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Comblike Complexes of Poly(itaconic acid) and Poly(mono methyl itaconate) and Alkyltrimethylamonium Cationic Surfactants

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Summary

A series of complexes from poly(itaconic acid) and poly(mono methyl itaconate) and alkyltrimethylammonium bromide surfactants with linear alkyl groups, containing even number of carbon atoms from 12 up to 22 were synthesized. The complexes were obtained in good yields and were soluble in organic solvents and stable up to temperatures near 150°C. On the other hand, the paraffinic side chains are able to crystallize depending on the methylene number of the surfactant *n*-alkyl chain.

Introduction

Comblike poly(itaconate)s have been widely studied because of their close similarity to poly(alkyl acrylate)s and poly(alkyl methacrylate)s and also, because itaconic acid has a low price and is easy to produce in large quantities [1-4]. Many works have been reported on the synthesis and the study of solution and solid-state properties of different types of poly(*n*-alkyl itaconate)s, such as poly(mono *n*-alkyl itaconate)s [5-9], poly(methyl *n*-alkyl itaconate)s [9-12] and poly(di *n*-alkyl itaconate)s [4, 9, 13-17]. Thermal degradation of these polymers was also studied indicating that in the main step of the degradation process of poly(mono *n*-alkyl itaconate)s, the formation of anhydrides with the release of the side chain takes place [18, 19], while for poly(di *n*-alkyl itaconate)s the depolimerization is the main reaction [20-23]. The side chains of poly(*n*-alkyl itaconate) derivatives are able to crystallize when they reach a minimum length. Thus for poly(mono *n*-alkyl itaconate)s and poly(methyl *n*-alkyl itaconate)s, it was found that at least 14 carbon atoms are needed to allow crystallization [9] whereas for poly(di *n*-alkyl itaconate)s only 12 carbon atoms were enough [4,9].

On the other hand, comblike structures of ionic nature can be easily formed by complexation of polyelectrolites with oppositely charged low molecular weight amphiphilic molecules. The wide variety of available polyelectrolytes and surfactants, as well as their possible use for tailoring the structure and the control of the properties of such complexes has increased the interest in this area [23]. Studies on some interesting type of stoichiometric comblike complexes prepared from the sodium salt of poly(α-L-glutamic acid), poly(γ-glutamic acid) and poly(β-malic acid) and different alkyltrimethylammonium bromide surfactants have been recently reported [23-29].

In this work we report on a series of stoichiometric complexes synthesized from poly(itaconic acid) (PIA) and poly(mono methyl itaconate) (PMI-1) with alkyltrimethylammonium bromide surfactants with linear alkyl groups, containing even number of carbon atoms from 12 up to 22. These complexes will be referred henceforth as *n*ATMA·PIA and *n*ATMA·PMI-1 where *n* is the number of carbon atoms in the alkyl side chain.

Experimental

Materials

Itaconic acid and linear alkyltrimethylamonium bromide surfactants ($RN^+Me_3 \cdot Br^-$) with $R=C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ and $C_{18}H_{37}$ were purchased from Aldrich Chemicals and those with $R=C_{20}H_{41}$ and $C_{22}H_{45}$ were synthesized according to literature procedures [30]. Organic solvents were of analytical grade and were used without further purification. Water used in the preparation of the complexes was distilled and deionized in a *Mili Q* water purification system and boiled before use.

Synthesis

Poly (itaconic acid) was prepared by polymerization of itaconic acid using potassium persulfate in water following the procedure described by Lárez, *et al* [31]. ^{1}H-NMR (in D_2O) (ppm) 2.8 (broad 2H C**H**$_2$-COO), 2.4 (broad 2H C**H**$_2$-C). ^{13}C-NMR (in D_2O) (ppm) 178.6 (C-**C**OOH), 174.2 (CH$_2$-**C**OOH), 46.2 (CH$_2$-**C**), 43.3 (**C**H$_2$-COO), 35.3 (**C**H$_2$-C).

Mono methyl itaconate (MI-1) was obtained by esterification of itaconic acid with a large excess of methanol using acetyl chloride as initiator.

