

# Synthesis and Characterization of Low-Molecular-Weight Polyacrolein

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**ABSTRACT:** Acrolein was polymerized in a polar solvent in the presence of *tert*- and *sec*-butyl lithium as initiators. Using a low monomer to initiator molar ratio and 1-h reaction time, cyclic structures were shown to be formed in the main chain of the resulting oligomers. The influence of different monomer to initiator molar ratios on molecular weight and on molecular weight distribution was investigated. Chain-transfer reactions toward the monomer resulted in lower molecular weights and narrower polydispersions as

[M]/[I] increased. The influence of initiator type on the polymer molecular weight was also evaluated. FTIR analysis of the degradation products at different heating temperatures indicated that the oligomers structure is composed of aldehyde, ether, and vinyl functional groups. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1771–1779, 2009

**Key words:** polyacrolein; anionic polymerization; alkyl lithium; thermogravimetric analysis

## INTRODUCTION

Functionalized polymers have been constantly studied because of their versatility toward the preparation of new materials. Several classes of polymers have been employed to achieve this goal, like polyamides, polyamines, polyacids, polyalcohols, polyaldehydes, among others. The interest in linear chain, soluble, and biocompatible polymers has grown considerably to attend to medical, pharmacological, and biotechnological requirements. Lynn et al.<sup>1</sup> proposed the synthesis of 140 poly( $\beta$ -amino ester); 70 of them were water-soluble and, within this group, 56 formed complexes with DNA molecules. Hartmann et al.<sup>2</sup> developed a new route to synthesize linear, monodisperse poly(amidoamines) from diamines and diacids, with well-defined monomer sequences. Several polysaccharides were modified for the production of bioconjugates.<sup>3–12</sup>

Polymers containing available aldehyde groups are particularly useful in protein modification and enzyme immobilization. Proteins can be immobilized through covalent bonding, and their conformation can be retained.<sup>13</sup> The aldehyde group easily reacts with primary amine groups in proteins originating

imines, which in turn can be reduced to amines, which are stable in physiological medium. Tunçel et al.<sup>14</sup> synthesized polymers containing imine groups, to be used as complexing agents for heavy metals. Shiomi et al.<sup>15</sup> printed the conformational space of hemoglobin in a silica matrix for the selective purification of this protein. They were able to achieve such results by anchoring aldehyde groups presented in hemoglobin to silica through covalent bonding.

Acrolein is a reactive monomer, which possesses a conjugated double bond system. It can be polymerized by radical, cationic, and anionic initiation, as well as by electrotechniques.<sup>16</sup> Synthesis via radical and cationic polymerization leads to insoluble polymers even at low conversion rates.<sup>17</sup> On the other hand, anionic polymerization, under certain conditions, may produce soluble polymers. The potential problems caused by the presence of polar side groups of acrolein are mainly the attack of either the initiator or the living end at the carbonyl group of the monomer, which may lead to termination. Also, activation of the protons in the  $\alpha$ -position to the carbonyl group may lead to monomer transfer reactions. Moreover, the bidentate character of the active centers may cause the monomer to be attacked not only by the carbanion (1,2-addition) but also by the enolate oxygen (1,4-addition). Therefore, acrolein may polymerize through opening of three different bonds: (1,2); (1,4); and (3,4) additions. Accordingly, aldehyde groups can be found in polyacrolein microstructure, as well as C=C double bonding, vinylic and aliphatic ether groups. The complexity of studying a monomer, which may produce a chained molecule with different structural units, is

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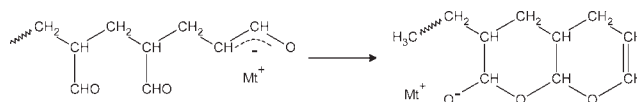
Contract grant sponsor: CNPq; contract grant number: Proc. 47.5320/2004-2.

that the synthesis of the desired molecule will strongly depend on the reaction conditions. Nevertheless, it is advantageous to use a molecule with differentiated groups, as it can add an amphiphilic character to the material, which is very much interesting from the cellular adhesion point of view. Teramura et al.<sup>18</sup> have studied the interaction of five water-soluble synthetic polymers with the living cellular surface and their respective elimination processes. It was verified that polymers with amphiphilic character presented good adhesion to the proteic cellular membrane, and therefore, they were good candidates for cellular transplant therapy.

