Polymerization of Diisopropyl Fumarate Under Microwave Irradiation

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ABSTRACT: Diisopropyl fumarate (DiPF), a representative monomer of dialkyl fumarates, was polymerized by microwave irradiation at three different powers (140, 210, and 280 W), using a domestic microwave oven. The nature and concentration of initiators [2,2′-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BP)], power and energy of microwave irradiation on the conversion, weight average molecular weight (M_w), and polydispersity index (M_w/M_n) were analyzed. The results indicate that the microwave conditions have a significant non-thermal effect in enhancing the polymerization rate of DiPF. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3785–3791, 2007

Key words: diisopropyl fumarate; radical polymerization; microwave; radiation

INTRODUCTION

Fumaric esters are representative members of 1,2-disubstituted ethylenic monomers that polymerize by a free radical mechanism.[1–3] Systematic and complete studies demonstrate that the nature of the alkyl ester group is reliable on its reactivity and on the high molecular weight polymers obtained.[4–5] The main characteristic of these monomers is their low polymerization rates, which are attributed to the strong steric hindrance of the propagation step.[6,7]

Because of the peculiar polymer characteristics (crystallinity and thermal stability),[2,8] together with the easiness of monomer synthesis (starting from maleic anhydride and the corresponding alcohols), it seems important to look for an alternative methodology to obtain the homopolymers at comparable velocities to those of other monomers.

The application of microwave energy in organic synthesis has been known for a long time and has been used in a great number of typical reactions of the organic chemistry.[9–11] The main advantages of this methodology with respect to the conventional methods are the decrease in the reaction times, the improvement of the yields, the reduction in the formation of secondary products, and, in some cases, selectivity in the stereochemistry of the obtained products. On the other hand, from the economic and the environmental security points of view, working at shorter reaction times and without a solvent constitute clear advantages.

The use of this methodology in the synthesis of polymers is more recent.[12,13] It has been demonstrated that it is possible to obtain polymers with good yields in shorter reaction times under irradiation with microwaves.[14] Although many monomers have been polymerized in these conditions, the effect of microwave irradiation on the mechanism and the rate of chemical reactions is still under debate and many investigators have mentioned the existence of a so-called nonthermal or specific microwave effect, responsible for the acceleration of the reaction rate and for which some theories have been proposed.[15]

The radical synthesis and the properties in solution of homo and copolymers of diisopropyl fumarate were studied in our laboratory.[16,17] Since the microwave polymerization appears to be promising by increasing the reaction rate of the monomers difficult of polymerize, we describe the polymerization of diisopropyl fumarate using this methodology.

EXPERIMENTAL

Materials and instruments

Fumaric acid was gifted by Maleic S.A. (Argentina) and purified by recrystallization of 1N HCl. Isopropanol (Merck, PA), was used as received. 2,2′-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BP)

were recrystallized from methanol. Other solvents were purchased from Merck and Sintogan (PA).

The control of purity and identification of the monomer were performed using infrared (IR) and gas chromatography–mass spectrometry (GC–MS).

A Shimadzu IR-435 spectrometer was used to record the IR spectra of the monomer as a capillary film.

GC–MS was performed on a HP 5890 Series II Plus Chromatograph couplet to an HP 5972A mass selective detector under the following conditions: column HP5-MS, 30 m × 0.25 mm × 5 μm; temperature set points: injector 200°C, oven 80°C, 10°C min^{-1}, 200°C, interface 300°C; ion source 185°C. The pressure in the mass spectrometer, 10^{-5} Torr, precludes ion-molecules reactions (electron energy 70 eV).

^{1}H and ^{13}C NMR spectra of polymer were obtained at 45°C in CDCl$_3$ by using a Bruker Avance DPX400 spectrometer (400 MHz for hydrogen and 100 MHz for carbon).

