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Novel Copolymer of Diisopropyl Fumarate and Benzyl Acrylate Synthesized Under Microwave Energy and Quasielastic Light Scattering Measurements

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Microwave assisted free radical copolymerization of diisopropyl fumarate (DIPF) and benzyl acrylate (BzA) with different copolymer compositions was performed using benzoyl peroxide as initiator. The effect of the reaction conditions on the macromolecular characteristics, monomer reactivity ratio and copolymer properties were studied. The monomer conversion and average molecular weights increase with the content of BzA units in the copolymer. The copolymers were characterized by IR, ^{1}H and ^{13}C-NMR spectroscopies and the molecular weights were analyzed with size exclusion chromatography (SEC). The reactivity ratios obtained from an extended Kelen-Tüdös method under microwave irradiations are a factor which is double than those obtained by thermal copolymerization. The product $r_1r_2 = 0.152$ suggests a preference of both propagating macroradicals toward consecutive homopolymerization. The hydrodynamic and polydispersity size were measured in ethylacetate, tetrahydrofuran and methylethylketone with a quasi-elastic light scattering (QELS) technique showing that the quality of the solvents increases in the order: EA < THF < MEK.

Keywords: Copolymer, microwave, diisopropyl fumarate, benzyl acrylate, quasielastic light scattering

1 Introduction

In recent years, research in microwave-assisted organic synthesis has been directed at increasing development in view of world interest in developing green chemistry, attempting to prevent pollution, safer chemistry, and a decrease in energy spending (1–3). In macromolecular chemistry, the microwave energy has been increasingly applied to a number of reactions, including step-growth, free radical and ring-opening polymerizations (4–6). Important homopolymers have been obtained by radical homopolymerization using this technique and recently it was extended to copolymers such as styrene-methyl methacrylate (7), styrene-butyl acrylate (8), bromophenylmaleimide-ethyl or butyl methacrylate (9), among others. Most of these works found an enhancement of the reaction conversion under microwave conditions, depending on the solvent, initiator and monomer compositions. Jung et al. (8) have shown that in the copolymerization of styrene and butyl acrylate the conversion rate increases at high ratio of butyl acrylate monomer feed under microwave irradiation conditions, and explained this behavior as a result of the different susceptibilities of both monomers to microwave irradiation. They found important differences in the monomer reactivity ratio in comparison to the energy source used.

The free radical homopolymerization of dialkyl fumarates (DRF) and benzyl acrylate (BzA) under microwave energy was systematically studied by our group (10–12). A significant enhancement on polymerization rates of both monomers was found in comparison with the reaction carried out under thermal heating. The aim of the present investigation is to report the copolymerization behavior of diisopropyl fumarate (DIPF) and benzyl acrylate (BzA) initiated with benzoyl peroxide (Bz_2O_2) as a free radical initiator under microwave conditions and the determination of the monomer reactivity ratios. The hydrodynamic size of a copolymer sample was analyzed through

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quasi-elastic light scattering measurements in three different solvents.

2 Experimental

2.1 Materials

Diisopropyl fumarate (DIPF) and benzyl acrylate (BzA) monomers were prepared and purified as previously described (10,12). Benzoyl peroxide (Bz_2O_2) was recrystallized from methanol. Other solvents were purchased from Merck and Sintorgan (PA).

2.2 Microwave Polymerization

Polymerization was carried out in bulk using specifically designed equipment for microwave synthesis, Synthos 3000 multimode batch reactor (Antor Paar). The instrument is equipped with two magnetrons, operating at a frequency of 2.45 GHz with continuous microwave output power from 0 to 1400 W. The reactor cavity encompasses an 8-vessel rotor (XQ80) and its protection lid. The rotor carries 8 reaction vessels, which are 80 ml PTFE-TFM, equipped with a pressure release valve seals and individually rests inside ceramic jackets, to enable reactions under high pressure (not necessary in the present case). The temperature is monitored using an internal gas balloon thermometer placed in one reference vessel and additionally by exterior IR thermography. Different amounts of both monomers were charged into each reaction vessels together with the previously weighed mass of the initiator (40 mM) and then purged with N_2 for 30 min. The reaction vessels were irradiated at 1200 W during 6 min; under those conditions the temperature attained 76°C after 2 min. After reaching room temperature, the polymer was isolated by methanol addition and purified by solubilization–precipitation (toluene: methanol, 1:5) and then dried at constant weight for conversion estimation.

