

New Copolymers of a Tautomerizable β -Ketonitrile Monomer: Synthesis, Characterization and Solution Tautomerism

Juan M. Giussi,^{1,2} Patricia E. Allegretti,² M. Susana Cortizo^{1,2}

¹Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CCT-La Plata, Argentina

²Laboratorio de Estudio de Compuestos Orgánicos (LADECOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata (1900), La Plata, Argentina

Correspondence to: M. Susana Cortizo (E-mail: gcortizo@inifta.unlp.edu.ar)

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ABSTRACT: The monomer 2-methyl-3-oxo-5-phenyl-4-pentenitrile (MOP) was prepared by reaction of ethyl cinnamate and propionitrile in alkaline mixture. This monomer exhibits three possible tautomeric forms. The tautomeric equilibria of MOP and its copolymers with styrene in different solvents were analyzed by ¹H NMR spectroscopy. The bulk and solution radical copolymerization initiated with azobisisobutyronitrile was carried out at 60 °C. The products were characterized by ¹H NMR, ¹³C NMR, HSQC NMR, HMBC NMR, and FTIR spectroscopies. The weight-average molecular weight and polydispersity index were analyzed with size exclusion chromatography. The monomer reactivity ratios were obtained with the Fineman-Ross method, obtaining a value of $r_1r_2 = 0.286$. MOP copolymer composition as well as the nature of the solvent significantly

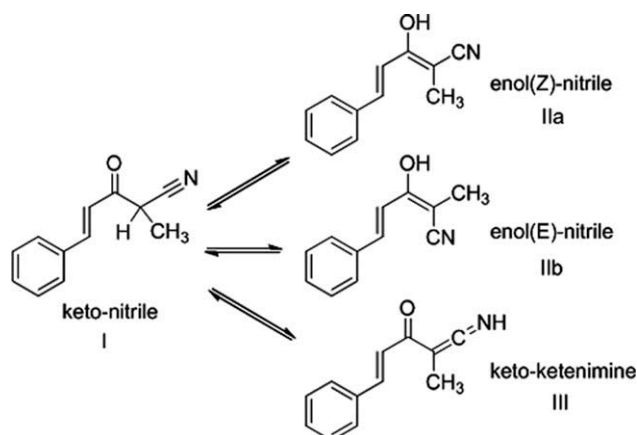
affected the tautomeric equilibrium. Regression analysis of the copolymer composition with solvatochromic parameters showed a good linear correlation, as quantitatively expressed by means of the linear solvation energy relationship using the empirical set of Kamlet-Taft solvent parameters. This behavior could be attributed to polymer–polymer or polymer–solvent interactions prevalent in solvents of different polarity, which are responsible for changes in macromolecular chain conformations, as confirmed by FTIR and viscometric studies. © 2012 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 000: 000–000, 2012

KEYWORDS: β -ketonitrile; FTIR; NMR; radical polymerization; viscosity; tautomeric equilibria

INTRODUCTION Tautomerism in organic chemistry has been extensively studied in condensed and gas phase by spectrometric methods in a wide variety of compounds such as carbonyl, nitro, and nitrile compounds.^{1–4} Among these, β -dicarbonyl compounds ($R-CO-CH_2-CO-R'$) are characterized by a considerable amount of both forms present in equilibrium and have therefore been the most studied. Comparatively, there are few works related to tautomeric equilibria in polymers. Mainly unsaturated β -diketones and β -ketoesters have been investigated as monomers in radical polymerization with the aim to clarify the effect of the relationship between the tautomeric structure and their polymerizability.⁵ A previous comprehensive and systematic study has shown that the monomer reactivity is a function of the polarity of the solvent and hydrogen bond donor acidity of the solvents, due to the percentage of each tautomeric form present in each solvent condition.⁵ Deviations of the kinetic behavior respect to the conventional model of radical polymerization have also been observed, as well as deviations on the reactivity ratios in copolymerization reactions. These findings demonstrate that the displacement of tautomeric equilibrium in the monomers significantly affects the

polymerization depending on the reaction conditions. Some researchers have studied such systems with a view to future applications. Mansri et al. synthesized 1-(*p*-vinylphenyl)-1,3-diketones and their copolymers, showing that the predominance of keto-enol forms observed for the monomers remained in the polymers, which could be later photocrosslinked.⁶ Amphiphilic diblock copolymers bearing β -dicarbonyl (acetoacetoxy) chelating residues have been prepared and characterized by different methodologies.⁷ These studies have shown that the aggregation behavior of those copolymers was dependent on different factors, such as the tautomeric form of the β -dicarbonyl ligand (keto/enol) and the nature and amount of the metal ion salt added.

To our knowledge, monomers exhibiting tautomeric structures derived from nitriles (unsaturated β -ketonitriles) have not been studied. These kinds of compounds are important because polymeric materials containing this functionality are known by their important technological applications due to their good mechanical properties, high chemical resistance, processing advantages, and self-adhesive properties.^{8–10} Previous systematic studies on structurally related β -ketonitriles



SCHEME 1 Nitrile–ketenimine and keto–enol equilibria for the MOP monomer.

by mass spectrometry have shown that steric and electronic effects influence the keto–enol and nitrile–ketenimine tautomeric equilibria (Scheme 1).^{11,12} Three unsaturated β -ketonitriles have been synthesized and their thermodynamic parameters of tautomerization in gas phase evaluated by mass spectrometry and compared with those obtained by theoretical calculations.¹³ This study showed that the keto–nitrile tautomer was favored with a good agreement between both methodologies.

Because the reactivity of a compound with tautomeric capacity can be determined from the proportion of each tautomer, the aim of this work was to study the polymerizability of an unsaturated β -ketonitrile monomer under different solvent conditions as well as the tautomeric equilibrium of the copolymers obtained. In addition, we analyzed the solution behavior of the polymers in two solvents of different polarity.