The molecular weight distribution and the average molecular weights were determined by size exclusion chromatography (SEC), using a LKB-2249 instrument at 25°C. A series of four μ-Styragel columns, ranging in pore size 10^5, 10^4, 10^3, 100 Å, was used with chloroform as an eluent. The sample concentration was 4–5 mg mL^{-1} and the flow rate was 0.5 mL min^{-1}. The polymer was detected by the carbonylic absorption of the ester group (5.75 μm), using an infrared detector (Miram 1A infrared Analyzer) and the calibration was done with poly(methyl methacrylate) (PMMA) standards supplied by Polymer Laboratories and Polysciences.

A domestic oven (ZENITH, ZVP-2819), which produced microwaves at a frequency of 2450 MHz and a maximal power of 700 W, was used.

Synthesis of the monomer

Diisopropyl fumarate (DiPF) was synthesized according method described elsewhere.[18] Fumaric acid and isopropanol were added to benzene in the ratio 1:2.65 and the mixture was refluxed for 22 h. Monomer characterization and identification was carried out by IR and MS. Yield 76%.

IR (ν cm^{-1}): 1720 (C=O), 1640 and 980 (RHC=CHR, trans), 1250 and 1100 (acyl—O—R). MS: m/z

= 158 (M$^+$—C$_3$H$_6$), 141 (M$^+$—OisPr), 113 (M$^+$—OisPr, —CO).

Microwave polymerization

Polymerization was carried out in bulk in a conical 25-cm^3 Pyrex flask closed by a septum. About 1 mL of monomer was added to a previously weighted amount of initiator (AIBN or BP) under nitrogen gas, using a hypodermic syringe. The initiator concentration was changed between 15 and 60 mM. The flask was purged with N$_2$ during 20 min, because an inert atmosphere is essential to obtain reproducible results. Then the flask with the sample was placed in the center of the turntable of the oven and irradiated with different powers (140, 210, 280 W) and times (between 2 and 20 min). After the treatment, the mixture is allowed to cool to room temperature, and then the polymer was isolated and purified by solubilization–precipitation (toluene–methanol) and identified by ^{1}H and ^{13}C NMR spectroscopy. The weight average molecular weight and polydispersity were determined using SEC. The measurement of the sample temperature was carried out with an accurate mercury thermometer on diethyl succinate and recorded in < 30 s at different conditions of power and time.[19]