Poly(mono methyl itaconate) (PMI-1) was prepared by bulk polymerization at 75°C during two and a half hours under nitrogen atmosphere using AIBN (1% mol/mol) as initiator. The polymer obtained was purified by dissolution in acetone and precipitation with chloroform. The purification procedure was repeated several times (yield 86.7%). ^{1}H-NMR (in D_2O) (ppm) 3.6 (s 3H COOC**H**$_3$), 2.7 (broad 2H C**H**$_2$-COO) , 2.3 (broad 2H C**H**$_2$-C). ^{13}C-NMR (in D_2O) (ppm) 178.4 (**C**OOH), 173.4 (**C**OOCH$_3$), 52,4 (COO**C**H$_3$), 46.2 (CH$_2$-**C**), 44.3 (**C**H$_2$-COO), 36 (**C**H$_2$-C).

Ionic complex of poly(itaconic acid) and poly(mono methyl itaconate) were prepared following the procedure described by Pérez-Gamero, *et al* [26]. A 0.05 N of an aqueous surfactant solution was slowly added to an equivalent amount of 0.05 N aqueous solution of the polymer sodium salt under magnetic stirring in a temperature range of 25 to 60°C (see Table 1). When the addition was completed, the mixture was allowed to rest at room temperature. The precipitated complexes were repeatedly washed with water and purified by reprecipitation with ether or acetone from chloroform solutions.

Characterization

Infrared spectra were registered on a Perkin-Elmer 2000 instrument from KBr discs samples or films prepared by casting.

NMR spectra were recorded on a Bruker DRX 400 spectrometer at the indicated temperatures from samples dissolved in deuterated solvents using tetramethylsilane (TMS) or trimethylsilylpropanesulfonate (TMPS) as internal references.

Solid-state ^{13}C CP/MAS NMR spectra were recorded at 75.5 MHz in the temperature range 20-60ºC. A Bruker AMX 300 instrument equipped with a CP-MAS accessory and variable temperature unit was used. Samples of 200 mg were spun at 4 kHz in a cylindrical ceramic rotor. All the spectra were acquired with contact and repetition times of 2 ms and 5 s, respectively and 256 to 1024 transients were accumulated. The spectral width was 31,2 kHz, and the number of data points was 4K. Chemical shifts were externally calibrated against the higher field peak of adamantane appearing at 29.5 ppm relative to TMS.

Calorimetric measurements were performed with a Perkin-Elmer DSC-7 calibrated with indium. Samples of about 5 mg were heated or cooled at rates of 10ºC min^{-1} under an ultra pure nitrogen atmosphere for temperatures ranging from –40 to 120ºC.

Thermo-gravimetric analysis, TGA, were carried out on a Perkin-Elmer TGA-7 thermobalance with similar conditions as those used in DSC runs but within a temperature range of 25 to 500ºC.

Wide angle X-rays scattering (WAXS) experiments were performed in a Philips automatic horizontal axis diffractometer using Cu Kα-Ni filtered radiation. Spectra were taken at various temperatures from -5 to 70°C with the scattering angle 2 θ varying from 3 to 50°.

Results and Discussion

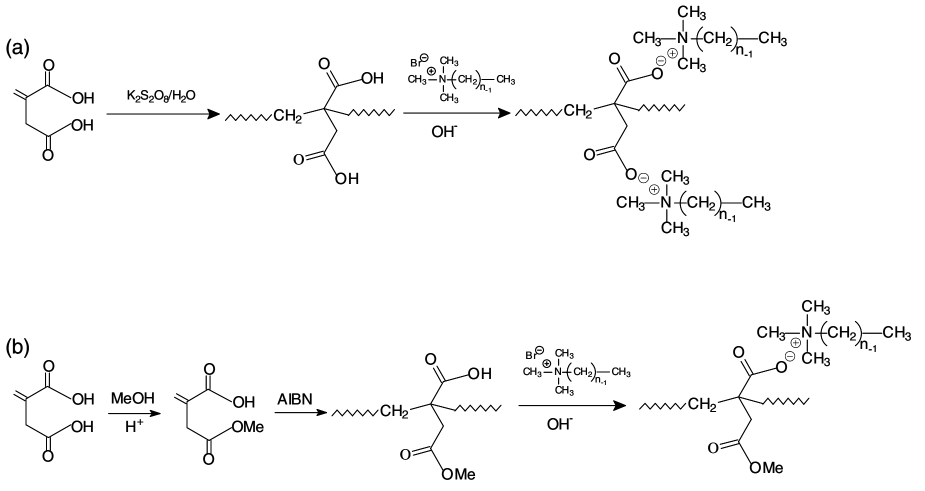
Synthesis and characterization of nATMA·PIA and nATMA·PMI-1

Poly(itaconic acid) and poly(mono methyl itaconate) prepared in this work were obtained in yields of 61.6 and 86.9%, respectively, and the synthetic route used allows to obtain polymers with molecular weights in the order of 5x10^5 Da.