EXPERIMENTAL

Materials

Styrene (98%, PASA S.A.) was freed from inhibitor by washing with aqueous NaOH solution (10 wt %) and then with water until neutrality, dried over anhydrous sodium sulfate, and distilled under reduced pressure before use. The initiator, 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Merck) was purified by recrystallization from methanol before use. Ethyl cinnamate (99%, Aldrich), propionitrile (99.0%, Fluka), sodium (99%, Aldrich), diethyl ether (99%, Merck), ethanol (99.9%, Carlo Erba), methanol (99.9%, Aldrich), chloroform (RPE, Carlo Erba), acetonitrile (HPLC, Sintorgan), tetrahydrofuran (RPE, Carlo Erba), hydrochloric acid (37%, Merck), sodium bicarbonate (99.5%, Fluka), and anhydrous sodium sulfate (99%, Anedra) were used as received without further purification.

Monomer Synthesis

2-methyl-3-oxo-5-phenyl-4-pentenitrile (MOP) was obtained through an adaptation of a method previously described,¹⁴ starting from ethyl cinnamate (Scheme 2). Sodium (11.5 g, 0.5 mol) and absolute ethanol (150 mL) were added in a 500-mL

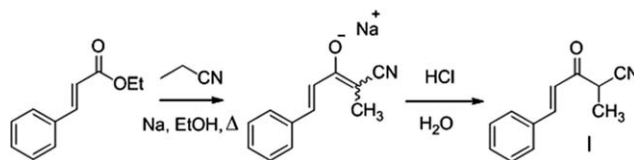
three-necked flask equipped with a stirrer, a condenser, and a dropping funnel. Although this solution was refluxing with stirring, a mixture of propionitrile (17.4 mL, 13.75 g, 0.25 mol), and ethyl cinnamate (51.5 mL, 53.9 g, 0.31 mol) was added through the dropping funnel over a period of 1 hour. The solution was refluxed for 3 hours, cooled, and poured into cold water (600 mL). The aqueous alkaline mixture was extracted three times with portions of diethyl ether (200 mL) and these extracts discarded. The aqueous solution was acidified with cold hydrochloric acid (10 vol %) and extracted three times with 200 mL portions of diethyl ether. Then, the ether fraction was extracted once with water (100 mL), twice with sodium bicarbonate solution (100 mL, 10 wt %), and once with water (100 mL); the aqueous extracts being discarded in turn. The organic phase was dried with anhydrous sodium sulfate, filtered through a fluted filter, and the ether removed by evaporation. The product was purified by recrystallization from methanol to give MOP as yellow crystals. Yield 31.45 g (68 wt %), mp: 44–46 °C. Purity was evaluated by high resolution mass spectrometry: m/z , (relative intensity, assignment) = 185.10 (7.21, $C_{12}H_{11}ON^+$), 131.00 (100, $C_9H_7O^+$), 103.10 (69.31, $C_8H_7^+$), 91.05 (9.65, $C_7H_7^+$), 77.05 (62.90, $C_6H_5^+$).

¹H NMR (200 MHz, Chloroform- d_1 , ppm) δ : 1.66 (>CH–CH₃ keto, d, 3H); 2.85 (=C–CH₃ enol, s, 0.14H); 3.45 (>CH–CH₃ keto, c, 1H); 7.07 (=CH–C=O, d, 1H); 7.5–7.8 (Ar–CH= and ArH, m, 6H). ¹³C NMR (200 MHz, Chloroform- d_1 , ppm) δ : 13.84 (–CH₃ keto); 14.72 (–CH₃ enol); 33.89 (>CH–CH₃ keto); 77.6 (=C–CN enol); 115.47(–CN enol); 116.78 (–CN keto); 117.91 (=CH–CO–); 123.60 (=CH–COH); 128.06 (*ortho*-C Ar); 129.02(*meta*-C Ar); 129.46 (*para*-C Ar); 134.03(Ar–CH=); 135.03 (ArC–CH= enol); 146.74(ArC–CH= keto); 176.82(HO–C= enol); 192.28(>C=O keto).

FTIR (KBr, cm^{-1}): 3400 (O–H enol form), 3050 (C–H, Ar), 2950 (C–H, Al), 2260 (C \equiv N saturated, keto form), 2230 (C \equiv N α,β -unsaturated, enol form) 1715 (C=O), 1680 (C=C olefin), 1660 (C=C enol form) 1600 (C=C Ar), 730 and 680 (C–H Ar monosubstituted).

Polymerization

The copolymers were synthesized by mass radical polymerization with azobisisobutyronitrile as a radical initiator, as previously reported.¹⁵ Briefly, different amounts of both comonomers (total weight 4 g) were introduced into a reaction tube with a preweighed amount of initiator (0.25 wt %). The mixtures were degassed by three freeze-pump-thaw cycles in a vacuum line system, then sealed and immersed into a thermostat at 60 °C for 24 hours in the absence of light. After the reaction, the polymers were purified by three



SCHEME 2 Synthesis of the MOP monomer.

steps of dissolutions in chloroform and precipitation in methanol, centrifuged, and dried under vacuum. This procedure was repeated until only the peak of the polymer was seen by size-exclusion chromatography (SEC). The solution radical polymerization was carried out with solvent addition (acetonitrile, ACN; tetrahydrofuran, THF; toluene, Tol; or chloroform, Chl) so that the monomer concentration was 70 wt %. The other reaction conditions were as described above for the mass radical polymerization.