In anionic polymerization, the monomer insertion to the growing chain end depends on the counterion size and also on the complexation or the dissociation power of the solvent. The polymerization of acrolein is very much dependent on the reaction temperature, and when it is performed at room temperature, gels may be formed. For reaction times longer than 6 h, gel production contributes to increase the difficulty of analysis.<sup>19</sup>

Gulino and Pascault<sup>20</sup> have studied the microstructure of polyacrolein produced by polymerizations initiated by naphthalene-Li and naphthalene-Na. For these polymerization reactions, they used a monomer to initiator molar ratio ( $[M]/[I]$ ) between 350 and 5000 and long reaction times (above 3 h). The authors suggested a mechanism to explain the existence of structural units in (1,2), (1,4), and (3,4) additions. They noted that for polymerizations initiated by bases containing  $\text{Li}^+$  as counterion, a higher (1,2) addition and, therefore, a higher amount of pendent aldehyde groups in polymer chain was obtained (amount of 1,2 units = 32%) when compared with the use of  $\text{Na}^+$  as the counterion (amount of 1,2 units = 12%). The effect of the counterion type on both polymer molecular weight and polydispersion was also evaluated. For the counterion  $\text{Li}^+$ , the molecular weight ( $M_n$ ) was within the 1200 to 3900 range, and the polydispersion values were higher than 10. On the other hand, for  $\text{Na}^+$ , the molecular weight fluctuated between 5000 and 15,000, and the polydispersion varied between 2.5 and higher than 10, when using the same reaction temperature range ( $-40^\circ\text{C}$  to  $5^\circ\text{C}$ ). Other important aspect in the polymerization of acrolein is that the vicinal (1,2) units may lead to the formation of cyclic structures by intramolecular chain-transfer reactions in accordance to what is presented in Figure 1.

The objective of this work was to investigate the reaction conditions to produce linear and low-molecular-weight polyacroleins, with available aldehyde groups, and considerable water solubility. Acrolein oligomers with such characteristics would be strong candidates to be used as modification agents for proteins aimed to be used as biomaterials.



**Figure 1** Intramolecular chain-transfer reactions in acrolein polymerization leading to the formation of cyclic structures.

## EXPERIMENTAL

### Materials and methods

Acrolein for synthesis was purchased from Spectrum Chemical (New Brunswick, NJ); both anionic initiators *sec*-BuLi and *tert*-BuLi were acquired from Acrós (Geel, Belgium) (1.3M in cyclohexane and pentane 92/8 solution) and from Aldrich (St. Louis, MO) (1.7M in hexane solution), respectively, and were used as received. THF was supplied by Vetec Química Fina (Brasil), and it was used after distillation under nitrogen from sodium/benzophenone just before use. Infrared spectra were recorded in a Perkin-Elmer (Norwalk, CT) 1720X, using KBr discs. DTA and TA analyses were performed with a TA Instruments (New Castle, DE) Q 500 thermal analyzer. The thermogravimetric measurements were performed at temperatures between 40 and  $700^\circ\text{C}$  (under nitrogen and at a heating rate of  $10^\circ\text{C}/\text{min}$ ). The oligomers' average molecular weights were determined by gel permeation chromatography (GPC) using Shodex SB804 columns (Miniato, Japan). Polyethylene glycol standards were used for calibration. The samples were eluted in a solution containing 0.05M LiCl 1 : 1 DMF :  $\text{H}_2\text{O}$  at a constant flow rate of 1 mL/min.

### Synthesis of low-molecular-weight polyacrolein

Tetrahydrofuran, previously dried and distilled in the presence of sodium, was introduced in a 120-mL flamed Schlenk flask containing a magnetic stirrer. After setting the desired polymerization temperature ( $-90^\circ\text{C}$ ) in a cryogenic bath, acrolein was added with a syringe. When the acrolein solution achieved thermal equilibrium, the initiator was quickly added. At the end of polymerization, after 1 h, 0.5 mL  $\text{H}_2\text{O}$  was introduced. The product was recovered by precipitation in hexane and dried in vacuum oven to constant weight.