Additionaly, carbonyl and quaternary carbon signals observed in ^{13}C-NMR spectra of PIA and PMI-1 are similar to those appearing in the spectrum previously reported by Lárez, *et al* [31] indicating that both polymers are almost atactic, with slight predominance of sindiotactic sequences. The synthetic routes used for the preparation of the complexes are shown in Scheme 1.

All complexes prepared in this work were solids and soluble in organic solvents as chloroform, methanol or ethanol but insoluble in water, which is a good solvent for PIA, PMI-1 and their sodium salts. This behavior is similar to that found for other ionic complexes [23-28] and may be considered as an evidence of the complexes formation. Yields were found to oscillate between 60 and 90% and some results obtained for *n*ATMA·PIA and *n*ATMA·PMI-1 are summarized in Table 1. On the other hand, films obtained by solvent evaporation of these complexes are not susceptible of orientation as usually occurs with most of their covalent analogs [9].

Figure 1 shows the IR spectra of *14*ATMA·PIA, and *14*ATMA·PMI-1 which may be considered representatives of the series, and compared with PIA, PMI-1 and tetradecyltrimethylamonium bromide (*14*ATMA·Br) spectra. The spectra of the complexes exhibit the characteristic absorptions of both, the poly(itaconic acid) or poly(mono methyl itaconate) and alkyltrimethylammonium moieties. The shifting of the carbonyl band of the acid, that appear at 1722 cm^{-1} to 1575 cm^{-1} which is characteristic of the carboxylate group and the absence of the OH stretching acid signal at 3600 cm^{-1} in the complexes spectra corroborate the complex formation. As for poly(γ,D-glutamic acid) complexes [26], water is also present in these complexes, as may be seen by the absorption centered at 3500 cm^{-1}, which could not be removed by drying under vacuum for days.



Scheme 1. (a) Synthesis of *n*ATMA·PIA. (b) Synthesis of *n*ATMA·PMI-1.

Table 1. Synthesis results and thermal behaviour of *n*ATMA·PIA and *n*ATMA·PMI-1.

Complex	T(a) (°C)	Yield (%)	T_d(b) (°C)	Weight-loss(c) (%)	ATMA moiety (%)(d)	T_m(e) (°C)	ΔH(e) (KJ/mol)	n_c(f)
*12*ATMA·PIA	25	61.6	234	67.7	39.0	-	-	-
*14*ATMA·PIA	25	76.5	237	69.4	40.0	-7.4	8.8	3.2
*16*ATMA·PIA	30	66.2	249	71.7	40.8	26	20.2	7.3
*18*ATMA·PIA	40	78.1	262	72.6	41.4	52	35.0	12.6
*20*ATMA·PIA	50	69.7	285	73.2	42.1	61	43.3	15.6
*22*ATMA·PIA	60	75.0	290	74.8	42.6	70	52.8	19.0
*12*ATMA·PMI-1	40	80.8	205	62.0	61.4	-	-	-
*14*ATMA·PMI-1	40	74.9	207	64.0	64.1	-	-	-
*16*ATMA·PMI-1	40	91.0	211	67.0	66.5	-	-	-
*18*ATMA·PMI-1	40	73.7	229	67.0	68.6	23	8.7	2.9(g)
*22*ATMA·PMI-1	40	65.2	240	60.0	72.0	57	11.7	3.8(g)

(a)Complex preparation temperature. (b)Decomposition temperature corresponding to the maximum of the DTGA curve. (c)Percentage of weight-loss in the main degradation step measured by TGA. (d)For *n*ATMA·PIA weight % of one chain. (e)Measured by DSC. (f)Estimated number of crystallized methylenes from DSC measurement. (g)Assuming a hexagonal lattice $n_c = \Delta H_f / 3.05$ KJ/mol.