In order to compare the previous method, we carried out a thermal copolymerization of the monomers at 76°C using a thermal bath and the same initiator concentration (40 mM).

2.3 Characterization Techniques

NMR (^1H and ^{13}C) spectra of copolymers were recorded with a Varian-200 MHz (Mercury 200) spectrometer operating at 200 and 50 MHz, respectively. Samples were dissolved in $CDCl_3$(10% w/v) and the spectra recorded at 35°C. A Shimadzu IR-435 spectrometer was used to record the infrared spectra of the polymers by casting a $CHCl_3$ solution (10% w/v) as a capillary film onto a sodium chloride (NaCl) window. The molecular weight distribution and the weight average molecular weights (M_w) were determined by size exclusion chromatography (SEC) with an 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 were used with chloroform as 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.

2.4 Quasielastic Light Scattering Measurements

The time correlation function G(q,t) of the light scattering intensity was measured at the scattering angle $\theta = 90°$ with a goniometer ALV/CGS-5022F with a multiple tau digital correlator ALV-5000/EPP covering a wide time range (10^{-6} – 10^3 s). The light source was a helium/neon laser ($\lambda = 632.8$ nm) operating at 22 mW. All of the measurements were carried out at room temperature. Solutions were prepared in ethylacetate (EA), methylethylketone (MEK) and tetrahydrofuran (THF); they were filtered through a 0.22 μm pore size PTFE membrane into the cell. The characteristic relaxation parameters were extracted by carrying out the inverse Laplace transform (ILT) of the measured G(q,t) using a superposition of exponentials (CONTIN) (13):

$$G^{1/2}(q,t) \approx \int_0^\infty L(\ln\,\tau)\,\exp(-t/\tau)\,d(\ln\,\tau) \qquad (1)$$

were $\tau = 1/Dq^2$, D is the diffusion coefficient and q, the scattering vector, is related to the scattering angle θ by $q = (4\pi n/\lambda)\sin(\theta/2)$. Here, n is the refractive index of the medium and λ is the wavelength of the vertically polarized light in vacuum.

3 Results and Discussion

3.1 Copolymer Synthesis and Characterization

The radical homopolymerization of DIPF and BzA monomers under microwave irradiation has been systematically studied using a domestic oven (10,12). Both systems exhibit an enhancement of the rate of the reaction and display differences in the tacticity of the obtained polymers, higher than that achieved with conventional radical polymerization. These results suggest that the polymerization reaction under microwave conditions proceeds with some stereospecificity, which is not the case for the reaction conducted in conventional thermal heating conditions. Similar results were found for other microwave assisted organic reactions (14, 15).

In this work, copolymers from these monomers with different relative content were synthesized, using Synthos 3000 equipment for organic synthesis. Under the selected conditions, the temperature quickly increased attaining 76°C in 2 min. Scheme 1 shows the structure of the copolymers confirmed by IR and ^{13}C-NMR spectra. IR (thin