Characterization

The ^1H NMR and ^{13}C NMR spectra of the monomer were recorded with a Varian Mercury Plus Spectrometer, 200 MHz. Toluene- d_8 , chloroform- d_1 , tetrahydrofuran- d_8 , and acetonitrile- d_3 were used as solvent. The typical spectral conditions were as follows: spectral width 3201 Hz, acquisition time 4.09 s and 8–16 scans per spectrum. The digital resolution was 0.39 Hz per point. The deuterium of the solvent was used as the lock and tetramethylsilane (TMS) as the internal standard. The sample concentration was 0.4 wt % and the spectra were recorded at 40 °C. For the polymers, experiments of NMR, heteronuclear single quantum coherence (HSQC) edited in distortionless enhancement by polarization transfer (DEPT), and heteronuclear multiple bond coherence (HMBC) were carried out. The spectra were recorded with a Bruker Spectrometer, 300 MHz, using chloroform- d_1 and acetonitrile- d_3 as solvent. The deuterium of the solvent was used as the lock and TMS as the internal standard. The polymer concentration was 6.0 wt % at 40 °C.

The Fourier transform infrared (FTIR) spectra of the polymer films deposited onto a sodium chloride window were recorded on a Nicolet 380 FTIR spectrometer between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and 32 accumulated scans. The films were prepared by the solvent casting method: first, a polymer solution in chloroform (5.0 wt %) was prepared and poured onto the sodium chloride window. Then the solvent was allowed to evaporate at room temperature, with the resulting films dried under vacuum until the weight remained constant. In addition, the FTIR spectra in solution were obtained with a Varian 660 IR spectrometer. For this purpose, a polymer solution in CHCl_3 or ACN (15 mg mL^{-1}) was measured inside the mountable liquid cells containing a KBr window. The spectra were recorded between 4000 and 500 cm^{-1} with a resolution of 4 cm^{-1} and 64 accumulated scans. The EZ-OMNIC software was used to analyze the spectra.

Gas chromatography–mass spectrometry (gc–ms) of the monomer was performed by the injection of methanol solutions (1 μL) in an HP 5890 Chromatograph coupled to an HP 5972 A mass selective detector under the following conditions:

- Column: HP5-MS, 30 m \times 0.25 mm \times 5 μm .
- Carrier gas: helium, 0.6 mL/min .

Temperature set points: injector: 200, 250, 275, and 300 °C; oven: 40 °C (5 min), 20 °C/min, and 290 °C; interface: 300 °C; ion source: 185 °C; quadrupole: 150 °C. Electron energy: 70 eV.

The pressure in the mass spectrometer, 10^{-5} Torr, precludes ion molecule reactions.

The average molecular weight and the molecular weight distribution were determined by SEC in a LKB-2249 instrument at 25 °C. A series of four μ -Styragel columns (10^5 , 10^4 , 10^3 , 100 Å pore size) were used with chloroform as eluent. The polymer concentration was 4–5 mg/mL , and the flow rate was 0.5 mL/min . The polymer was analyzed using double detection as previously reported.¹⁶ Mass chromatograms of the polymers were detected by a Shimadzu (SPD-10A) UV/VIS detector at 254 nm (for the phenyl group), whereas the carbonyl group from the MOP comonomer was detected by infrared (IR) absorption at 5.75 μm with a Miram IA spectrophotometer detector. Polystyrene standards supplied by Polymer Laboratories and Polysciences were used for calibration.

The intrinsic viscosity ($[\eta]$) was determined by dissolving the polymer in Chl or ACN under mechanical agitation for 24 h at room temperature. After that, dilutions were prepared from a stock solution such that $0.3 < \eta_{\text{sp}} < 0.8$ (η_{sp} being the specific viscosity).

The viscosities of the dilutions were measured with an Ostwald capillary viscometer ($t_0 > 120$ s) at 25 °C.

RESULTS AND DISCUSSION

Copolymer Synthesis and Characterization

The radical copolymerization of MOP with styrene produces a new copolymer which structure, ^1H NMR spectrum (in acetonitrile) and assignments of resonance signals are shown in Figure 1(a,b). To accomplish the assignment of the signals, a two-dimensional NMR was used. The structure was confirmed by FTIR (NaCl, thin film, cm^{-1}): 3050 (C–H, Ar), 2950 (C–H, Al), 2220 (C \equiv N), 1715 (C=O), 1600 (C=C Ar), 730 and 680 (C–H Ar monosubstituted).

The copolymer compositions were estimated from the integral ratio of the peaks of aliphatic, $I(\text{Al})$, and aromatic, $I(\text{Ar})$, hydrogen close to 2.0 and 7.0 ppm, respectively, using eq 1.

$$F_{\text{MOP}} = \frac{5I(\text{Al})/I(\text{Ar}) - 3}{3} \quad (1)$$

where F_{MOP} represents the MOP composition of the copolymers.

Table 1 shows the polymerization conditions [solvent and MOP monomer mole fraction in the initial mixture of the monomer (f_{MOP}), MOP monomer mole fraction in the polymer (F_{MOP}), conversion, weight-average molecular weight (M_w), and polydispersity index (PDI) of the copolymers synthesized. Here, the decrease in the reaction conversion and the M_w are clearly stated as the content of MOP in the feed increases, which suggests that the MOP monomer has a lower reactivity than styrene. A similar behavior was observed during the copolymerization of other systems including 1,2-disubstituted ethylenic monomers.^{17,18} For all f_{MOP} values, the PDI was close to 2, suggesting, based in theoretical predictions,¹⁹ that the disproportionation or chain