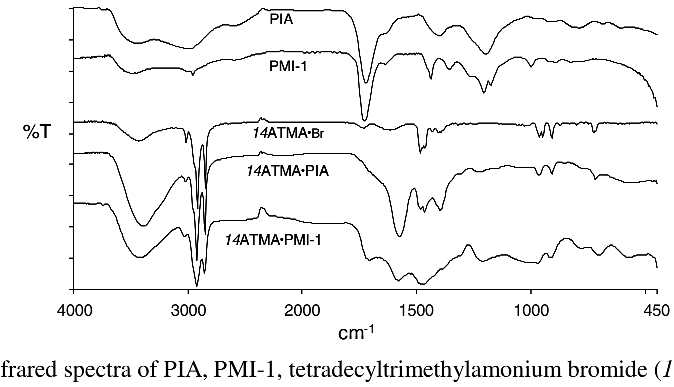


Figure 1. Infrared spectra of PIA, PMI-1, tetradecyltrimethylamonium bromide (*14*ATMA·Br), *14*ATMA·PIA and *14*ATMA·PMI-1.

^{13}C-NMR spectra of, *14*ATMA·PIA, *16*ATMA·PIA, *18*ATMA·PIA, are shown in Figure 2. All carbons of the surfactant moiety are present, as well as the carbonyl groups carbons and the carbons of the main chain which appear as very broad signals, as it happens in the case of the covalent analogs [9]. The ^{1}H-NMR spectra for *n*ATMA·PIA whereas ^{1}H and ^{13}C-NMR spectra for *n*ATMA·PMI-1 only show the signals corresponding to the surfactant moiety when they were carried out in deuterated benzene or chloroform regardless of the temperature at which they were performed. The main chain carbons appear also as broad bands. This broadening could be related with the restricted mobility of the main chain.

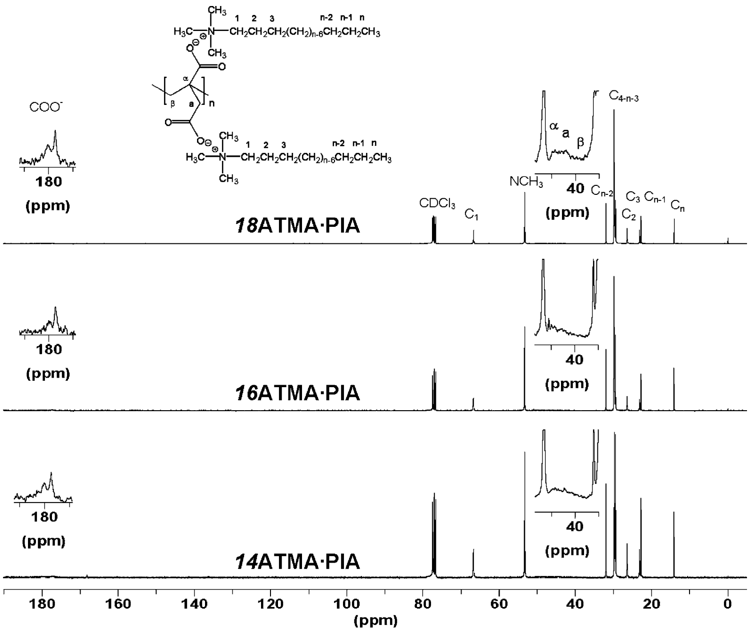


Figure 2. ^{13}C NMR spectra in deuterated chloroform at 50°C of some *n*ATMA·PIA.

Thermal properties

The thermal stability of the complexes was evaluated by TGA. As representative members of both series, TGA traces of *12* and *18*ATMA·PIA and *16* and *22*ATMA·PMI-1 are shown in Figure 3 A and B, respectively. As it may be appreciated, complexes appeared to be stable up to 150°C with a maximum decomposition in the range of 200 to 250°C. Below 200°C the little weight loss shown in the TGA traces is attributed to the release of hydration water which was previously observed in the IR spectra (see Fig. 1). For *n*ATMA·PMI-1 the % weight loss in the main step decomposition is close to the proportion of alkyltrimethylammonium moiety in the complexes and the weight loss for *n*ATMA·PIA is rather than the proportion of one surfactant chain, as may be seen in Table 1. On the other hand, a preliminary analysis by IR spectroscopy was carried out to examine the volatiles and the solid insoluble residue produced at this stage. The volatile fraction showed the presence of hydrocarbon and CO_2 bands, while in the solid residue a significant decrease of the C-H bands and the lack of carboxylate groups was observed. These facts strongly suggest that during the thermal decomposition, surfactant chains are released followed by the fragmentation of the surfactant alkyl chain encompassed by the destruction of the ionic complex. It is well known that in the thermal degradation of poly(mono *n*-alkyl itaconate)s the degradation mechanism involves anhydride formation with the release of the side chain and decarboxylation [18,19]. Elimination of water and formation of poly anhydride followed by decarboxylation has also been reported for thermal degradation of PIA [32]. Similar processes may be occurring here, but more work must be done to have conclusive results.