RESULTS AND DISCUSSION

Effect of nature of initiator

The radical polymerization under microwave irradiation of DiPF produces an homopolymer consisting of a poly(isopropoxycarbonylmethylenic) chain as shown in Scheme 1. Figure 1(a,b) show the ^{1}H and ^{13}C NMR spectra of this polymer together with the corresponding assignation. In the first, the three different integral signal exhibited a 1 : 1 : 6 ratio, consistent with the expected number of hydrogen. The ^{13}C NMR spectra shows almost two signal for the >C=O and the —CH— of the main chain resonances at 170 ppm and 46 ppm respectively. This signal corresponds to the different configurational possibility of the atactic polymer. Similar conclusions were obtained by thermal radical polymerization, confirming its identity.[18,20]
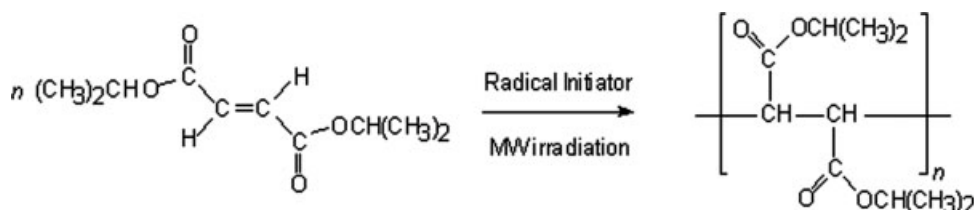
Scheme 1 Free radical polymerization of diisopropyl fumarate under microwave irradiation.
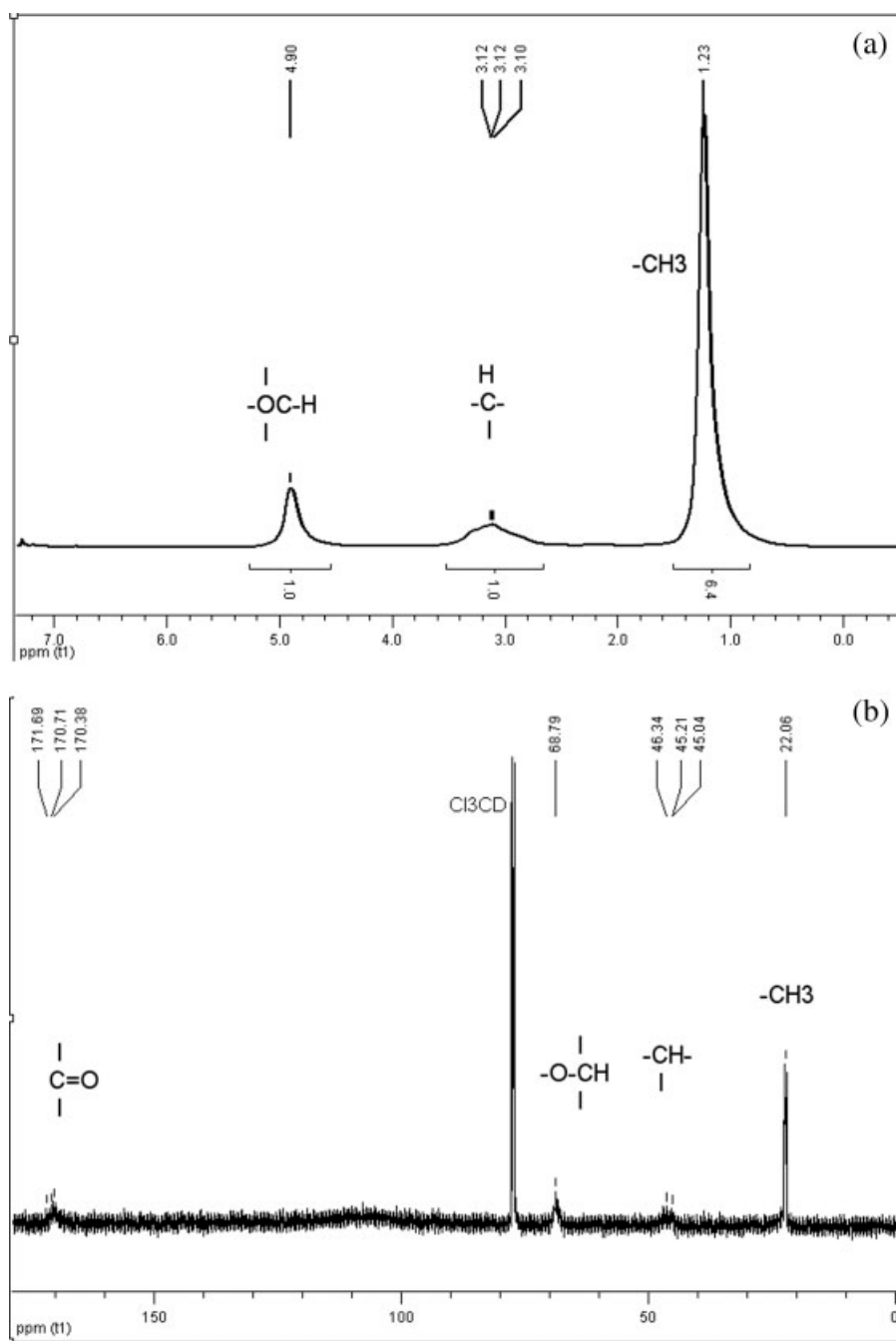
Figure 1 NMR spectra of polyDiPF obtained under microwave conditions: (a) ^{1}H and (b) ^{13}C.

