms are the predominant termination modes.

Fig. 5(a–c) shows the SEC chromatograms of the polymer obtained at different power irradiation in function of time. At 136 W, a shift of the maximum of peak to higher elution volume in function of time was observed, indicating a decrease of average molecular weight. Besides, the chromatographic profile became bimodal, as a result of a new second macromolecules population. The weight average molecular weight M_w and the polydispersity index (M_w/M_n) are listed in Table 1. M_w/M_n was near to two at conversion lower than 20%, suggesting that chain transfer

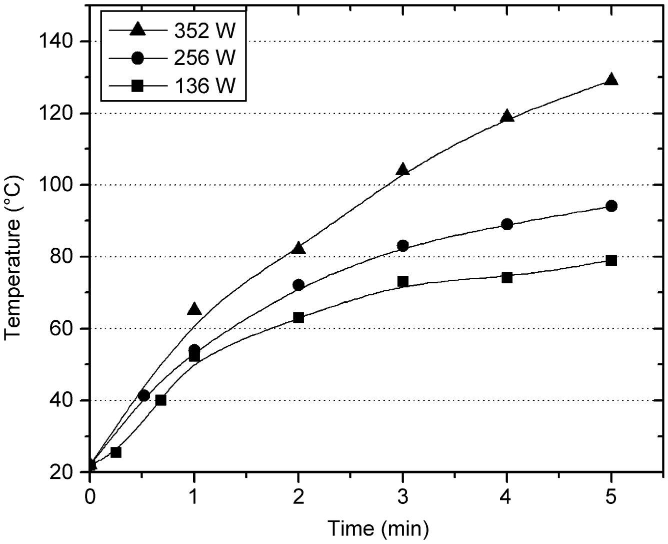


Fig. 3. Temperature profiles at different power irradiation.

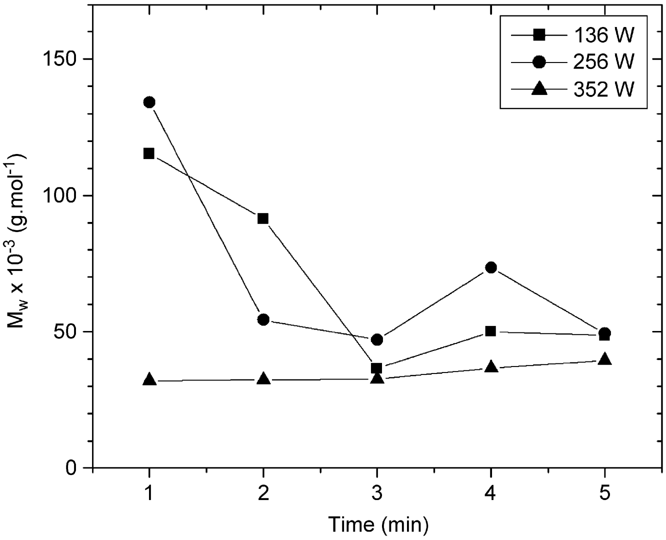
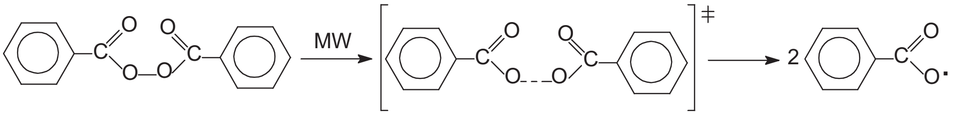


Fig. 4. Weight average molecular weight (M_w) as a function of the time at three different power irradiation. [BP] = 40 mM.



Scheme 1. Radical decomposition of benzoyl peroxide, indicating the possible transition state.