## RESULTS AND DISCUSSION

The influence of the anionic initiator type (*tert*-BuLi or *sec*-BuLi) on both molecular weight and polydispersion of the obtained polyacrolein samples was studied at constant temperature of  $-90^\circ\text{C}$  in THF, for monomer/initiator molar ratios varying between 10 and 100. The polymerization mixture turned to dark blue with the monomer addition, and this color

TABLE I  
Experimental Conditions and GPC Results for the Polymerization of Acrolein

Sample	Acrolein (mmol)	Initiator system		[Monomer]/ [Initiator]	Molecular weight (g/mol)		$M_w/M_n$
		Type	mmol		$M_w$	$M_n$	
PA13	89.3	<i>tert</i> -BuLi	8.9	10	–	–	–
PA14	89.3		4.5	20	983	358	2.74
PA15	178.6		5.9	30	–	–	–
PA16	89.3		2.2	40	650	307	2.11
PA17	178.6		3.5	50	473	275	1.72
PA18	178.6		2.2	80	408	310	1.54
PA28	178.6	<i>sec</i> -BuLi	29.7	6	1,481	504	2.93
PA29	178.6		22.3	8	–	–	–
PA27	178.6		17.8	10	–	–	–
PA21	89.3		4.5	20	1,057	368	2.87
PA22	178.6		5.9	30	743	334	2.21
PA23	89.3		2.2	40	670	330	2.03
PA24	178.6		3.0	60	605	304	1.99
PA25	178.6		2.2	80	–	–	–
PA26	89.3		0.9	100	361	196	1.84

Solvent (THF) = 60 mL;  $T_{\text{reaction}} = -90^\circ\text{C}$ .

was maintained until all monomer was consumed. The resulting oligomers were initially characterized by GPC.

### Gel permeation chromatography analysis

The experimental conditions used for the polymerization of acrolein, as well as GPC results, are presented in Table I.

Contrarily to expected results, the molecular weights of the obtained oligomers decreased with the increase of the [monomer]/[initiator] ( $[M]/[I]$ ) ratio for both initiator systems used in this study, as can be observed in Figures 2 and 3. Moreover, the

molecular weights obtained from reactions in which *sec*-BuLi was the initiator were slightly higher than those of the oligomers obtained with *tert*-BuLi, keeping constant all other reaction conditions. At least within the  $[M]/[I]$  range studied, this result may be explained by the increase of chain-transfer reactions with the acrolein monomer as the  $[M]/[I]$  ratio increased, leading to decreasing molecular weights.

Molecular weight distributions for the oligomer samples were relatively narrow when compared with the data reported in the literature.<sup>18</sup> Also, the increase of  $[M]/[I]$  molar ratio promoted the decrease of polydispersity for both initiator systems (down to values lower than 2), as can be observed in

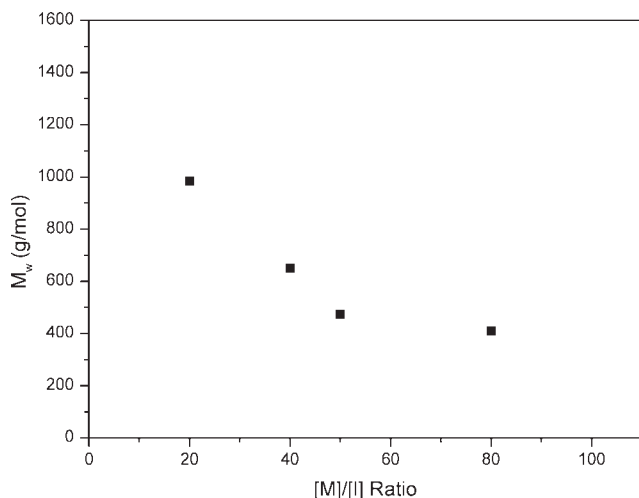


Figure 2 Molecular weight ( $M_w$ ) versus  $[M]/[I]$  ratio for the polymers obtained with *tert*-BuLi as initiator.