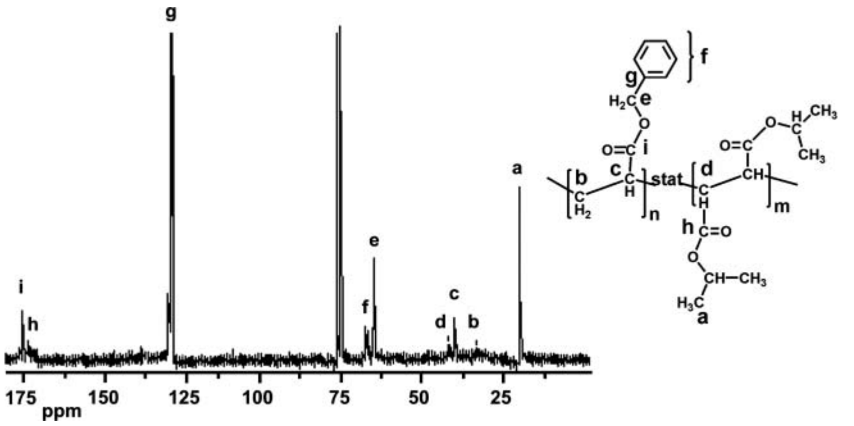
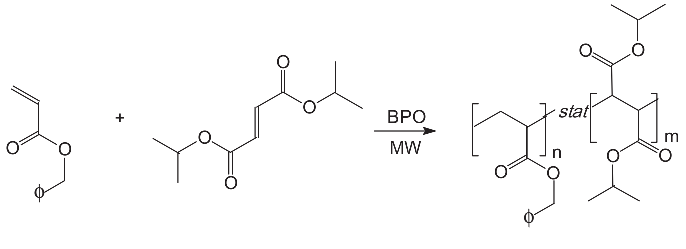


Fig. 1. ^{13}C-NMR spectrum of poly(DIPF-*stat*-BzA) prepared from $f_1 = 0.48$ under microwave polymerization.

film): (cm^{-1}), 3060, 3020 and 2880 (C-H), 1715 (C=O), 1585 (C=C Ar), 1250 and 1100 (CO-OR). The assignments of ^{13}C-NMR peaks were done according to the corresponding homopolymer spectrum. Figure 1 shows a characteristic spectrum.



Sch. 1. Free radical copolymerization under microwave (MW) irradiation with benzoyl peroxide (BPO) as initiator.

^{13}C-NMR (CDCl$_3$): δ (ppm), 21.84 (CH$_3$), 35.42 (CH$_2$), 41.63 (*C*H-COOBz), 43.98 (-*C*H-COOisP), 66.56 (OCH$_2$-), 128.35–128.65 (4 ArC), 136.12 (ArC, α-CH$_2$), 172.49 (*C*O-OisPr), 174.37 (CO-Bz). Splitting of peaks of backbone methines of DIPF units were observed for different composition copolymers, while the peak of carbonyl carbons and backbone methylene do not show splitting. Figure 2 shows the chemical shifts (δ, ppm) observed as a function of the mole fraction of BzA in the copolymer (F_1) as calculated below. It is evident that the resonance signals of backbone methines of DIPF units decrease with the increase of F_1. Since the splits are a result of configurational and sequence distribution effects, this tendency appears to indicate that the magnetic environment changes when the composition changes (16).

Figure 3 presents the ^{1}H-NMR of poly[(diisopropyl fumarste)-*stat*-(benzyl acrylate)] copolymer along with assignments of various resonance signals. Composition was estimated from the integral ratio of the peaks at 7.21 and 1.12 ppm corresponding to aromatic hydrogen (Ar) of BzA and methyl hydrogen (CH_3) of DIPF, respectively, using the following ratio:

$$F_1 = \frac{12\ I(Ar)}{12\ I(Ar) + 5\ I(CH_3)} \tag{2}$$

Where F_1 is the mole fraction of BzA in the copolymer and $I(Ar)$ and I(CH_3) represent the ^{1}H-NMR resonance peak areas at 7.21 and 1.12, respectively. Table 1 summarizes the feed (f_1), copolymer (F_1) compositions, and the properties of the obtained copolymer. Here, the growth of the reaction conversion is clearly stated when the content of BzA in the feed increases. The higher reactivity of BzA was also noticed when comparing the microwave homopolymerization of both monomers at a similar initiator concentration ([Bz$_2$O$_2$] = 20 mM): 44.0 and 30.2 % conversion were attained at 40.8 kJ and 168 kJ of microwave energy for BzA and DIPF, respectively (11, 12). On the other hand, the copolymerization carried out under microwave conditions shows an important acceleration of