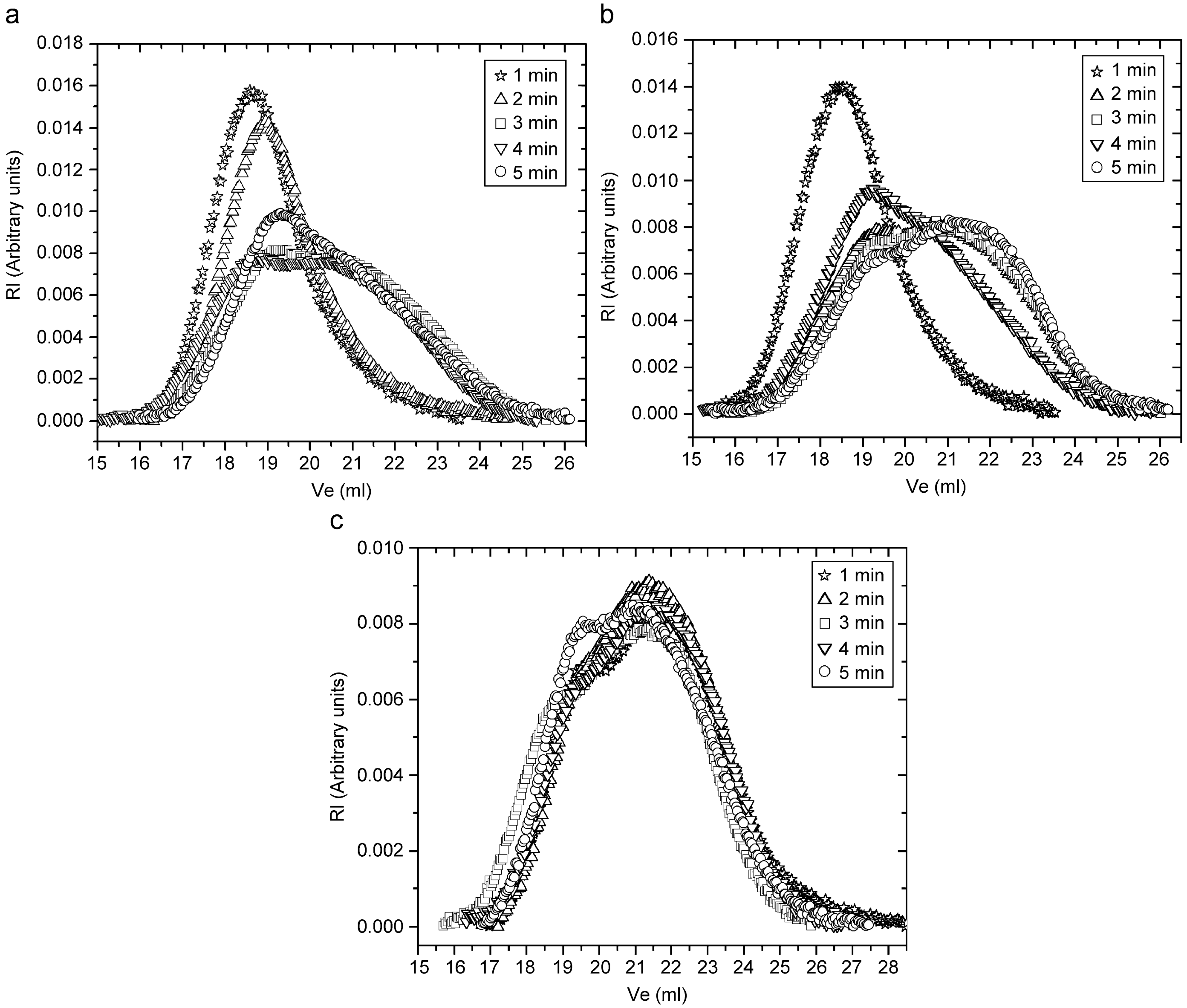


Fig. 5. Chromatographic profile of poly(benzyl acrylate) in function of time: (a) 136 W, (b) 256 W, (c) 352 W. [BP] = 40 mM.

reactions are more important at higher conversions. This kind of behavior has been observed in free radical polymerization of other alkyl acrylates and, in fact, is the main reason of the difficulty found in the kinetics analysis of those systems (Castignolles et al., 2006).

