

Polymerization of p-nitrobenzyl acrylate under microwave irradiation and their optical properties

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Received: 16 July 2010 / Accepted: 2 November 2010 / Published online: 19 November 2010
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Abstract p-Nitrobenzyl acrylate was polymerized under microwave irradiation initiated by benzoyl peroxide. The effect of the reaction conditions on the conversion, average molecular weights and the polydispersity index (M_w/M_n) were investigated. The polymers were characterized by IR, ^1H and ^{13}C -NMR spectroscopies and molecular weights were analyzed with size exclusion chromatography (SEC). Optical properties in seven solvents were studied. The most outstanding characteristics of this monomer were slow kinetics of polymerization and low average molecular weight ($M_w \sim 3000$) as result of the chain transfer reaction to monomer, as it was demonstrated by experimental test and theoretical calculations. Solvatochromic effect of polymer solutions by changing the solvent polarity was quantitatively expressed by means of the linear solvation energy relationship using the empirical Kamlet-Taft solvents parameters set. The analyses demonstrated that the solute-solvent dipolar interactions were mainly responsible of the observed shift of ν_{\max} and attributed to the *para*-nitrobenzyl group of the monomer, which enhanced the optical properties of the polymer.

Keywords p-nitrobenzyl acrylate · Microwave polymerization · Computational calculation · Optical properties

Introduction

The use of the microwave energy as a new methodology for to carry out more safety, clean and efficient chemical reactions was known for a long time [1–3] and has spread rapidly to the field of polymer [4–6]. The mechanism of energy transfer using a microwave field is considerably different from the well-established modes (radiation, conduction, and convection) of heat transfer. The use of microwave energy is a very original procedure for heating materials. Its main advantage derives from the almost instantaneous heating of them, homogeneously and selectively, especially in those with poor driving properties and in which local overheating is a major inconvenience. Another important aspect related to the environmental impact is the reduction in energy consumption compared to the usual means of heating and the absence of solvent in the reaction.

As the free radical polymerization is the most important industrial polymerization technique, the effect of the microwave energy onto the behavior of polymerization of styrene, methacrylates and fumarates, among others, was studied [7–10]. However, few of these studies have been conducted systematically in order to understand the effect of the experimental variables (power and time) on the kinetics of polymerization as well as on the molecular weight and the molecular weight distribution [9, 10]. These studies provided relevant information about the monomer structure-reactivity relationship under the above conditions, as it was demonstrated for the case of fumaric esters [11].

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Polymers with functional groups are very important because of their specific end applications [12, 13]. Among them, acrylic and methacrylic esters with aromatic substituents which present high thermal stability and good optical properties were used as a nonlinear optical polymer as well as photobase generators in photo-induced polymerization, depolymerization, and crosslinking [14–16].

The aim of the present study was to analyze the effect of the different experimental variables (power, time, solvent and initiator concentrations) on the polymerization behavior and the macromolecular characteristic of poly(*p*-nitrobenzyl acrylate) obtained under microwave conditions. In addition, we investigated the optical properties of this polymer in different solvents in relationship to their structural characteristics.

Experimental part

Materials and instruments

Acrylic acid (Diransa) and *p*-nitrobenzyl alcohol (Aldrich 99%) were used as received. Benzoyl peroxide (BP) and 2,2'-azobisisobutyronitrile (AIBN) were 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.

¹H-NMR and ¹³C-NMR spectra of monomer and polymers were recorded on a Variam-200 MHz (Mercury 200) at 35 °C in CDCl₃.

UV-visible absorption spectra were obtained with a double-beam Cary 3 (Varian, Australia) spectrophotometer with 1 cm optical path cell using spectroquality solvents. The following solvents were used: 1,4-dioxane (DX), chloroform (CL), ethyl acetate (EA), tetrahydrofuran (THF), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMA) and acetonitrile (ACN). The polymer concentration was ca. 10⁻⁴–10⁻⁵ mole l⁻¹ (moles of polymer repeat unit per liter).

The molecular weight distribution and the average molecular weights were determined by size exclusion chromatography (SEC) with a LKB-2249 instrument at 25 °C and UV-Visible detector (SPD-10A Shimadzu). A series of four μ-Styragel columns, ranging in pore size 10⁵, 10⁴, 10³, 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 calibration was done with polystyrene standards supplied by Polymer Laboratories and Polysciences, Inc.