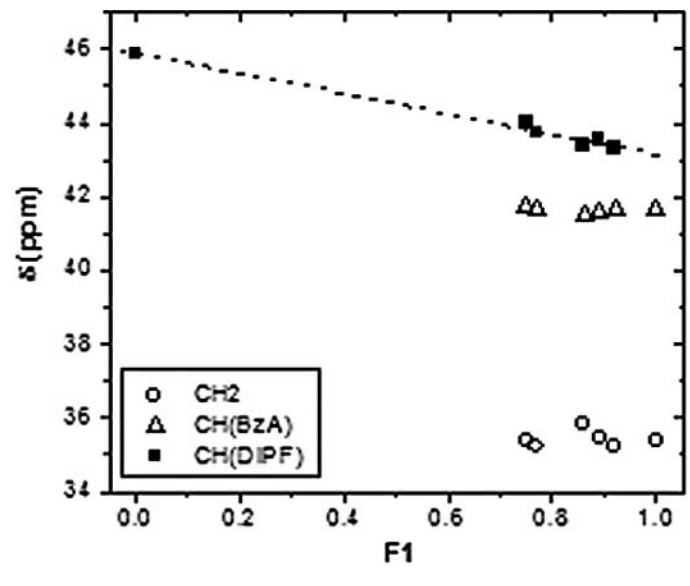


Fig. 2. Chemical shift of C=O, CH$_2$ and CH signals of poly(DIPF-*stat*-BzA) with different compositions.

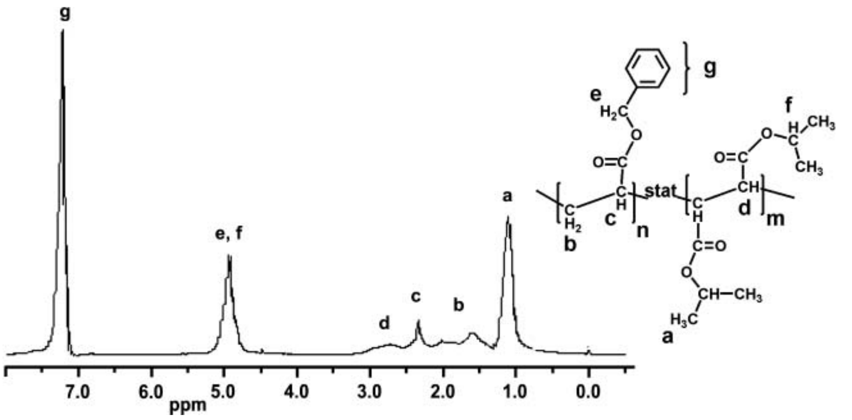


Fig. 3. ^{1}H-NMR spectrum of poly(DIPF-*stat*-BzA) prepared from $f_1 = 0.48$ under microwave polymerization.

the rate of reaction: 1.3 and 0.023% conversion/min for microwave and thermal conditions respectively, under similar conditions (76°C, $[Bz_2O_2] = 40$ mM).

Changes in the molecular weight (M_w) and polydispersity index (M_w/M_n) exhibited similar tendencies as observed in the reaction conversion with increasing f_1 (Table 1). Figure 4 shows the change in the chromatographic profile with the increase of the BzA content in the copolymer, which is close to the poly(benzyl acrylate) homopolymer distribution, characterized by bimodal distribution at high conversion (12). This behavior is possibly due to polymer chain transfer reactions, as was demonstrated for the BzA homopolymerization. Besides, a decrease by a factor four in the Bz_2O_2 concentration produces an increase in the number average molecular weight M_n only from 8200 to 11720, indicating that the relationship between M_n and initiator concentration is weaker than that expected for a chain radical polymerization mechanism, according to the classical expression (17):