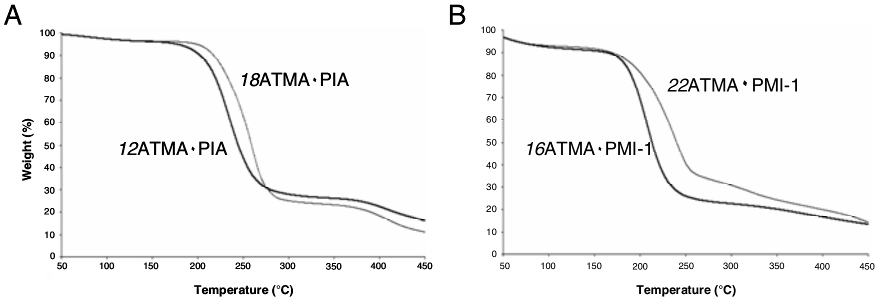


Figure 3. TGA traces of (A) *12*ATMA·PIA and *18*ATMA·PIA and (B) *16*ATMA·PMI-1 and *22*ATMA·PMI-1.

As for comblike polymers, it is well known that *n*-alkyl chains of the surfactant moiety are able to crystallize when they reach a minimum length [23, 26]. In order to determine if the *n*-alkyl chains of the surfactant moiety are able to crystallize in *n*ATMA·PIA and *n*ATMA·PMI-1 complexes, a DSC study was carried out. As it can be observed in Figure 4, DSC heating scan recorded for *12*ATMA·PIA did not show any endotherm. Nevertheless for *14*ATMA·PIA to *22*ATMA·PIA endothermic peaks at temperatures between -7 to 70°C are displayed and attributed to the fusion of the paraffinic phase made of *n*-alkyl side chains. As it illustrated in the insert of Figure 4, these transitions were reversible on cooling and reheating. At it happens with melting temperature, T_m, the enthalpy involved in the fusion also increased with the value of *n*.

For *n*ATMA·PMI-1, the endothermic peaks are smaller than those measured for *n*ATMA·PIA and are only observed when $n \geq 18$. These results indicate that the minimum length of the *n*-alkyl chain of the surfactant moiety required for crystallization is 14 carbon atoms in *n*ATMA·PIA and 18 in *n*ATMA·PMI-1. The values of T_m and ΔH_m for both series are summarized in Table 1.

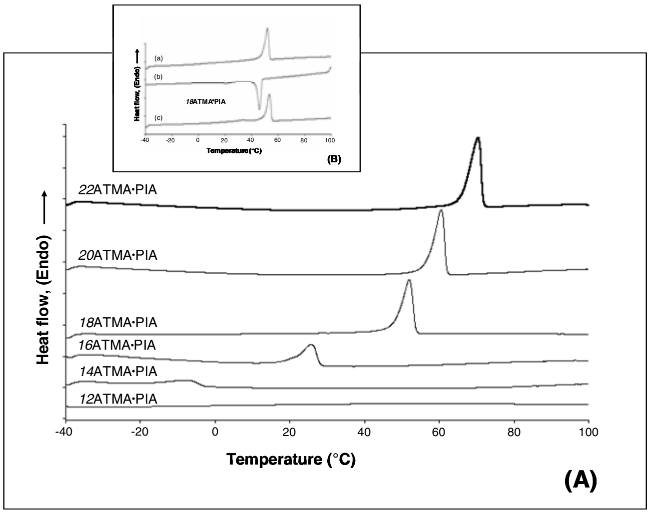


Figure 4. (A) DSC heating scans at 10°C/min for series of *n*ATMA·PIA. (B) Insert *18*ATMA·PIA (a) first heating, (b) cooling, (c) second heating.