A microwave oven (Zenith, ZVP-2819), which produced microwaves at a frequency of 2,450 MHz and a maximal

power of 700 W, was used to carry out the polymerization reaction.

Monomer synthesis

p-Nitrobenzyl acrylate (pNBA) was synthesized by esterification starting from acrylic acid and *p*-nitrobenzyl alcohol together with a catalytic amount of sulfuric acid [17]. Acrylic acid and *p*-nitrobenzyl alcohol were added to benzene in the ratio 1:2:1. Sulfuric acid was used as catalyst and the mixture was refluxed for 22 hs while nitrogen was bubbled. The product was purified by column chromatography using chloroform as eluent. The yield was 60 % (mp: 50–51 °C). Monomer characterization and identification were carried out by spectroscopic methods. IR (ν, cm⁻¹): 1730 (C = O), 1635 (H₂C = CHR), 1600 (C = C Aromatic), 1280 and 1140 (acyl-O-R), 740 (C-H Aromatic), 830 (C-NO₂). ¹H-NMR (δ_H, ppm): 5.30 (–CH₂–benzyl), 5.85 (–CH₂–), 6.25 (>CH–), 6.60 (–CH₂–), 7.50–8.50 (aromatic). ¹³C (δ_C, ppm): 168.83 (C = O), 143.35 (C-NO₂), 132.17 (C_{Ar}, α-CH₂), 128.57 (C = C), 127.93 and 124.04 (Ar), 65.01 (O-CH₂-Ar), confirming the corresponding structure.

Polymerization

The general procedure to produce the polymerization under microwave conditions was described [9]. Briefly, the reaction was carried out in bulk in a conical Pyrex flask of 25 cm³ closed by a septum. Two grams of monomer were added to a previously weighted amount of the initiator (BP). The initiator concentration was changed from 0.1% to 0.98% w/w. The flask was purged with N₂ during 30 min and then was placed in the centre of turntable of the microwave equipment and irradiated at different power (70, 140, 210 W) and time (between 4 and 30 min).

Alternatively, the reaction was carried out under thermal heating conditions using a thermostated bath at 70 °C to compare both heating methods.

After reaching room temperature, the polymer was isolated and purified by chloroform solubilization and precipitation on methanol, dried at constant weight and the conversion determined gravimetrically. The polymer was identified by nuclear magnetic resonance spectroscopy and its weight average molecular weight and polydispersity index were determined by SEC. In some cases the reaction was carried out in a vacuum sealed tube, in order to evaluate the effect of each atmosphere.

Computational method

In order to understand the behavior of pNBA polymerization, thermodynamic calculations were performed on

monomers and polymers in comparison to benzyl acrylate (BA) polymerization, previously studied [9].

The conformational space of the species studied was investigated using genetic algorithm as implemented in Balloon software [18]. The conformers obtained were optimized using the semiempirical PM6 method with MOPAC2009 software [19]. The lowest-energy conformer of each species was further optimized using tools from the density functional theory as implemented in the Gaussian 03 package [20]. The optimizations were accomplished using the Becke's three parameters hybrid density functional with the gradient-corrected correlation functional due to Lee, Yang, and Parr, a combination that gives rise to the well known B3LYP method [21]. The 6-31 + G* basis set was used. A vibrational analysis at same level of theory was performed for all the optimized geometries to verify their local minima on the potential energy surface of the molecules and obtain thermodynamic information.

Results and discussion

Structural analysis

Figure 1 shows the $^1\text{H-NMR}$ spectrum of the poly(p-nitrobenzyl acrylate) and its structure. The following are the corresponding H assignments (δ_{H} , ppm): 8.10 and 7.41 ($\underline{\text{H}}\text{-Ar}$), 5.10 ($\underline{\text{H}}_2\text{C-Ar}$), 2.73 ($>\underline{\text{C}}\text{H-C}=\text{O}$), 2.35, 1.97 and 1.52 ($-\underline{\text{C}}\text{H}_2-$). The spectrum shows the splitting due to the signals of hydrogen $-\text{CH}_2-$ of the main chain resonances between 2.35 and 1.52 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: 13.5% of syndiotactic and 86.5% of isotactic configuration of the polymer [22]. This