$$\nu = \frac{k_p\,[M]}{2\,(f k_d k_t\,[I])^{1/2}} \tag{3}$$

Where ν is the kinetic chain length, k_d, k_p, k_t are the rate constants for the initiator decomposition, propagation and termination steps, respectively; f is the initiator efficiency, $[M]$ and $[I]$ are the monomer and initiator concentrations, respectively. ν is related with M_n through $\nu = M_n/M_o$ or $\nu = M_n/2M_o$ for coupling or disproportionation termination mode, respectively (M_o is the molecular weight of the monomer). The average molecular weights of the copolymers obtained under microwave radical copolymerization were one order of magnitude lower than those obtained by thermal copolymerization (Table 1). These results suggest that a higher radical concentration was obtained under microwave conditions, according to the known radical polymerization mechanism, taking into account that M_n decreases with the increase of radical concentration. In fact, previous work demonstrated that under microwave conditions the rate constant for the initiator, k_d, was one order of magnitude higher than that considered in thermal conditions (10).

Table 1. Copolymerization of diisopropyl fumarate (DIPF) with benzyl acrylate (BzA), $[Bz_2O_2] = 40$ mM. Microwave conditions (MW): P = 1200 W, 6 min (76°C); thermal conditions: 76°C, 1440 min

Conditions	f_1	F_1	*Conv (%)*	$M_w \times 10^{-3}$	M_w/M_n
MW	0.00	0.00	1.8	18.6	1.96
	0.31	0.75	7.8	31.1	2.05
	0.48	0.77	20.5	26.9	2.70
	0.58	0.89	28.2	37.7	4.60
	0.67	0.86	23.4	32.8	3.80
	0.81	0.92	54.4	29.9	4.90
	1.00	1.00	69.7	57.5	6.90
Thermal	0.31	0.59	32.7	350.0	4.60
	0.67	0.77	59.3	262.0	8.80

3.2 Monomer Reactivity Ratio Determination

In order to determine the copolymerization behavior at high conversion polymerization, the reactivity ratio was calculated by using the conversion based modified methods of Kelen and Tüdos (18,19). Applying that methodology to comonomer-copolymer composition curve (Fig. 5), the monomer reactivity ratios, r_1 and r_2 (BzA and DIPF respectively) were determined and listed in Table 2. The values obtained, $r_1 >> r_2$, indicated that DIPF shows a low reactivity toward BzA, an electron-accepting monomer. Similar behavior was found in the radical copolymerization of DIPF with methyl acrylate (MA) and phenyl acrylate (PhA) carried out under thermal conditions (20). The product $r_1r_2 = 0.152$ with $r_1 >> 1$ and $r_2 << 1$ indicates that both propagating macroradicals have a preference to the addition of BzA monomer, suggesting a tendency toward consecutive homopolymerization of the two monomers (21).Then, the structure of the copolymer

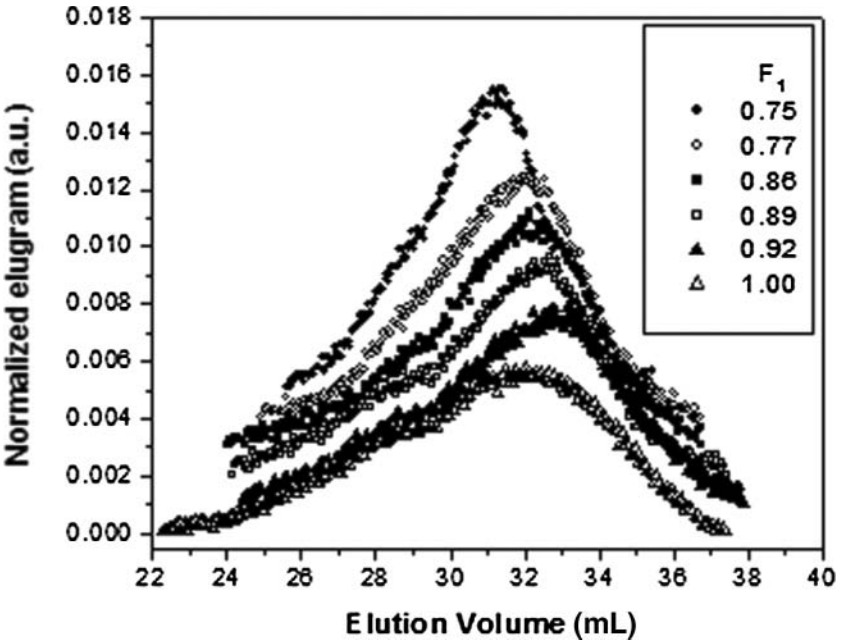


Fig. 4. Chromatographic profile of poly(DIPF-*stat*-BzA) in function of F_1. 1200 W, 6 minutes, $[Bz_2O_2] = 40$ mM.