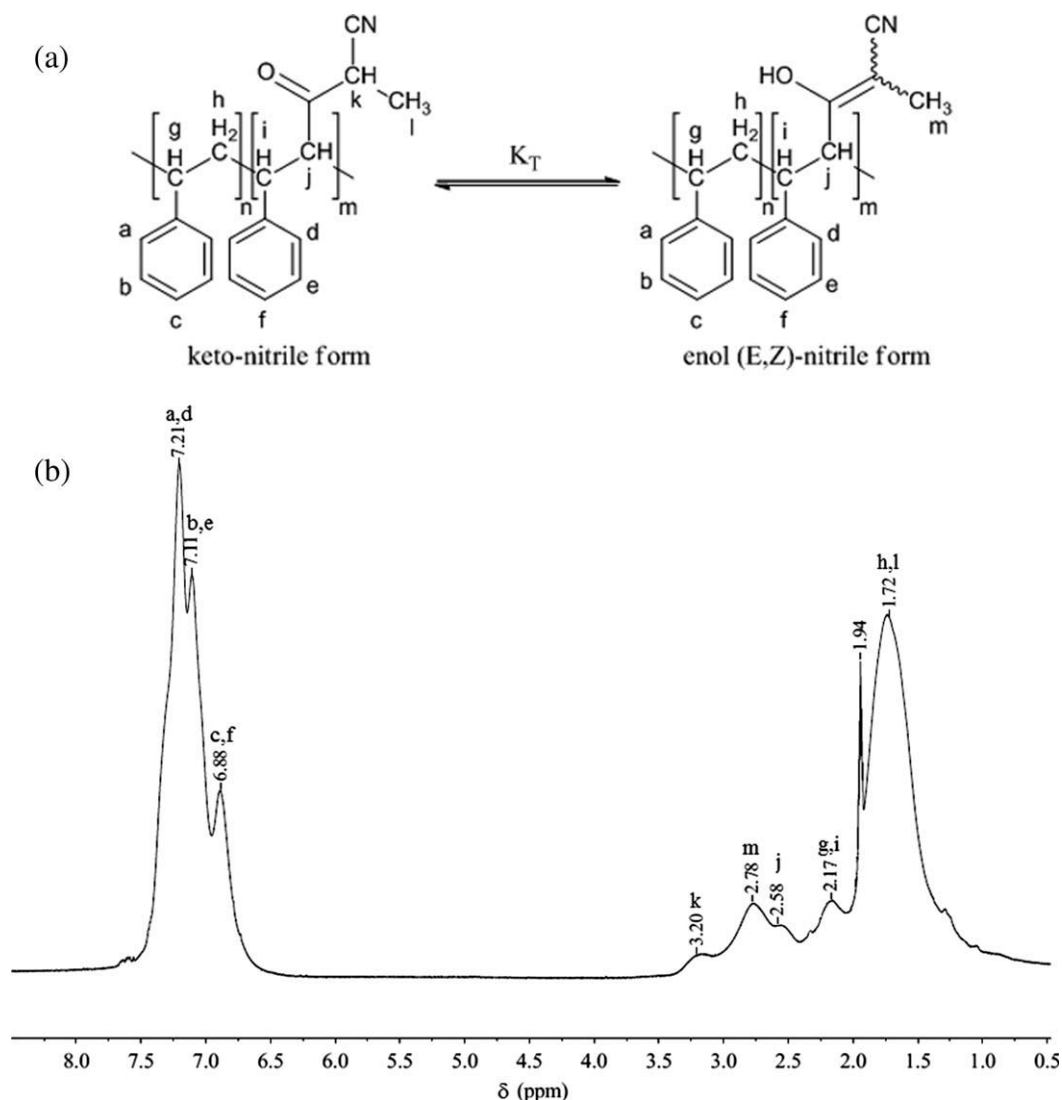


FIGURE 1 Structure of poly(St-co-MOP) (a) and ^1H NMR spectrum of the copolymer prepared from $f_{\text{MOP}} = 0.67$ (b). MOP: 2-methyl-3-oxo-5-phenyl-4-pentenitrile.

transfer mechanisms are the predominant termination modes. This proposal was confirmed by the HSQC-DEPT spectrum (Fig. 2). The insert shows an enlarged region in the HSQC spectrum (between 1 and 3.7 ppm in 1H-axis) represented in trace mode, which revealed the presence of a weak signal localized at $\delta_{\text{H}} = 2.75$ ppm and $\delta_{\text{C}} = 32$ ppm corresponding to terminal methylene group ($-\text{CH}_2-\text{Ph}$) assignable to proposed disproportionation or chain transfer termination mechanisms, as suggested by other researchers.^{20,21}

In relation to the reactions carried out in solution, it is possible to see a significant effect of the solvents on the reaction conversion and F_{MOP} (compounds 6–9). The highest conversion was attained in THF, whereas the lowest was observed in the most polar solvent (ACN). Similarly, the mole fraction of MOP in the copolymer was higher in THF and Tol than that in ACN. These results suggest that the different structures of MOP and/or the different monomer-solvent interactions could influence the copolymerization behavior.

To explain the solvent effect on the copolymerization behavior, we used the simplified form of the Kamlet-Taft linear solvation energy relationship:²²

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \quad (2)$$

where XYZ is the property to be correlated, XYZ_0 is the property related to a standard process, π^* is the dipolarity/polarizability term, α is the hydrogen-bond donating (HBD) capacity, and β is the hydrogen-bond accepting (HBA) capacity. The coefficient of the individual interaction contributions can be determined by using multiple linear correlation analysis. The solvatochromic parameters π^* , α , and β of different solvents for the square multiple correlation analysis were taken from ref. 22.

The Kamlet-Taft equation was applied to our copolymerization system in solution F_{MOP} as the property to be correlated with the solvents: Tol, Chl, THF, and ACN (Compounds 6–9,

TABLE 1 Copolymerization of MOP with Styrene, Conversion (Conv), Weight Average Molecular Weight (M_w), and Polydispersity Index (PDI) of the Copolymers Synthesized

Compounds	Solvent	f_{MOP}^a	F_{MOP}^a	Conv (%)	M_w^b (g/mol)	PDI ^b
1	–	0.2	0.17	34.3	82,400	1.99
2	–	0.5	0.38	22.1	52,500	1.88
3	–	0.67	0.52	16.5	32,600	1.80
4	–	0.75	0.62	14.5	33,200	2.07
5	–	0.9	0.77	18.7	23,300	1.70
6	Tol	0.9	0.83	5.7	9,100	1.54
7	Chl	0.9	0.75	5.8	9,050	1.59
8	THF	0.9	0.87	11.9	19,300	1.65
9	ACN	0.9	0.68	2.71	8,700	1.48
10	–	1	1	1.05	1,900	1.30

Reaction conditions: [AIBN] = 0.25 wt %, 60 °C, 24 hours.