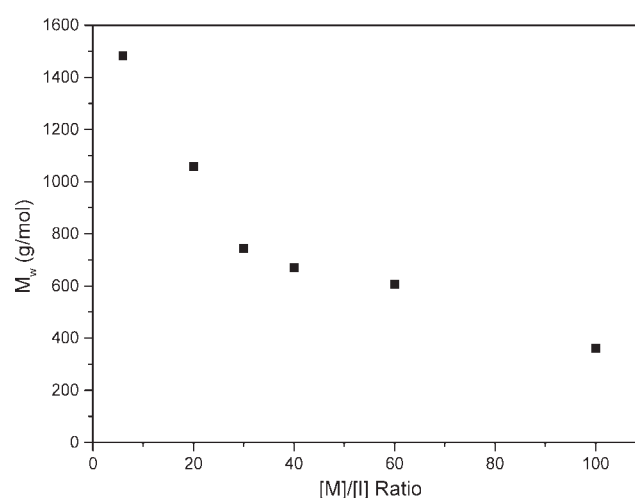
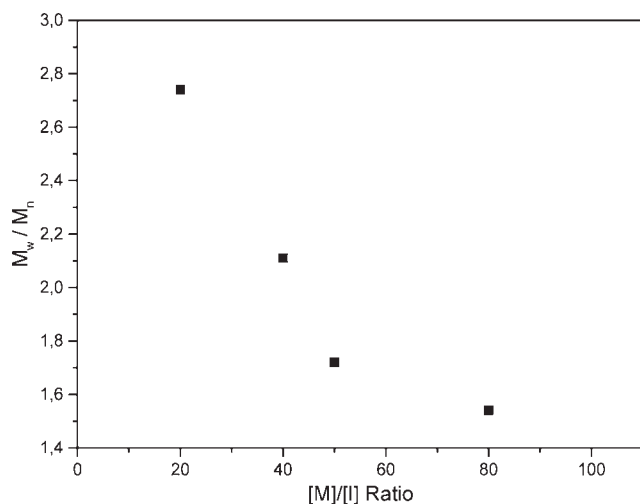


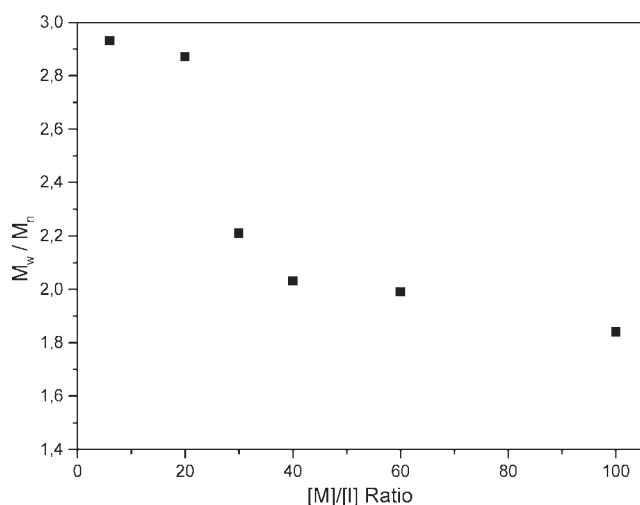
Figure 3 Molecular weight ( $M_w$ ) versus  $[M]/[I]$  ratio for the polymers obtained with *sec*-BuLi as initiator.



**Figure 4** Polydispersity versus  $[M]/[I]$  ratio for the polymers obtained with *tert*-BuLi as initiator.

Figures 4 and 5. For the products obtained with *tert*-BuLi, polydispersity values varied within the 1.5 and 2.8 range, whereas for oligomers obtained with *sec*-BuLi, polydispersity values were between 1.8 and 2.9. The narrowing of molecular weight distribution at high  $[M]/[I]$  ratios was attributed to the low occurrence of intramolecular transfer reactions under these conditions.