The SEC chromatograms of the polymer obtained at higher power irradiation shows similar behavior to those obtained at 136 W, as can be seen in Fig. 5(b and c). At 256 W bimodal molecular weight distributions appears after 2 min of polymerization, when the conversion reaches 44%. On the other hand, at 352 W, all chromatographic profiles were bimodal due to the conversion was higher than 20% at all the analyzed times. These results suggest the importance of the chain transfer reaction at higher conversions. In order to verify this hypothesis we investigated the polymer microstructure by ^{13}C NMR. Fig. 1(b) exhibits some signals of quaternary and tertiary branch adjacent carbons, and CH of branch benzyl group at 48.55, 39.54 and 68.77, respectively. Scheme 2 shows the corresponding structure resulting of the chain transfer reaction. A posterior confirmation of chain transfer reaction to benzyl group was obtained by the two-dimensional gHSQC spectrum (Fig. 6). This spectrum shows two different signals assigned to the benzyl C of regular structure and branched (66.64 and 68.77, respectively) associated to the corresponding hydrogen (5.09 and 4.97, respectively). Similar structures derived of the chain transfer reaction during the free radical polymerization had been demonstrated by other authors (Ahmad et al., 1998).

Table 1
Conversions and size exclusion chromatographic data of PBzA at [BP] = 40 mM

Power (W)	t (min)	% Conversion	M_w (g mol^{-1})	M_w/M_n
136	1	1.6	115,300	2.2
136	2	13.4	91370	2.6
136	3	49.0	36,500	5.8
136	4	59.0	49,950	5.8
136	5	53.0	48,500	5.6
256	1	3.9	134,200	2.3
256	2	44.0	54,300	5.1
256	3	41.0	46,950	5.9
256	4	43.0	73,450	4.7
256	5	51.0	49,300	5.3
352	1	42.0	31,950	2.5
352	2	47.0	32,300	4.2
352	3	57.0	32,500	6.0
352	4	55.5	36,600	5.1
352	5	57.0	39,500	5.2

3.3. *Effect of the initiator concentration*

Table 2 presents the results of the change of initiator concentration on the conversion, the weight average molecular weight M_w and M_w/M_n values under two different power irradiation conditions and constant energy. The energy (E) was evaluated as the product of the power and time of irradiation. It is possible to see that at 136 W an increase of the initiator concentration produces an increase of conversion, but at 352 W a similar conversion was attained.

The effect of the initiator concentration on the M_w exhibited a decrease when the [BP] was increased, according to the expected kinetic behavior for a free radical polymerization.

Under all conditions the M_w/M_n values were higher than 2, suggesting that chain transfer mechanism is the dominant one.

3.4. *Solution properties*

In order to evaluate the solution behavior of the PBzA, viscometry was carried out in two different solvents: butanone and nitromethane as a good and theta solvent at 35 and 46.6 °C, respectively. Fig. 7 shows the viscosity measurement for PBzA (obtained at 136 W, 5 min). Within the concentration range of the viscometric determination, $2 < c < 30\,\mathrm{mg\,ml^{-1}}$, plots are lineal. The intrinsic viscosity $[\eta]$ was conventionally obtained from double extrapolation of the Huggins and Kramer equations:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \tag{2}$$

$$\frac{\ln \eta_r}{c} = [\eta] + k_K[\eta]^2 c \tag{3}$$

where η_r is the relative viscosity k_H and k_K are the Huggins and Kramer coefficients, respectively. $[\eta]$ was estimated as the average of the two ordinate intercepts from the two extrapolations. A value of $(15.6 \pm 0.3)\,\mathrm{ml\,g^{-1}}$ for $[\eta]$ and of 0.30 and 0.19 for k_H and k_K constant, respectively, were obtained in butanone. The found values for the k_H and k_K constants are similar to those of other polyacrylates in thermodynamically good solvents. The viscosity average molecular weight calculated from the $[\eta]$ was of $1.025 \times 10^5\,\mathrm{g\,mol^{-1}}$, while a 48,500 value was found by SEC. This difference may be attributed to two possible effects. On the one hand, the hydrodynamic volume of a branched polymer is smaller than a linear one (Bondanecký and Kovár, 1982a), and its elution volume is higher, resulting in a lower weight average molecular weight. The M_w obtained by SEC was based in a calibration curve by means of lineal polystyrene standard as references, so it is a possible explanation for the different M_w values found between both methodologies.

On the other hand, it is known that polydisperse polymer exhibits a higher intrinsic viscosity than a monodisperse one (Bondanecký and Kovár, 1982b), as in the present case, where the M_w/M_n values are higher than 4. Both effects contribute to increase the viscosity average molecular weight estimated by viscometry measurement.