^a f_{MOP} and F_{MOP} are the mole fraction of MOP in the feed and in the copolymer, respectively.

^b Weight-average molecular weight (M_w) and polydispersity index (PDI) determined by SEC according to the ratio M_w/M_n .

Table 1). Because none of the solvents has hydrogen bond donating power, the a term was vanished. As shown in Figure 3, the regression analysis of the monomer mole fraction in the polymer (F_{MOP}) with the solvatochromic parameters gave a good linear correlation according to eq 3:

$$\ln F_{\text{MOP}} = 0.386 - 1.139\pi^* + 0.255\beta \quad (3)$$
$$n = 4 \quad r = 0.994 \quad \text{SD} = 0.007$$

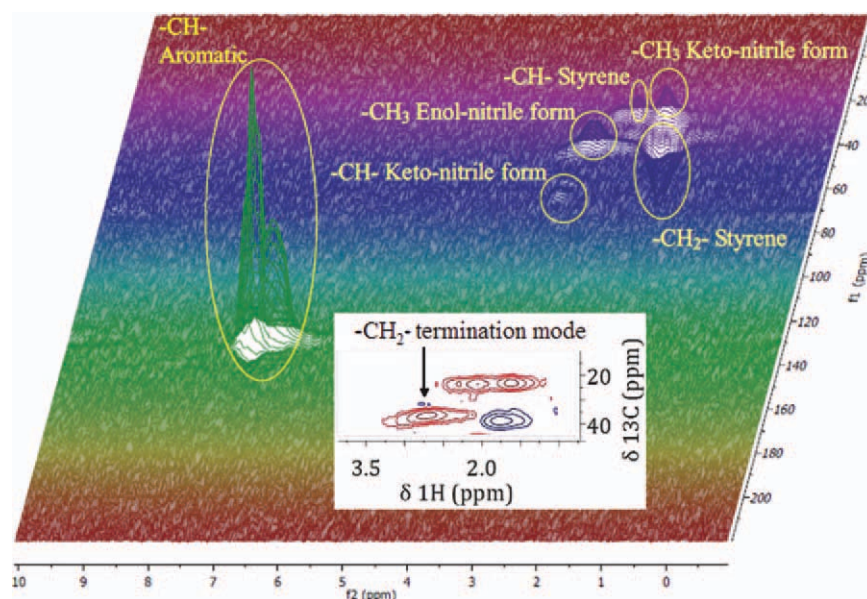
where n is the number of solvents, r the correlation coefficients, and SD the standard deviation. The influence of π^* on F_{MOP} is more important than the β term, indicating that the

solute-solvent dipole-dipole interactions occur preferably. The highest value of F_{MOP} in THF could be explained considering its highest HBA capacity. This result may be related to the content of the enol tautomeric form present in this solvent. To verify this proposal, the MOP enol tautomeric fraction (x_{enol}) contained in the solvents studied was determined by ^1H NMR, which will be explained in the section of tautomeric analysis from monomer and polymers.

In contrast, the M_w of the copolymer obtained in solution condition was lower than that of the copolymer synthesized in bulk (compound 5), which could be attributed to the dilution effect. The PDI was close to 1.5. This results shows, based in theoretical predictions,¹⁹ that the combination of macroradicals is the predominant mechanism of termination of radical growth. In these cases, there was no evidence of terminal methylene groups in the corresponding spectra, confirming that the termination proceeds through the combinations of macroradicals, similar to found by others investigators.²³

Determination of the Monomer Reactivity Ratio

The determination of the reactivity ratios of monomer pairs allows understanding the copolymerization behavior of monomers. The typical comonomer-copolymer composition curve obtained is illustrated in Figure 4, which shows that MOP composition in the copolymer is always smaller than that in the feed. The application of the Fineman-Ross method²⁴ allowed us to obtain the following reactivity ratios: $r_{1(\text{MOP})} = 0.303 \pm 0.015$ and $r_{2(\text{St})} = 0.943 \pm 0.16$. The values obtained, $r_1 < r_2$, indicate the lowest reactivity of the MOP monomer and the preference of the poly(MOP) radical toward the styrene monomer ($1/r_1 = 3.30$). The product $r_1 r_2 = 0.286$ suggests a random distribution of the monomeric units along the chain copolymer and a low tendency towards alternation, contrary to that observed for other 1,2-disubstituted monomers.^{17,25}

**FIGURE 2** Two-dimensional HSQC-DEPT spectrum of copolymer 5 in ACN.

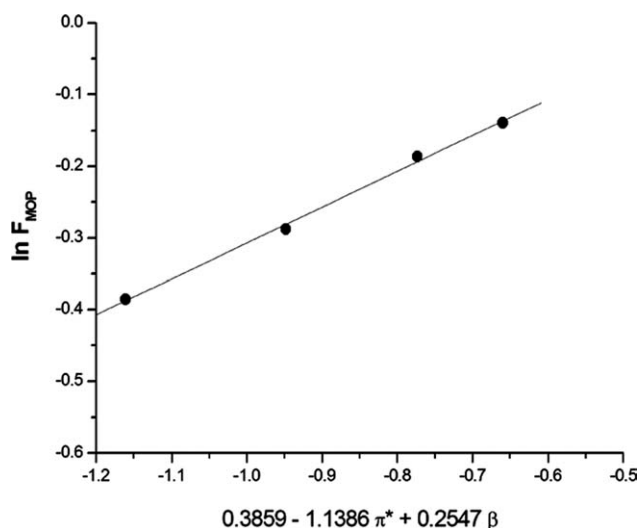


FIGURE 3 Regression analysis of the monomer mole fraction (F_{MOP}) with the solvatochromic parameters.