would consist of containing more or less long sequences of the most reactive comonomer (BzA) separated with occasional DIPF comonomers. Only when the BzA monomer has been consumed completely, the homopolymerization of the residual DIPF would occur. A confirmation of the proposed structure is given by the observed changes in NMR spectra, where the resonance signals of backbone methines of DIPF units decrease with the increase of F_1.

The values of the monomer reactivity ratio increased a two factor under microwave conditions in both monomers (Table 2). These results are related with the increase of the mole fraction of BzA in the copolymer as shown in Figure 5. Similar results were observed in other systems (8, 9).

3.3 Quasielastic Light Scattering Measurements

The elastic light scattering measurements of copolymer solutions in single solvents as a function of the scattering angle and concentration (through the Zimm plot, for instance) gives apparent macromolecular parameters (molecular weight, radius of gyration, second virial coefficients) (23). A complete characterization of the copolymer requires the collection of data in three different solvents and a fitting procedure to get the real parameters. Instead, quasielastic light scattering techniques, by probing the temporal fluctuations of the scattered intensity light at fixed scattering angles, provides information about the main relaxation times of the system and the hydrodynamic radius. Monodisperse homopolymers in dilute solutions have a single relaxation time $\tau = (Dq^2)^{-1}$, where D is the translational diffusion coefficient of the macromolecule, related to the hydrodynamic

Table 2. Values of reactivity ratios r_1 and r_2 and the product r_1r_2 for radical copolymerization of alkyl acrylate monomers (M_1) with DIPF (M_2)

M_1	Conditions	r_1	r_2	r_1r_2	*Reference*
BzA	MW	2.456	0.062	0.152	this work
BzA	Thermal	1.160	0.028	0.032	this work
MA	Thermal	1.900	0.091	0.173	17
PhA	Thermal	3.400	0.070	0.238	17

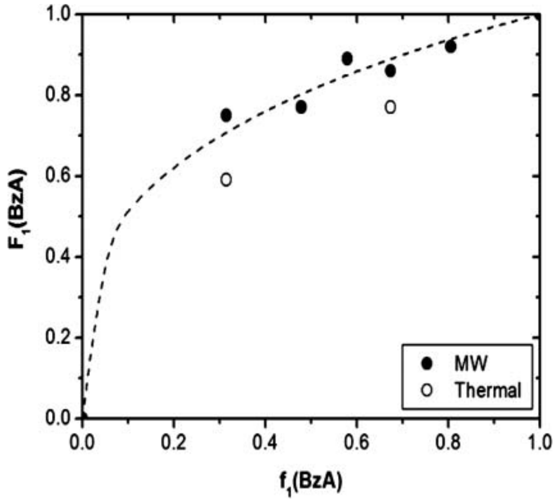


Fig. 5. Copolymer composition plot for the DIPF-BzA system. Microwave conditions: P = 1200 W, 6 min (76°C); thermal conditions: 76°C, 1440 min. The dotted line is the theoretical composition curve.

radius R_h through the Stokes-Einstein relationship:

$$D = \frac{k_B T}{6\pi \eta \, R_h} \tag{4}$$

Here, η is the solvent viscosity and $k_B T$ is the thermal energy. In the present experimental setup ($\theta = 90^{\circ}$, $\lambda = 632.8$ nm), the magnitude of the scattering vector (in nm^{-1}) is $q = 0.0140$ n. The translational diffusion coefficients are obtained from the relaxation times τ (in ms) as $D = 0.196\, n^2/\tau$. A cumulant expansion analysis (24) of the scattered intensity correlation function is used to get the mean relaxation time τ and a polydispersity index Δ. The method is appropriate whenever $\Delta \leq 0.3$; otherwise, other methods must be selected (25). Polydisperse samples in the same dilute regime display a distribution of relaxation times with a peak centered around a mean value. In the semidilute region, a second peak appears at longer times, called "slow" mode, to distinguish it from the previous one, the "fast" mode.