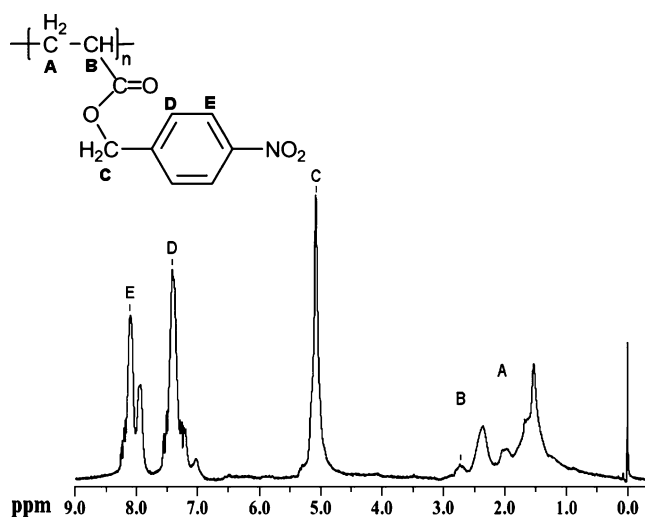


Fig. 1 $^1\text{H-NMR}$ spectra of poly(p-nitrobenzyl acrylate)

result seems to indicate certain stereospecificity of the polymerization reaction under microwave conditions, similar to the results observed for other acrylates [9].

From the $^{13}\text{C-NMR}$ spectrum (not shown), the following C assignments were obtained (δ_{C} , ppm): 173.94 ($\underline{\text{C}}=\text{O}$), 148.08 ($\underline{\text{C}}\text{-NO}_2$), 143.17 ($\underline{\text{C}}\text{Ar}$, $\alpha\text{-CH}_2$), 128.53 and 129.99 (Ar), 65.41 ($\text{O-}\underline{\text{C}}\text{H}_2\text{-Ar}$), 41.57 ($-\underline{\text{C}}\text{H}_2-$), confirming the corresponding structure.

Microwave and thermal polymerization

The conditions of reaction employed and the characteristics of polymers obtained are shown in Table 1. The effect of the initiator nature was evaluated starting from two different compounds, AIBN and BP. Higher conversion was reached using BP under the same experimental conditions (run 1 and 2), while the M_w were comparable in both cases. For this reason, the other polymerization reactions were performed using BP. Similar results were formerly found and explained by other monomers studied [11].

It is noteworthy that the kinetics of polymerization is very slow (run 2 to 6) compared to poly(benzyl acrylate) (PBA) and poly(methyl acrylate), previously studied under similar conditions [9, 23]. On the other hand, the M_w was much lower than the M_w of PBA obtained under similar conditions. These results seem to indicate some impediment to the growth of macroradical chain.

In order to clarify this behavior, additional experimental and computational tests were undertaken. The effect of different experimental variables was examined. The tests realized at the lowest power irradiation (70 W) during different times (4–30 min) showed no reaction under these conditions. When the reaction was carried out using dioxane as solvent, a decrease on the conversion but the same M_w were observed (run 5 and 7). This result can be attributed to a dilution effect. The reaction realized in vacuum-sealed tubes (in dioxane) produced a small increase in the reaction conversion and almost double increment in the molecular weight (run 8). While the increase in conversion could be due to increased reaction time (4 to 7 min), the effect is most noticeable on the molecular weight. The atmosphere obtained in vacuum conditions favors the growth macroradical because of the more efficient evacuation of oxygen. The increase of the power irradiation did not produce a significant improvement on the conversion or on the M_w (run 8 and 9). In order to see whether this effect was specific of the microwave energy, a reaction using conventional thermal heating (run 2 and 10) was performed. The temperature was selected according to preliminary examination under the same microwave conditions (data no shown). There was an important decrease of the conversion rate: 0.19% conversion/minute (run 10)

Table 1 Experimental polymerization conditions and characterization of PpNBA. Initiated by BP under microwave and thermal condition

Run	P (W)	Time (min)	Atmosphere	Solvent (%w/w)	[I] (%w/w)	%C	M _w	M _w /M _n
1	140	7	N ₂	–	0.98 ^(a)	4.0	3,300	1.1
2	140	7	N ₂	–	0.98	21.2	2,300	2.1
3	140	6	N ₂	–	0.98	17.4	2,700	1.7
4	140	5	N ₂	–	0.98	14.0	3,300	1.6
5	140	4	N ₂	–	0.98	14.3	2,500	1.7
6	140	3	N ₂	–	0.98	11.0	3,200	1.7
7	140	4	N ₂	Dioxane (42)	0.98	5.4	2,400	1.2
8	140	7	Vacuum	Dioxane (42)	0.70	8.8	5,600	1.7
9	210	7	Vacuum	Dioxane (42)	0.70	4.3	3,100	1.2
10	70 °C ^(b)	7	Vacuum	–	0.98	1.3	4,200	1.1

^a Azobisisobutyronitrile^b Thermal conditions

respect to 3.03% (run 2) under microwave conditions. Other thermal reactions tested at different times and initiator concentrations showed no significant improvement on the M_w.