Tautomeric Analysis from Monomer and Polymers

As mentioned earlier, the polymerizability of monomers that include tautomeric groups depends on the contents of each tautomeric form. Scheme 1 shows the theoretical tautomeric equilibria for MOP: the keto-enol tautomerism through the keto-nitrile (I) and enol (E and Z)-nitrile (II) forms and nitrile-ketenimine tautomerism through the keto-nitrile (I) and keto-ketenimine (III) forms. The existence of all these tautomeric forms in gas-phase has been previously demonstrated by gc-ms.¹³ Through ^1H NMR spectroscopy, the nitrile-ketenimine equilibrium for structurally related compounds could not be observed, due to the lower sensitivity of this method.¹²

The tautomeric equilibria between (I) and (II) tautomers were studied by ^1H NMR using four solvents of different polarity (toluene, chloroform, tetrahydrofuran, and acetonitrile). Figure 5 shows the ^1H NMR spectra (extended zone

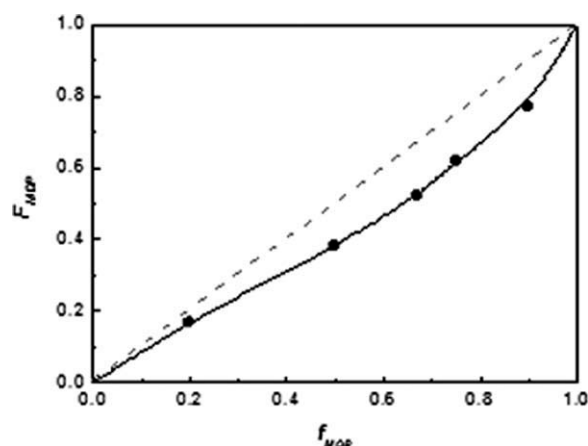


FIGURE 4 Copolymer composition plot for the styrene-MOP system. Polymerization conditions: $[\text{AIBN}] = 0.25 \text{ wt } \%$, 60°C , 24 hours.

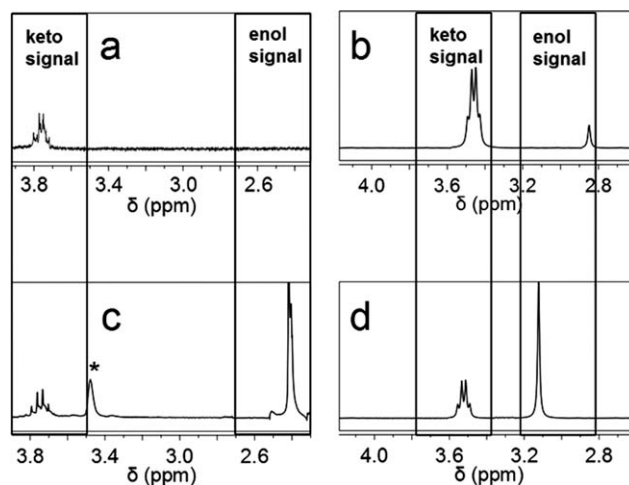


FIGURE 5 ^1H NMR spectra of MOP in: toluene (a), chloroform (b), tetrahydrofuran (c), and acetonitrile (d). Chemical shift corresponding to the hydrogen involved in the tautomeric equilibrium (see Scheme 1).

between 2 and 4 ppm) for the MOP monomer in the four solvents together with the assignment of signals for the keto-nitrile (I) and enol-nitrile (II) form. It is worth noting that this methodology does not allow distinguishing between the geometric isomers (IIa and IIb), and thus these equilibria were not evaluated individually. The rate of keto-enol interconversion is sufficiently slow on the NMR time scale to calculate the tautomeric equilibrium constant (K_T) from the areas (I) obtained by integration of the selected peaks on each spectrum. Thus, the signals at $\delta = 2.85$, 2.42, and 3.12 ppm were assigned to the methyl hydrogen of enol-nitrile (II) form in chloroform, tetrahydrofuran and acetonitrile, respectively. The corresponding signal in toluene was not observed. In contrast, the signals at $\delta = 3.74$, 3.45, 3.73, and 3.52 ppm were assigned to the methine hydrogen of keto-nitrile (I) tautomeric form in toluene, chloroform, tetrahydrofuran, and acetonitrile, respectively. To obtain K_T , it is necessary to divide the value of the integral ratio of the peaks of both tautomeric forms (I_{keto} and I_{enol}) by the number of hydrogen for which integrates, using eq 4.

$$K_T = \frac{I_{\text{enol}}/3}{I_{\text{keto}}} \quad (4)$$

Table 2 present the x_{enol} and K_T values for MOP in the four analyzed solvents. As can be seen, the enolic fraction and K_T

TABLE 2 Tautomeric Constant (K_T) and Enol Molar Fraction (x_{enol}) of MOP in Different Solvents

Solvent	x_{enol}	K_T
Toluene	0	0
Chloroform	0.041	0.005
Tetrahydrofuran	0.161	0.192
Acetonitrile	0.289	0.406

TABLE 3 Chemical Shift of Selected Signals Used to Evaluate the Tautomeric Equilibria in Both Solvents (Chloroform and Acetonitrile)

Compound	Chloroform		Acetonitrile	
	$\delta_{\text{C-H}}$ (keto-nitrile) (H_k)	δ_{CH_3} (enol-nitrile) (H_m)	$\delta_{\text{C-H}}$ (keto-nitrile) (H_k)	δ_{CH_3} (enol-nitrile) (H_m)
2	3.30	2.86	3.33	2.95
5	3.12	2.78	3.20	2.85
10	2.99	2.63	3.17	2.81

grows as far the polarity of the solvents increases, suggesting a highest stabilization of enol tautomeric form in more polar solvents. In contrast, considering the F_{MOP} values obtained in solution polymerization (Table 1), a dependence of copolymer composition with a content of enol form is evident. When the x_{enol} increase, F_{MOP} decrease, suggesting that the enol tautomeric form of MOP exhibited lower reactivity than keto tautomeric form. An exception was observed in THF solvent (highest F_{MOP} value), which was attributed to the highest capacity of this solvent to stabilize the enol tautomeric form through hydrogen bond.