All the copolymer samples obtained by microwave energy have similar molecular weight and composition, with dominant contribution from the BzA comonomer. Hence, one dilute copolymer solution (mole fraction $f_1 = 0.48$, $M_w = 26900$ g mol^{-1}, $c = 3.1$ g l^{-1}) in ethyl acetate was analyzed by QELS at the scattering angle 90° and room temperature. A cumulant expansion analysis (24)of the scattering intensity time correlation function (Fig. 6), gives a polydispersity index $\Delta \approx 0.45$; for this reason, the relaxation times were obtained from the maximum of the continuous time distribution spectrum with CONTIN (13). The time distribution spectra display a bimodal shape with two well separated peaks (Inset in Fig. 6). The maximum of the short time peak is located at 0.025 (±0.001) ms, giving an intensity average hydrodynamic radius $R_{h.u} = 5.1$ nm (±0.2), obtained by direct application of the Stokes-Einstein equation. Similar patterns were obtained at lower concentrations confirming that the measurements were carried out at the dilute region.

No attempt was made to compare the size with that of the PBzA homopolymer because of the extremely high polydispersity of the actual microwave synthesized sample. A search in the literature gave no complementary information about this system. On the other side, only high molecular weight PFIP homopolymers were studied with elastic light scattering (26), theoretically described as semi-flexible chains, but these results can scarcely expect to be extrapolated to low molecular weight samples as those obtained in this work.

In order to obtain appropriate estimations of the size of the copolymers, number and weight average hydrodynamics radii were calculated from the time correlation function with CONTIN. In this step, it is assumed that the polymer chains behave as hard spheres in the Rayleigh-Debye scattering regime, giving: $R_{h,n} = 1.49$ (±0.06) nm and $R_{h,w} = 2.33$ (±0.11) nm, respectively. A measure of the size polydispersity of the sample was obtained from the ratio $R_{h,w}/R_{h,n} = 1.5$ (±0.2).

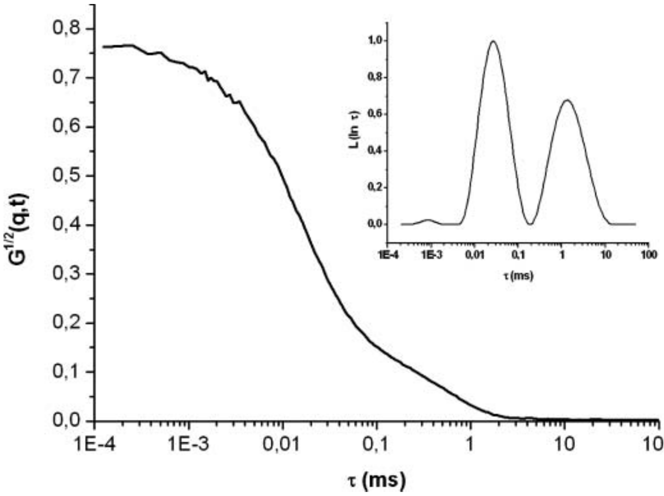


Fig. 6. Intensity autocorrelation function G(q,t) of poly(DIPF-*stat*-BzA), (M_w 26900 g mol^{-1}) in EA, concentration $c = 3.1$ g l^{-1}. The inset shows the representative relaxation time distribution L(ln τ) vs. time.

The same sample was measured in MEK and THF at the same temperature and similar concentrations. Again, bimodal time distribution spectra were obtained and the data was analyzed with the same methods. Table 3 collects the results in the three solvents.