Transfer constant evaluation

Since under all experimental variables, low weight average molecular weights were always obtained it, is possible that some type of chain transfer reaction could be competitive with the chain propagation reaction. To test this hypothesis the variation in the degree of polymerization with monomer concentration was analyzed, considering that the transfer to monomer would be the most probable chain transfer

reaction. The analysis was carried out according to the following equation [24]:

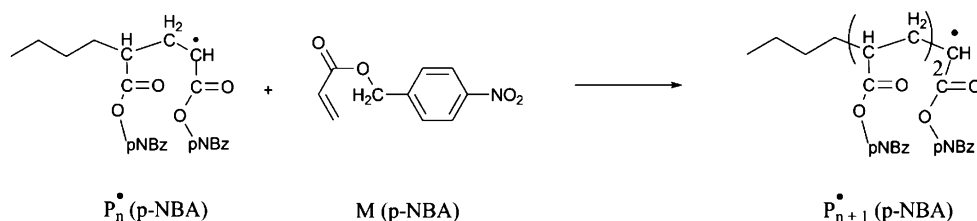
$$\frac{1}{DP_n} = \frac{k_t R_p}{k_p^2} \frac{1}{[M]^2} + C_M \quad (1)$$

where DP_n is the number average degree of polymerization, k_t and k_p are the termination and propagation constants respectively, R_p is the polymerization rate, $[M]$ is the monomer concentration and C_M is the monomer chain transfer constant.

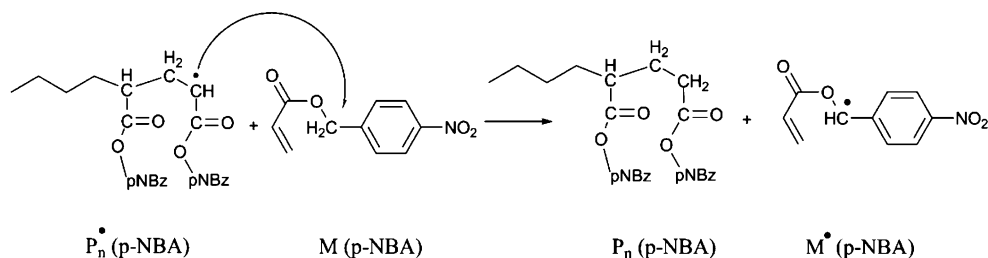
Scheme 1 shows both chain propagation and monomer benzyl hydrogen chain transfer reactions. In order to estimate the C_M value, different polymers were synthesized

Scheme 1 Propagation step and chain transfer reaction of pNBA monomer

a PROPAGATION STEP



b CHAIN TRANSFER REACTION



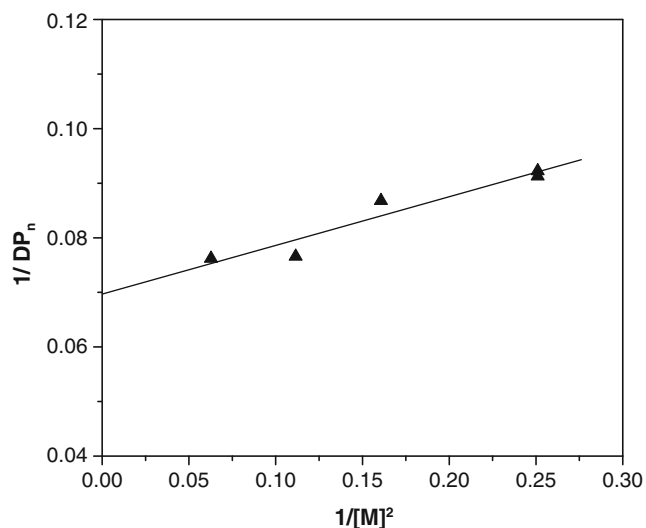


Fig. 2 Evaluation of chain transfer constant to monomer (C_M) according to Eq. 1. Experimental conditions; $P=140$ W; $t=10$ min; $[BP]=0.1\%$ w/w