Two different initiators have been tested: AIBN and BP. Their effect on the conversion, weight average molecular weight (M_w), and polydispersity index (M_w/M_n) are shown in Table I. Higher conversion is reached using BP under the indicated conditions, while the M_w were similar at each power studied.

To investigate if these results are a consequence of the different behavior of initiators under microwave conditions, the decomposition rate constants (k_d) were estimated following the methodology of Ng and Chee, based on the polymerization kinetics.[21] In that framework, the relationship between the degree of conversion (p) and the time of reaction (t) can be expressed by the following equation:

$$-\ln(1-p)/t = V_0 - V_0(k_d/4)t \tag{1}$$

where the parameter V_0 is defined by

$$V_0 = k_p(fk_d/k_t)^{1/2}[I]_0^{1/2} \tag{2}$$

TABLE I
Effect of the Kind of Initiator on the Conversion, Weight Average Molecular Weight and Molecular Weight Distribution at 10 min ([I] = 60 mM)

Run	Initiator	Power (W)	Conversion (%)	M_w ($\times 10^3$)	M_w/M_n
1	AIBN	140	4.9	32.4	1.6
2	AIBN	210	4.5	61.2	1.7
3	BP	140	38.6	36.9	1.7
4	BP	210	26.1	43.9	2.0

k_d, k_p, and k_t are the rate constants for the initiation, propagation and termination steps, respectively; f is the initiator efficiency, and $[I]_0$ is the initial concentration of the initiator.

A graphical representation of the left-hand side of the eq. (1) versus t allows to get an estimation of k_d values. Figure 2 shows the experimental data at 140 W power irradiation and 60 mM of initiator concentration expressed according the aforementioned methodology. k_d values of 1.95×10^{-3} and 2.59×10^{-3} s^{-1} were calculated, while 4.96×10^{-4} and 1.52×10^{-3} s^{-1} were reported under normal heating (benzene/100°C)[22] for BP and AIBN, respectively. These results indicate that in both conditions the kinetics with BP is a bit slower than that with AIBN, and so the observed differences can be attributed to the highest efficiency of the first initiator. It has been found that the overall polymerization reactivities of the dialkylfumarates change dramatically, depending on the structure of the primary radicals used.[23] The authors demonstrated that in the case of DiPF, the polymerization reactivity in the reaction with dimethyl 2,2'-azobis(isobutyrate) (MAIB) was 7.13 times higher than that obtained with AIBN, due 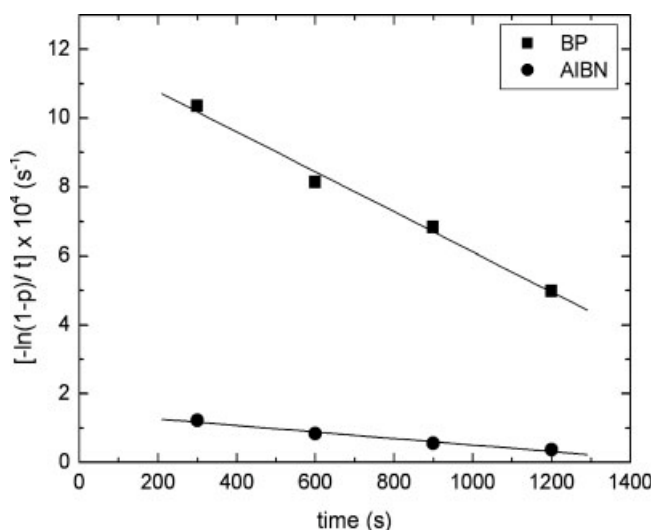to the primary radical of AIBN partially participates in primary radical termination and inactivates outside the cage; i.e., the real initiator efficiency of AIBN is lower than that of MAIB. In our case, the observed differences may be attributed to a similar effect of the primary radicals toward the monomer.