The tautomeric equilibrium of the selected polymers (2, 5, and 10, Table 1) was evaluated in chloroform and acetonitrile through a deconvolutional analysis of the hydrogen signals in the ^1H NMR spectra. HSQC-DEPT and HMBC-DEPT experiments were carried out to determine the signal assignments to each tautomeric form. The first technique allowed discriminating between positive signals, belonging to the methyl and methine groups and negative signals assigned to the methylene groups of styrene. The second technique (data not shown) allowed discriminating the signals corresponding to H methines in position α to carbonyl group (H_j and H_k , Fig. 1). Figure 2 shows the HSQC-DEPT spectrum for copolymer 5 in acetonitrile. The tautomeric equilibrium constant (K_T) in the polymers (Fig. 1a) was calculated, similarly to the monomer, from the I_{keto} and I_{enol} . The position of the hydrogen signal associated with each tautomeric form was dependent on the polymer composition and solvents. For this reason, Table 3 presents the chemical shift of the H selected to evaluate the tautomeric equilibria in both solvents (chloroform and acetonitrile). Thus, Table 4 shows the equilibrium constant values for the samples selected. It is possible to see that for all the compounds the equilibrium constants in acetonitrile are higher than those in chloroform.

This behavior indicates that in the most polar solvent, the enol form is favored respect to the keto form, which is evident from the enol content evaluated as molar fraction of this tautomer (x_{enol}). In ACN, the enol form can participate in hydrogen bond because the hydrogen-bond accepting (HBA) capacity of this solvent through electronic pairs of N, promoting the displacement of the equilibrium to the enol form. The HBA capacity of chloroform to this type of interaction is much smaller, as demonstrated by analyzing the solvent effect on F_{MOP} . A similar behavior was found for other β -ketonitriles.¹²

As it can be seen in Table 4, for the polymers, the K_T values in chloroform increase as the mole fraction of MOP in the copolymer increases. The K_T (ACN)/ K_T (CDCl_3) ratio allowed us to estimate the effect of the macromolecular structure on the tautomeric equilibrium (column 7 of Table 4). This ratio is not constant but highest for the monomer and decreases as F_{MOP} increases.

The K_T (ACN)/ K_T (CDCl_3) relation showed that F values are important in the tautomerism and probably attributed to the prevalent interaction between two MOP units in comparison with the polymer-solvent interactions. A similar behavior has been found by other researchers.²⁶

To confirm this hypothesis, we measured the intrinsic viscosities in CHCl_3 and ACN for a representative sample (copolymer 2, Table 1) and presented them in Figure 6. It is possible to see that within the concentration range of the viscometric determination, $5 < C < 25 \text{ mg mL}^{-1}$, plots are linear. The intrinsic viscosity $[\eta]$ was conventionally obtained from double extrapolation of the Huggins and Kramer equations:

$$\frac{\eta_{\text{sp}}}{C} = [\eta] + k_H[\eta]^2 C \quad (5)$$

$$\frac{\ln \eta_r}{C} = [\eta] + k_K[\eta]^2 C \quad (6)$$

where η_r is the relative viscosity, and 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 and the results are presented in Table 5. It is possible to see that $[\eta]$ in chloroform is almost double that determined in acetonitrile, indicating that the polymer chain acquires more expanded conformation in the first solvent. From the $[\eta]$ data, it is possible to evaluate the hydrodynamic radius R_h , assuming that the polymer coil is a hard sphere so that the radius of the hydrodynamically equivalent rigid sphere is obtained from the following expression:²⁷

TABLE 4 Tautomeric Constant (K_T) and Enol Molar Fraction (x_{enol}) for Selected Samples

Compound	F_{MOP}	K_T (CDCl_3)	x_{enol}	K_T (ACN)	x_{enol}	K_T (ACN)/ K_T (CDCl_3)
MOP	–	0.08	0.074	1.00	0.500	12.5
2	0.38	0.44	0.305	4.00	0.800	9.09
5	0.77	0.71	0.415	3.66	0.785	5.15
10	1	0.88	0.468	2.16	0.683	2.45

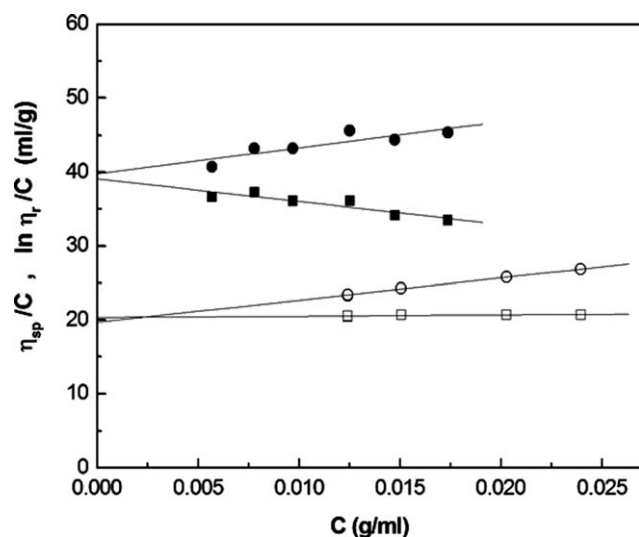


FIGURE 6 Viscosity of poly(St-co-MOP), $f_{\text{MOP}} = 0.50$, as a function of the concentration at 25 °C. Chloroform: (●) η_{sp}/C , (■) $\ln(\eta_r)/C$; acetonitrile: (○) η_{sp}/C , (□) $\ln(\eta_r)/C$.