From the viscometric measurements in nitromethane at 46.6 °C, a value of intrinsic viscosity in theta solvent ($[\eta]_\theta$) of $(10.2 \pm 0.5)\,\mathrm{ml\,g^{-1}}$ and of 1.04 and 0.14 for k_H and k_K constant, respectively, were obtained. The intrinsic viscosity expansion factor is determined by

$$\alpha_\eta^3 = \frac{[\eta]}{[\eta]_\theta}. \tag{4}$$

The value obtained for PBzA is 1.53, while other researchers (Mathakiya et al., 2003), working in dioxane at 30 °C found a value of 1.49 for this parameter. This small difference indicated that the chain of PBzA is more expanded in butanone than in dioxane.

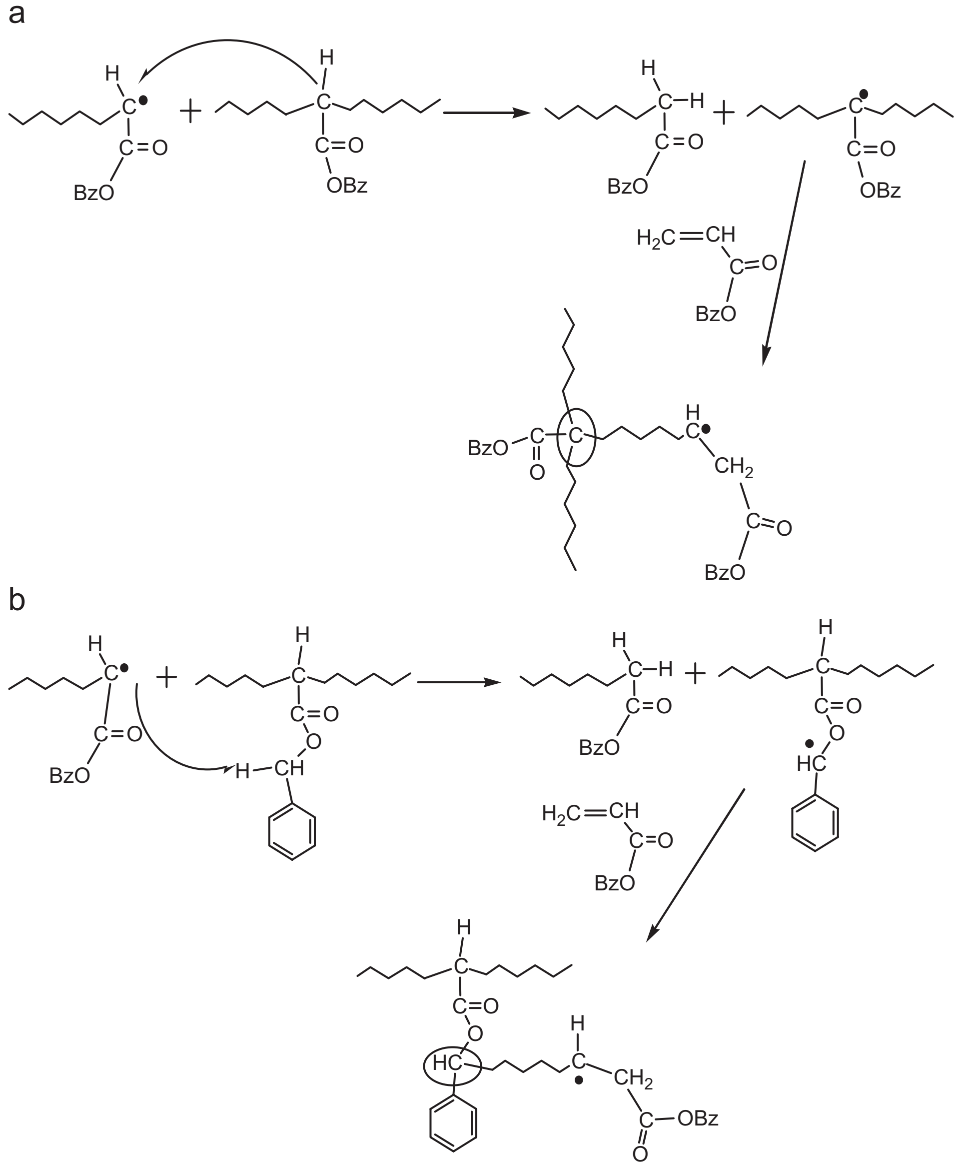
4. Conclusions

The microwave irradiation methodology has been successfully applied to free radical polymerization of benzyl acrylate using benzoyl peroxide as an initiating system showing an enhancement of the rate of the reaction.