changing the initial monomer concentration and keeping the conversion $<10\%$. Figure 2 shows the data obtained from which C_M was determined as: 0.070 ± 0.003 ($r=0.96$, $n=5$, $p=0.009$). This value is several orders of magnitude higher than other C_M previously reported in the literature: 0.955×10^{-4} and 0.332×10^{-4} for benzyl and ethyl acrylate, respectively [25], indicating the relevance of the chain transfer reaction as a termination mechanism of macroradical growth. In order to clarify the observed differences during the polymerization of pNBA and BA, homopolymerization and chain transfer enthalpy of reaction were calculated for both monomers, as follows:

$$\Delta H_{\text{HOMOP.}} = H(P'_{n+1}) - H(P'_n) - H(M) \quad (2)$$

$$\Delta H_{\text{TRANSF}} = H(P_n) + H(M') - H(P'_n) - H(M) \quad (3)$$

where $H(P'_{n+1})$, $H(P'_n)$, $H(M)$, $H(P_n)$ and $H(M')$ are enthalpies for macroradical with $n+1$ units, macroradical with n units, monomer, polymer with n units and radical monomer obtained by chain transfer, respectively (see Scheme 1).

In these calculations, the P'_n macroradical was estimated as consisting of a one repeating unit with a methyl group instead of a methylene group [26]. This approach does not significantly alter the results and it is necessary due to computational cost of applying the theory of density functional to large systems. Results of the calculated enthalpy (Table 2) put in evidence that the chain transfer reaction is favored with respect to the propagation reaction in the case of pNBA. This means that the products of the first reaction are thermodynamically more stable. An inverse result was found in the case of BA, where the

Table 2 Propagation and chain transfer reaction enthalpies for benzyl acrylate BA and p-nitrobenzyl acrylate pNBA calculated with B3LYP/6-31 + G*

ΔH (kcal mol $^{-1}$)	BA	pNBA
Propagation	-9.67	-14.06
Chain transfer	-7.91	-18.32

lower enthalpy corresponds to the propagation reaction of macroradical, according to the observed experimental results.

Optical properties

Figure 3 shows the UV spectra of PBA and PpNBA polymers in chloroform solution. A small bathochromic shift of the peak was observed from 256 to 264 nm, respectively, attributed to the larger conjugation of pNBA structural unit containing a nitro group and which characterizes the chromophore present in the macromolecule. A difference of two orders of magnitude higher in concentration of PBA respect to PpNBA, was necessary to measure the same absorbance intensity on the UV spectra which highlights the optical properties of PpNBA.

The absorption spectra of PpNBA in seven solvents were measured at 298 K. A shift of the peak maximum at a longer wavelength was observed with the increase of the solvent polarity (see Fig. 4 and Table 3). This bathochromic effect occurs when the dipolar moment of the solute in the ground state is smaller than in the excited state [27].