The enthalpy associated with the melting process may be used to estimate the fraction of methylene units participating in the paraffinic crystalline phase using the following equation [33]:

$$\Delta H_m = \Delta H_{m(e)} + nk$$

Where *n* is the number of methylene units and methyl terminal group in the alkyl chain, $\Delta H_{m(e)}$ is the contribution from the chain ends and *k* is the fusion enthalpy per mol of CH_2 unit.

When the measured fusion enthalpies (ΔH_m) were plotted *vs.* *n* a linear correlation was found as it can be seen in Figure 5, and the approximate number of methylene units that are crystallized (n_c) can be estimated by using the equation:

$$n_c = \Delta H_m / k$$

Values obtained for *n*ATMA·PIA are listed in Table 1. In all cases values for both, ΔH and the number of crystallized methylenes, are lower than those calculated for their covalent analogs [9]. In the case of *18* and *22*ATMA·PMI-1 the number of crystallized methylenes in the *n*-alkyl chain was estimated assuming that they crystallize in an hexagonal lattice, whereas the fusion heat reported for a crystal-liquid transition of lineal alkanes is in the order of 3 KJ/mol·CH_2 [34] (see Table 1).

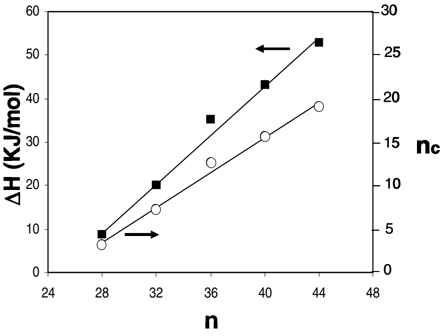


Figure 5. Variation of the number of crystallized CH_2 (o) and enthalpy (■) *vs.* *n* for *n*ATMA·PIA.

Further studies about the crystallization of the *n*-alkyl chains of the alkyltrimethylammonium moiety were performed by solid state ^{13}C NMR and WAXS. Figure 6 shows the ^{13}C CP/MAS NMR expanded spectra of *18*ATMA·PIA in the region where most of the side chain carbons appear. In the spectrum performed at 25°C (Fig. 6 A), a temperature lower than the transition observed by DSC, a peak located at around 33 ppm and assigned to the inner methylenes of the long alkyl chains in all *trans* conformation can be observed. At 60°C, temperature above the transition, this signal completely disappears and a new peak located at approximately 30 ppm emerges as it may be observed in the spectrum presented in Fig. 6 B. This new peak can be assigned to methylene units in fast equilibrium between *trans* and *gauche* conformations characteristic of a molten state. These results are similar to those previously reported for poly(*n*-alkyl itaconate)s [9, 12] and corroborate that the endothermic signal observed in the DSC traces, is due to the melting of the paraffinic phase of the surfactant.

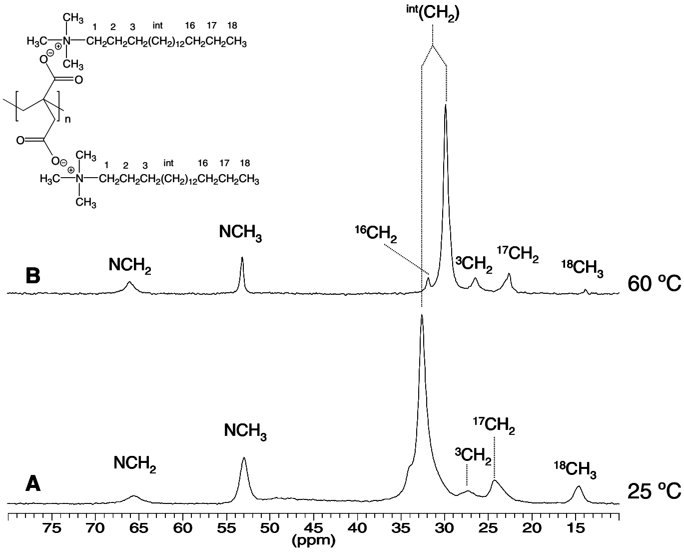


Figure 6. Solid state ^{13}C CP/MAS NMR of *18*ATMA·PIA at (A) 25°C and (B) 60°C.