The NMR spectrum analysis indicates that atactic polymers were obtained although a small tendency to syndiotacticity was observed, indicating certain stereospecificity of the polymerization mechanism under microwave conditions.

Branched polymers are obtained at higher reaction conversions through a chain transfer mechanism. This result is in accord with the high polydispersity index obtained under those conditions.

It is possible to choose the weight average molecular weight by the appropriate selection of irradiation power of microwave and the initiator concentration, in order to



Scheme 2. Structures of the PBzA obtained by intermolecular chain transfer reactions: (a) to main chain polymer and (b) to benzyl group.

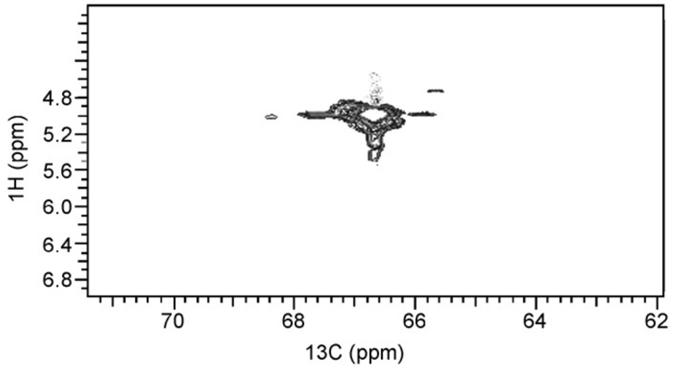


Fig. 6. Two-dimensional gHSQC spectrum corresponding to benzyl group chemical shift.

Table 2
Effect of the initiator concentration on the conversion, M_w and M_w/M_n at two different power irradiation conditions

P (W)	t (min)	E (kJ)	[BP] (mM)	% C	M_w (g mol^{-1})	M_w/M_n
136	5	40.8	20	44.0	79,700	5.8
136	5	40.8	40	53.0	48,500	5.6
352	2	42.2	20	52.0	40,810	4.1
352	2	42.2	40	47.0	32,300	4.2

obtain samples with the predetermined macromolecular characteristic.

The polymer solution behavior in good or theta solvent is similar to the one obtained under thermal conditions,

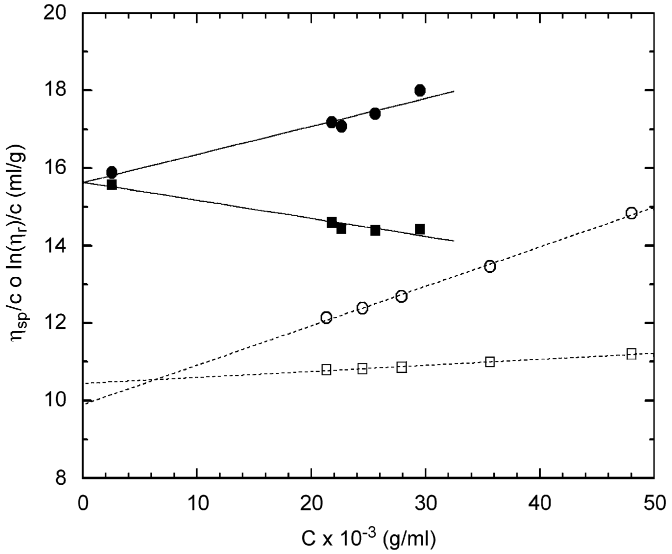


Fig. 7. Viscosity of PBzA as a function of concentration—butanone at 35 °C: (●) η_{sp}/c, (■) ln(η_r)/c; nitromethane at 46.6 °C: (○) η_{sp}/c, (□) ln(η_r)/c. Polymerization conditions: 136 W, 5 min, [BP] = 40 mM.

making evident that microwave polymerization do not modify the polymer thermodynamic properties.

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