As expected, the size polydispersity parameter is the same in all the solvents within experimental errors. Assuming a square root relation between average hydrodynamic radii and average molecular weights (27), the usual polydispersity index would read $M_w/M_n = 2.2$ (±0.3), in close agreement with that calculated by size exclusion chromatography. Moreover, the quality of the solvent increases in the order EA, THF, MEK, as revealed by the swelling of the number and weight averaged radii (28).

The presence of a second peak of similar height at longer times (i.e., 1.2 ± 0.1 ms for the EA solution) in the time distribution spectra deserves a comment. The time distribution spectrum is equivalent to an "intensity weighted

Table 3. Hydrodynamic radius (intensity, number and weight averages, respectively) and size polydispersity obtained from QELS of the copolymer sample with molar fraction $f_1 = 0.48$, $M_w = 26900$ g mol^{-1} in three solvents

	EA $\eta = 0.420$ *mPa·s*	*THF* $\eta = 0.454$ *mPa·s*	*MEK* $\eta = 0.381$ *mPa·s*
$R_{h,u}$ (nm)	5.1 (0.2)	5.0 (0.2)	5.6 (0.6)
$R_{h,n}$ (nm)	1.5 (0.1)	2.0 (0.3)	2.4 (0.6)
$R_{h,w}$ (nm)	2.3 (0.1)	2.9 (0.3)	3.3 (0.5)
$R_{h,w}/R_{h,n}$	1.5 (0.1)	1.5 (0.2)	1.4 (0.4)

size distribution". In this case, the first peak is centered at 5.1 nm and the second peak would correspond, assuming idealistically an extended Rayleigh scattering regime, to an intensity weighed radius some forty times bigger, around 200 nm. In fact, the angular dependence of this mode follows a power law $\tau \sim q^{-\alpha}$, with $\alpha = 2.1$ (± 0.3), compatible with a translational diffusive mode. In dilute solutions, a second mode appears in block copolymers dissolved in poor solvents for one of the monomers (29). This is not the case for the present system, because the solvents are thermodynamically good for both homopolymers. The origin of the slow modes found in the QELS measurements is currently under investigation.

Nevertheless, the calculation of the corresponding mass or number weighed distributions decreases exponentially the contribution of the second peak to insignificant values, well below the experimental errors. Hence, the contribution of this additional mode is completely irrelevant during the averaging processes to obtain the hydrodynamic radii because the corresponding weighting factors favour smaller sizes. The QELS measurements provide, under these circumstances, accurate estimations of the polymer size, overcoming the known limitations of elastic light scattering method for low molecular weights.

4 Conclusions

Copolymer of BzA and DIPF obtained under microwave conditions, initiated by Bz_2O_2 shows significant enhancement of the rate of reaction in comparison with the thermal polymerization conditions. The monomer reactivity ratios r_1 and r_2 are twofold higher under microwave conditions than those obtained under thermal conditions, indicating a change of the radical reactivity according to the heating mode. The product $r_1 r_2 = 0.152$ suggests a preference of both propagating macroradicals toward consecutive homopolymerization. The increase of the mole fraction feed of BzA induces an increase of the average molecular weights and polydispersity index, probably due to the polymer chain transfer reaction as happens to be in the BzA homopolymerization. The analysis of the hydrodynamic radius of a typical copolymer sample in EA, THF and MEK with QELS techniques shows that the quality of the solvents increases in the order: EA < THF < MEK and the polydispersity size was the same in the three solvents, as expected.

Acknowledgments

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28. The information on the quality of each solvent from the molecular weight dependence of the hydrodynamic radius (i.e, from the exponent ν in the power law $R_h \approx M^{\nu}$) would require a range of molecular weights wider than that obtained in this work. Moreover, the exponent ν (different from 0.5) is sensitive only to extremely high values of molecular weights ($M > 10^6$ g mol^{-1}), as demonstrated by Weill and Des Cloizeaux. This result was implicitly used in the text to estimate the molecular weight polydispersity of the copolymer sample from the size polydispersity obtained from QELS measurements.
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