An additional observation from the NMR spectra is that the chemical shifts at room temperature of the methyl and terminal methylene, $^{18}CH_3$ and $^{17}CH_2$ in spectrum A of Fig. 6, appear near 14.5 and between 24-25 ppm respectively. These chemical shifts are close to those reported for *n*-alkanes crystallized in hexagonal form [35]. The fact that these values are similar to the observed ones for the equivalent carbons in the alkyl side chains of poly(*n*-alkyl itaconate)s [9, 12], strongly suggests that the side chains of this series are also crystallized in an hexagonal lattice.

Finally WAXS experiments were carried out for all samples. The diffractograms of both complexes *n*ATMA·PIA and *n*ATMA·PMI-1 with $n \geq 18$ were recorded at various temperatures and they showed similar features: the sharp reflection corresponding to an interplanar spacing of at 4.2Å, characteristic of a crystalline paraffinic hexagonal phase exists at room temperature and up to temperatures below the melting temperature determined by DSC. At higher temperatures the amorphous regions contribution to the scattered intensity increases drastically as shown by the wide signal at 4.5 Å, together with an important intensity reduction from the crystalline reflection. These changes in the crystallinity degree may be appreciated in Figure 7 for *18*ATMA·PIA. The scan labeled (c) is obtained after the recrystallization which occurs during the cooling from 60ºC to room temperature and it is readily seen that the crystallinity degree is now lower than on the first run (a) before reaching the molten state (b). However, for *14* and *16*ATMA·PIA although by DSC a weak endotherm was detected, the diffractograms taken at low temperatures did not show any significant contribution from crystalline regions. This discrepancy might be due to the imperfect crystallization which occurs for these short chains which render them less noticeable by diffraction methods.

WAXS, DSC and solid state NMR results confirm that the *n*-alkyl chains of the surfactant moiety are able to crystallize forming hexagonal lattices when they reach

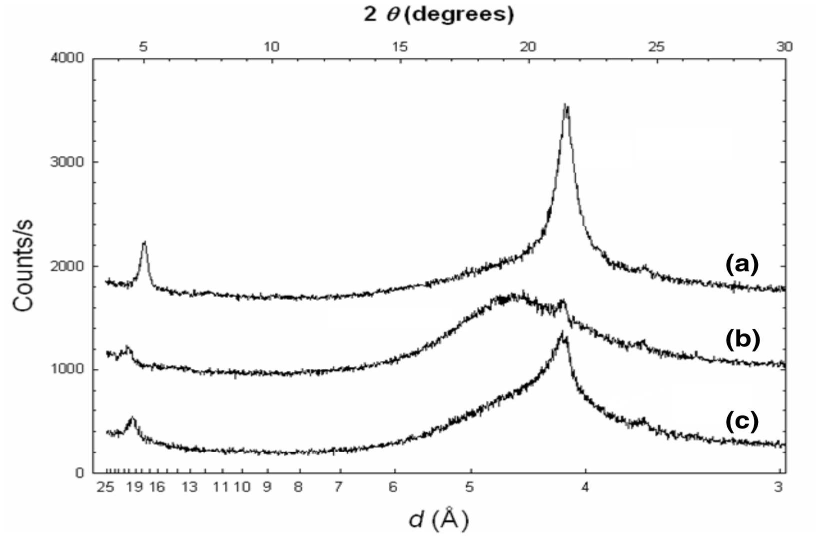


Figure 7. Diffractograms of *18*ATMA·PIA complex at different temperatures. (a) 25°C, (b) 60°C, (c) 25°C after heating.

a minimum length. Unfortunately oriented films of these materials could not be obtained to gather more information on their crystalline structure or about the conformation adopted by the main chain in the complexes.

Conclusion

In this work it has been shown that it is possible to synthesize complexes from poly(itaconic acid) or its methyl ester and alkyltrimethylammonium bromide surfactants with relative good yields. All complexes are soluble in organic solvents, insoluble in water and are stable up to temperatures near 150°C. In solid state, the alkyl side chains of complexes derived from PIA are able to crystallize when they contain are at least 14 carbon atoms long. For PMI-1 derivatives crystallization only occurs for *n*-alkyl side chains with 18 o more carbon atoms.