On the other hand, Table I also shows that an important acceleration of the rate reaction in microwave conditions was obtained. In fact, the thermal radical polymerization of the DiPF with BP (60 mM) at 80°C attained a conversion of 31% of polymer after 19.5 h.[18]

Comparison with other radiation polymerization methodologies is not easy because of the different experimental conditions published in the literature. The bulk polymerization of DiPF under UV radiation has not been studied, but is known that di-*tert*-butyl fumarate (a monomer with higher reactivity than DiPF) does not polymerize photochemically without being sensitized.[24] The photopolymerization of DiPF in benzene sensitized with 1,1'-azocyclohexane-1-carbonitrile at 30°C has been studied by Yamada et al.[6] After that 20 min, a conversion of 2.7% was found, while the radical thermal initiator reaction under similar conditions (concentration and solvent) produces < 0.1% at the same time of reaction.[18] Even if the UV radiation induces an acceleration of the rate of the reaction, its effect is not as noteworthy as the one observed under microwaves polymerization conditions.

Although in the microwave reactions thermal and nonthermal effects operate concurrently,[25] we attribute the observed result to the nonthermal effect, taking into account that an increase of conversion was observed at low power irradiation, while an increase of temperature was recorded at higher power, as seen in the Figure 3 at different times.
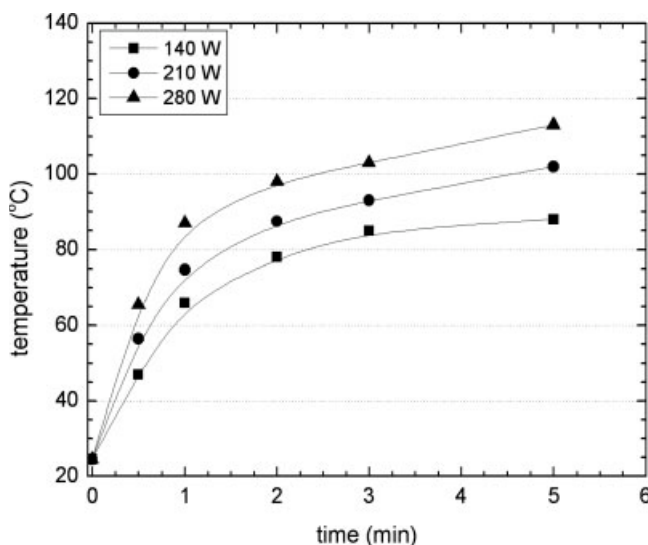

Figure 2 Plots of eq. (1) with $-\ln(1 - p)/t$ versus t with BP and AIBN initiators. 140 W power irradiation and $[I]_0$ = 60 mM.

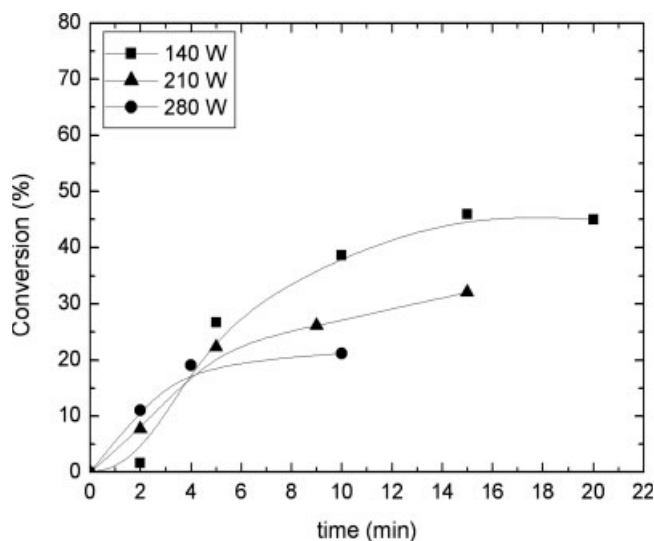**Figure 3** Temperature profiles at different power irradiation.

Figure 4 Conversion versus time plots at three different power irradiation. [BP] = 60 mM.

On account of these results BP was selected as the initiator for the following studies.