$$R_h = \left(\frac{3}{10\pi N_A} \right)^{1/3} ([\eta] M_w)^{1/3} \quad (7)$$

The R_h value (Table 5) confirms that the polymer coil is more expanded in CHCl_3 than in ACN. In contrast, the value of 0.22 for the Huggins coefficient (k_H) in CHCl_3 suggests that it is a good solvent, in which polymer-solvent interactions prevail; while the higher value (0.77) obtained in ACN suggests possible interchain interactions, as found in other systems.^{28,29} Because viscosity was measured under a dilute regime, due to $0.3 < \eta_{\text{sp}} < 0.7$ and $C < \text{critical chain overlap concentration}$ ($C^* = 60 \text{ mg mL}^{-1}$ in ACN), the intrachain interactions are more likely, and could be due to intermolecular hydrogen bonding between the OH group of the enol tautomeric form of the MOP unit and the carbonyl group of the corresponding ketonic form of other MOP units within the same chain. Such interactions may be responsible for a more contracted polymer chain conformation with a smaller hydrodynamic radius in acetonitrile, as found in this work.

To confirm the existence of hydrogen bonding interactions, FTIR spectra in solution were obtained. Figure 7 displays the FTIR spectra of copolymer 2 in CHCl_3 and ACN with a range of selected wave numbers. Both spectra showed a band of O—H stretching at 3623 and 3537 cm^{-1} in CHCl_3 and ACN, respectively. However, in the latter solvent, the increase in intensity and width of this band, together with the shift at lower wave numbers, indicated the presence of a hydrogen bond. Bands at

TABLE 5 Intrinsic Viscosity, Huggins and Kramer Constant for the Copolymer 2 ($f_{\text{MOP}} = 0.5$) in Chloroform and Acetonitrile

Solvent	$[\eta]$, mL g^{-1}	R_h (nm)	k_H	k_K	$k_H - k_K$
CHCl_3	39.4 ± 0.5	6.9	0.22	−0.20	0.42
ACN	20.0 ± 0.5	5.5	0.77	0.04	0.73

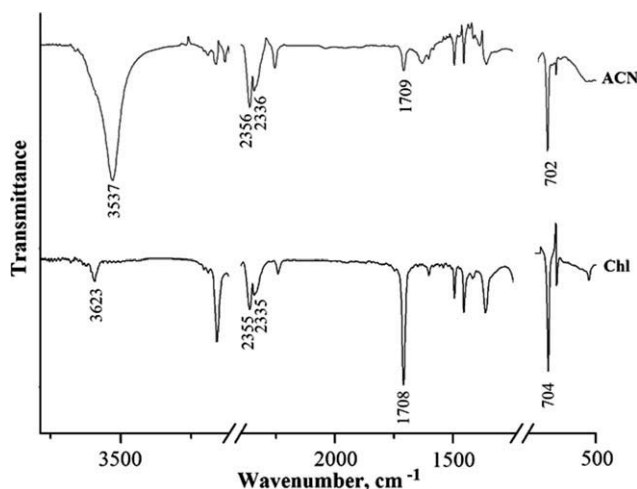


FIGURE 7 FTIR spectra of copolymer 2 in chloroform and ACN.

2355 and 2335 cm^{-1} were assigned to stretching frequencies of nitrile groups present in a saturated structure (keto forms) and in another $\alpha\beta$ -unsaturated structure (enol form), respectively, as observed in the case of our monomer (see experimental part) and by another researcher.³⁰ The stretching frequencies of the carbonyl group are evident at 1708 and 1709 cm^{-1} in CHCl_3 and ACN, respectively, showing a decrease in the intensity in the latter solvent, as expected based on the lower keto molar fraction (highest x_{enol} , Table 4). In absorbance mode, we calculated the integration of C=O and the O—H band respect to the bands at 704 and 702 cm^{-1} corresponding to C—H out of plane deformation frequencies in both solvents. Table 6 presents the values of these relationships, which evidence the differences between both solvents. We could see the higher proportion of enol tautomer in ACN, in agreement with the results obtained by NMR spectrometry.

These interesting results encourage us to think about their potential applications, considering that their functionality can be modeled by changes in the solvent polarity. Recently, Demetriu and Krasia-Christoforou presented an interesting study using a copolymer containing a monomer with a β -ketoester moiety, which exhibited tautomeric forms, and was able to act as an effective metal-ion sensor in a specific solvent.³¹ Thus, our future studies are aimed in this direction.

CONCLUSIONS

New copolymers of MOP with styrene were synthesized and characterized by a number of techniques. The values of

TABLE 6 FTIR Bands Relationship CO/CH(Ar) and OH/CH(Ar) in Different Solvents, Assigned to Tautomeric Form of Copolymer 2 ($f_{\text{MOP}} = 0.5$)

Solvent	CO/CH(Ar)	OH/CH(Ar)
CHCl_3	1.468	0.370
ACN	0.401	17.885

CO and OH bands corresponding to keto and enol form, respectively.

reactivity ratio, r_1 and r_2 , and $r_1.r_2$, showed a tendency toward statistical copolymerization of both monomer and that the MOP monomer is less reactive than styrene and has a low tendency to give homopolymers.

The analysis by NMR, through ^1H NMR, ^{13}C NMR, HSQC, and HMBC allowed quantifying the displacement of tautomeric equilibrium through the deconvolutional analysis of tautomeric signals. The results show that the increase in solvent polarity increases the enol content both in the monomer and in the polymers and the $K(\text{ACN})/K(\text{CDCl}_3)$ relationship showed that the F values are important in the tautomerism.

The viscometric data and FTIR spectra gave further evidences about the existence of tautomerism in the synthesized copolymers and confirm the presence of intramolecular interaction in nonpolar solvents.

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