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References

1. Tate B.E. (1967) Adv. Polym. Sci., 5: 214
2. Cowie J.M.G, Haq C. (1977) Br. Polym. J., 9: 241
3. Cowie J.M.G. (1979) Pure and Appl. Chem., 51: 2331
4. Cowie J.M.G., Haq Z, Mc Ewen I.J., Veličković J. (1981) Polymer, 22: 327
5. León A, Gargallo L, Horta A. (1991) J. Polym. Sci., 27: 2337
6. Gargallo L, Radić D., León A. (1985) Makromol. Chem., 186: 1289
7. León A, Gargallo L, Radić D., Horta A. (1991) Polymer, 32: 761
8. Ribes-Graus A., Díaz-Calleja R., Gargallo L., Radić D. (1990) Polymer 32: 2755
9. López-Carrasquero, F., Martínez de Ilarduya A., Cárdenas A., Carrillo M., Arnal M.L., Laredo E., Torres C., Mendez B., Müller A., (2003) Polymer, 44: 4969
10. León A., López M., Gargallo L., Radić D., Horta A. (1990) J. Macromol. Sci., Phys., B29: 351
11. León A., Gargallo L., Radić D., Bravo J., Horta A. (1992) Makromol. Chem., 193: 593
12. Carrillo M., Martínez de Ilarduya A., Arnal M.L., Torres C., López-Carrasquero F. (2002) Polym. Bull., 48: 59
13. Cowie J.M.G., Henshall S.A.E., Mc Ewen I.J., Veličković J. (1977) Polymer, 18: 612
14. Veličković J., Filipović J. (1984) Makromol. Chem., 185: 569
15. Arrigí V., Mc Ewen I.J., Colmes P.F. (2004) Macromolecules, 37: 6210
16. Hirano T., Tateiwa S., Seno M., Sato T. (2000) J. Polym. Sci. Part A Polym, Chem. 38: 2487
17. Genix A.-C, Lauprétre F. (2005) Macromolecules, 38: 2786
18. Velada J.L., Hernaez E., Cesteros L.C., Katime I. (1996) Polym. Degrad. and Stab., 52: 273
19. Velada J.L., Cesteros C., Madoz A., Katime I. (1995) Macromol. Chem. Phys., 196: 3171
20. Bošković G., Katsikas L., Veličković J.S., Popović I.G. (2000) Polymer, 41: 5769
21. Popović I.G., Katsikas L., Veličković J.S. (2005) Polym. Degrad. and Stabil., 89: 153
22. Popović I.G., Katsikas L., Veličković J.S. (2005) Polym. Degrad. and Stabil., 89: 164
23. Ponomarenko E.A., Tirrell D.A., MacKnight W.J. (1996) Macromolecules, 29: 8751
24. Ponomarenko E.A., Waddon A.J., Bakeev K.N., Tirrell D.A., MacKnigth, J. (1996) Macromolecules, 29: 4340

25. Ponomarenko E.A., Waddon A.J., Tirrell D.A., MacKnigth J. (1996) Langmuir, 12: 2169
26. Pérez-Gamero G., García-Alvarez M., Martínez de Ilarduya A., Fernández C., Campos L., Muñoz-Guerra, S. (2004) Biomacromolecules 5: 144
27. García-Alvarez M., Alvarez J., Alla A., Martínez de Ilarduya A., Herranz C., Muñoz-Guerra S. (2005). Macromol. Biosci., 5: 30
28. Portilla-Arias J.A., García-Alvarez M., Martínez de Ilarduya A., Holler E., Muñoz-Guerra S. (2006). Biomacromolecules, 7: 161
29. Alemán C., Muñoz-Guerra S. (2003) Polímeros: Ciencia e Tecnología, 14: 250
30. Hendrix W.T., von Rosenberg J.L. (1976) J. Am. Chem. Soc., 98: 4850
31. Lárez V.C., Canelón F., Millán E., Perdomo G., Katime I. (2002) Polymer Bull., 49: 119
32. Filipović J.M., Katsikas L., Popović I.G., Veličković S.J., Djakov T.A., Petrović-Djakov D.M., (1997) J. Thermal Analysis, 49: 335
33. Jordan E.F. Jr., Feldeisen D.W., Wrigley A.N. (1971) J. Polym. Sci. Part A-1, 9: 1835
34. Broadhurst M.G. (1962) J. Res. Natl. Bur. Stand. Sect. A, 66: 241
35. VanderHart D.L. (1981) J. Mag. Reson., 44: 117