Effect of irradiation power

Figure 4 shows the conversion profiles using an initiator concentration of 60 mM, under three different power irradiations. The monomer conversion increases drastically at the beginning and then reaches a constant value at 10 min of the reaction. The interesting feature of this polymerization is that the limit conversion achieved by using a lower power (140 W) was greater than using a higher power (280 W). A similar result was observed in another system.[14,26] It
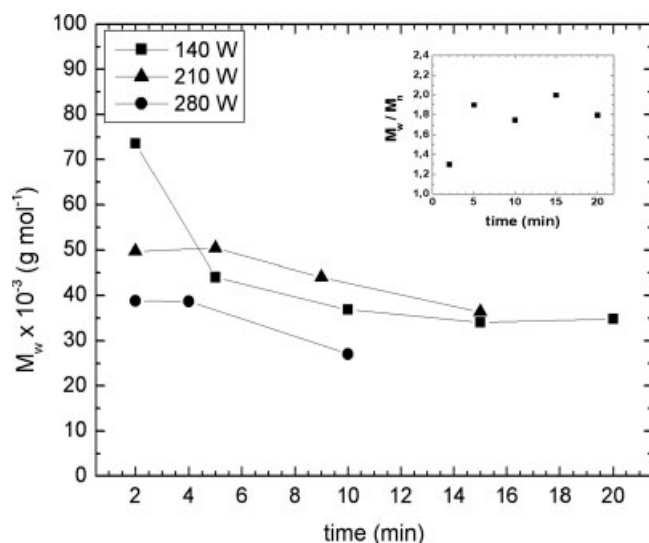
TABLE II
Effect of Initiator Concentration on the Conversion,
M_w, **and** M_w/M_n **at Three Different Power**
Irradiation Conditions

Run	Power (W)	Time (min)	[BP] (mM)	Conversion (%)	M_w ($\times 10^3$)	M_w/M_n
5	140	15	15	28.0	40.08	1.8
6	140	15	30	25.8	39.52	1.8
7	140	15	60	45.9	34.03	2.0
8	210	5	15	15.1	35.90	1.8
9	210	5	30	12.2	69.90	1.9
10	210	5	60	22.3	50.40	1.9
11	280	4	15	5	30.52	1.9
12	280	4	30	4.5	31.74	1.9
13	280	4	60	19.1	38.70	1.6

seems to be a nonthermal effect of microwave irradiation on the radical polymerization of DiPF initiated by BP. It has been proposed that the specific effects of microwaves can be important in systems where the steric effects are involved slowing the reaction rates,[25] as in the present case.

Figure 5 presents the time effect on the weight average molecular weight at different power irradiations. At 140 W, M_w decreases drastically from the beginning of polymerization and then it slowly tends to a constant value. In the other two power irradiation examined, the decrease in M_w was less sharp. This behavior seems to indicate that the monomer polymerize and then degrade during the course of reaction, attaining an equilibrium molecular weight distribution with a M_w/M_n near to 2, as seen in the insert of Figure 5 corresponding to a 140 W power irradiation. This kind of behavior has been demonstrated for methyl methacrylate theoretically and
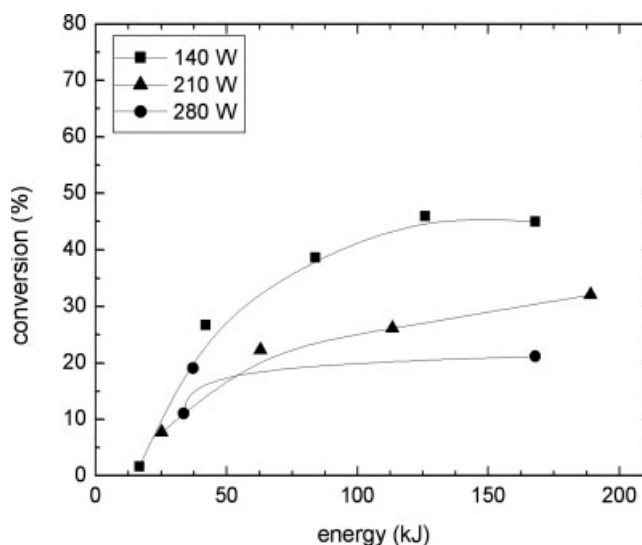

Figure 5 Weight average molecular weight (M_w) as a function of the time at three different power irradiation. [BP] = 60 mM.