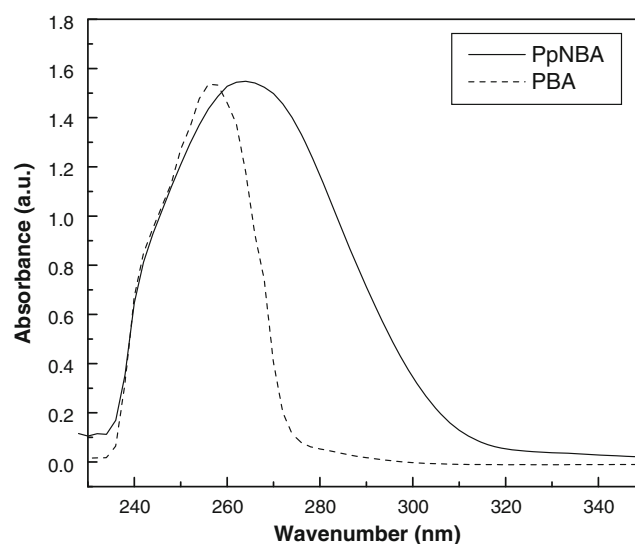


Fig. 3 UV absorption spectra of PBA and PpNBA polymers in chloroform solution

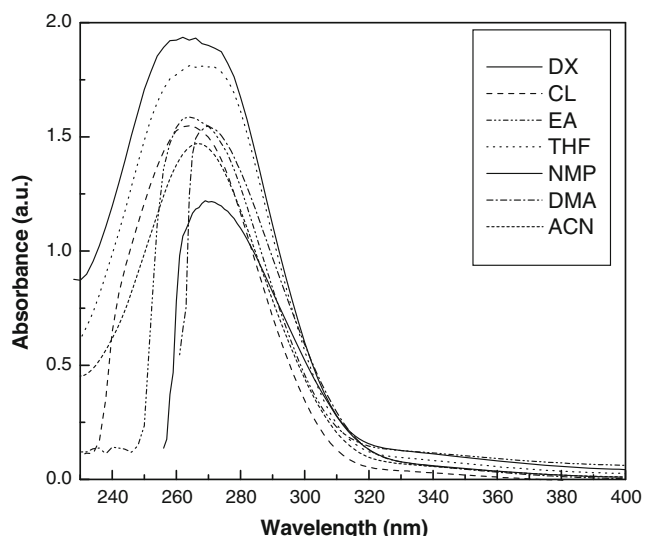


Fig. 4 UV absorption spectra of PpNBA in different solvents (acronyms in the “Experimental part”)

To evaluate the local interactions between the solute and the solvent, the simplified form of the Kamlet-Taft linear solvation energy relationship was used [28]:

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (4)$$

where XYZ is the property to be correlated, in our case the wave numbers of the absorption maxima (ν_{\max}), XYZ_0 is the property related to a standard process, π^* is the dipolarity/polarizability term, δ represents a polarizability correction term, α is the hydrogen-bond donating (HBD) capacity and β is the hydrogen-bond accepting (HBA) capacity. The coefficient of δ (the d term) is zero for all electronic spectra that are shifted bathochromically with the increasing solvent dipolarity, as in this case [28].

The solvatochromic parameters π^* , α and β for the square multiple correlation analysis were taken from references 28 and 29 as shown in Table 3. The results show that the solvent effect on the wave numbers of the absorption maxima may be well correlated by the following expression:

$$\nu_{\max}(10^3 \text{ cm}^{-1}) = 39.711 - 2.293\pi^* - 0.983\beta - 1.153\alpha \quad (5)$$

$n = 7 \quad r = 0.988 \quad SD = 0.115 \quad F = 0.007$

Table 3 UV absorption maxima for PpNBA in different solvents and their solvatochromic parameters

Solvent	λ_{\max} (nm)	ν_{\max} (10^3 cm^{-1})	π^*	α	β
1,4-Dioxane	262	38.17	0.55	0.00	0.37
Chloroform	264	37.88	0.58	0.44	0.00
Ethyl acetate	264	37.88	0.55	0.00	0.45
THF	264	37.88	0.58	0.00	0.55
NMP	272	36.76	0.92	0.00	0.77
DMA	270	37.04	0.88	0.00	0.76
Acetonitrile	267	37.45	0.75	0.19	0.31

Solvatochromic parameters α , β and π^* were taken from refs. [28, 29]

where n is the number of tested solvents, r the correlation coefficient, SD the standard deviation and F the significance.

The influence of the π^* on the bathochromic shift of ν_{\max} of PpNBA is more important than the other two terms (α and β), indicating that the solute-solvent dipole-dipole interactions occur preferably in the excited-state of the PpNBA.

Besides, comparing the absolute value, “b” coefficient is smaller than “a” coefficient for the calculated relationship. This result demonstrates that the ability of the solute to donate hydrogen bonds is weaker than its ability to accept hydrogen bonds through the heteroatoms and so a slighter influence of “b” term on the bathochromic shift of ν_{\max} is observed.

Conclusions

The polymerization behavior of pNBA initiated by BP under microwave energy was systematically studied, and showed significant enhancement of the rate of reaction respect to the thermal conditions. The most outstanding characteristic of this monomer is slow kinetics of polymerization and low average molecular weight, in comparison to BA. Both experimental results and theoretical calculations demonstrated that this behavior is a consequence of the chain transfer reaction to monomer, suggesting that the nitro group plays an important role in the stabilization of free radical monomer.

The optical properties of PpNBA were studied in different solvents showing a solvatochromic effect, which can be quantitatively expressed by means of the linear solvation energy relationship using the empirical Kamlet-Taft solvents parameters set. The analyses demonstrated that the solute-solvent dipolar interactions are mainly responsible of the observed shift of ν_{\max} . These results imply that the substitution of the nitro chromophoric group on the aromatic ring of the monomer unit enhances optical properties of the polymer and so its future applications.

Acknowledgment The authors wish to thank Mrs. Silvia Moya for language improvement of this manuscript. This work was supported by Universidad Nacional de La Plata (Projects 11/X515), Argentina.

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