Figure 6 Conversion versus irradiation energy plots at three different power irradiation. [BP] = 60 mM.
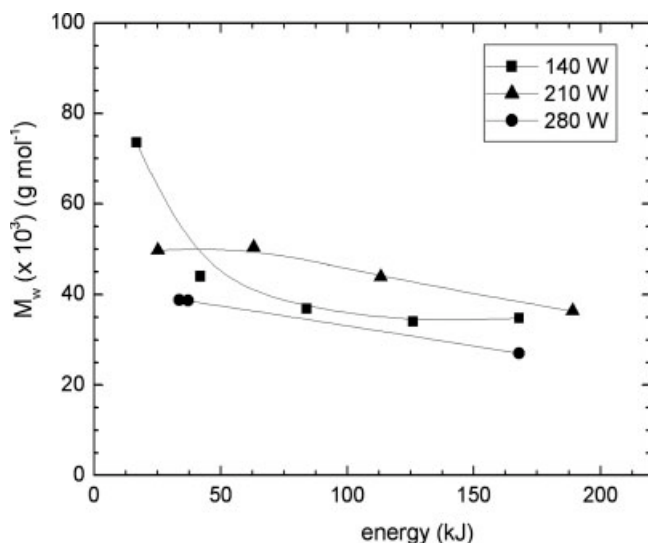
Figure 7 Weight average molecular weight (M_w) as a function of the irradiation energy at three different power irradiation. [BP] = 60 mM.

experimentally under microwave irradiation conditions of radical polymerization.[27]

Effect of initiator concentration

Table II 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 three different power irradiation conditions of polymerization. Between 15 and 30 mM of initiator concentration a similar conversion was attained, but an increase of conversion was obtained at 60 mM.

The effect of initiator concentration on the M_w exhibited a variable behavior depending on the applied power irradiation. At 140 W a decrease of M_w was observed while the initiator concentration increased, similar to the thermal radical polymerization. At 280 W the opposite effect is verified: the M_w increased up to 25% in the same concentration range. Finally, at 210 W no systematic dependence on M_w with the initiator concentration was observed. These results suggest that, a transfer radical mechanism could be more relevant at a higher power irradiation.

Under all conditions the polydispersity index (M_w/M_n) was close to 2, similar to that obtained in thermal conditions,[18,28] suggesting that the disproportionation or transfer chain mechanisms are dominant.

Effect of irradiation energy

Figure 6 shows the conversion curve at different irradiation energy (E) evaluated as the product of the power and time of irradiation. It is possible to see that, with the same E, the limit conversion achieved using a lower power (140 W) was always greater

than that using a higher power (280 W). Again, this behavior suggests a nonthermal effect characterizing the DiPF polymerization.

Figure 7 shows the change in M_w with the different tested irradiation energy. At all studied power, M_w decreases at higher irradiation energy, but approaches to a limiting value with higher E.

CONCLUSIONS

Microwave irradiation has been successfully applied to radical polymerization of diisopropyl fumarate using benzoyl peroxide as an initiating system. This methodology has demonstrated to be especially useful with a monomer that is difficult to polymerize and that exhibits slow kinetic of polymerization, as a representative of the fumaric esters. It has been demonstrated that the rate of polymerization under microwave irradiation has been significantly faster than the one under thermal conditions.

The molecular weight distribution, close to 2, is similar to that obtained under thermal conditions and indicates that the same radical mechanism of polymerization is operating.

A systematic study of radical polymerization under microwave irradiation of other fumaric esters is under progress in order to understand the effect of the monomer structure on this kind of polymerization.

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