Lower  $[M]/[I]$  ratios led to the formation of higher amounts of cyclic structures in the chain, which in turn increased polydispersity. These relationships can be explained, as the formation of cyclic structures involves an intramolecular reaction, a low monomer/initiator molar ratio favors its formation rather than propagation, and thus, the formation of cyclic structures increases polydispersity. In fact, in the oligomerization of acrolein, cyclization competes



**Figure 5** Polydispersity versus  $[M]/[I]$  ratio for the polymers obtained with *sec*-BuLi as initiator.

with propagation and occurs as frequently as the  $[M]/[I]$  ratio decreases.

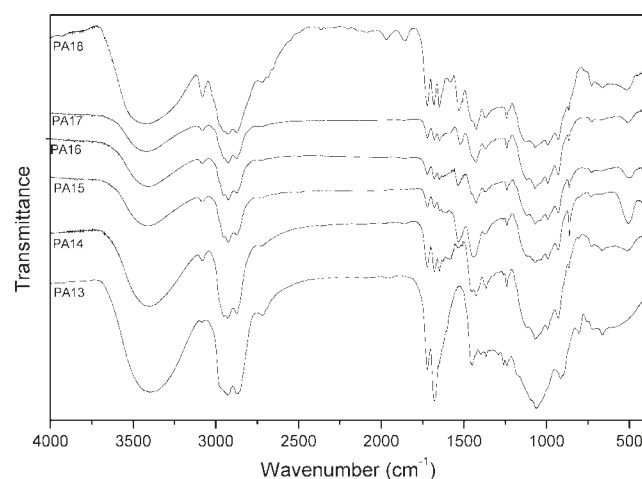
### Infrared absorption spectrometry analysis

The FTIR analysis of the low-molecular-weight polyacrolein samples revealed the presence of microstructures corresponding to three possible monomer insertions in the polymer chain: (1,2) monomer insertions were confirmed by the occurrence of absorptions referring to the carbonyl aldehyde group; (3,4) insertions were confirmed by the mono-substituted vinyl group absorption; and the (1,4) additions are related to the presence of vinyl ether groups in the polymer backbone.

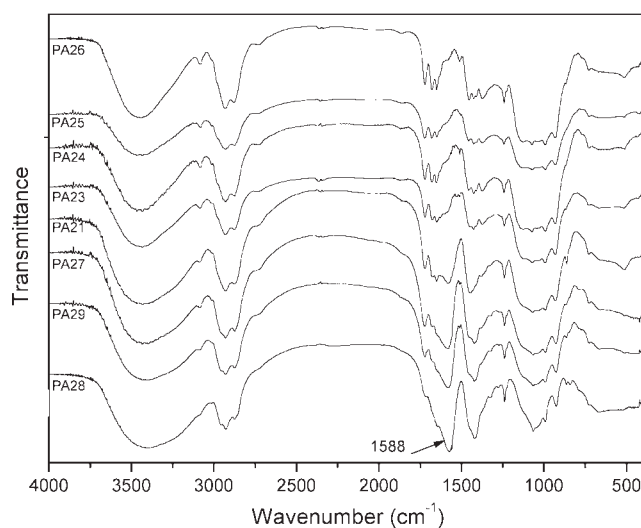
The presence of aldehyde groups can be confirmed by the appearance of bands in the 1740–1720  $\text{cm}^{-1}$  range, attributed to C=O stretching, by absorptions corresponding to the asymmetrical deformation of —CH between 1410 and 1380  $\text{cm}^{-1}$ , and also by the presence of a characteristic doublet at 2830–2810  $\text{cm}^{-1}$  and 2720–2695  $\text{cm}^{-1}$ . In all samples, the presence of aldehyde groups was evidenced, as can be observed in the spectra shown in Figures 6 and 7. Consequently, (1,2) monomer addition occurred during oligomerization.

The monosubstituted vinyl groups were confirmed by the absorption at around 3080  $\text{cm}^{-1}$ , which can be attributed to the stretching of =CH<sub>2</sub> at the vinyl end groups. The (3,4) monomer insertion in polyacrolein microstructure could be verified in all samples synthesized in this study.

A band around 3400  $\text{cm}^{-1}$  can be observed in the spectra obtained for all the samples. This band can be attributed to the presence of terminal —OH groups. It can also be noticed that for both initiators, as the  $[M]/[I]$  ratio increases, the FTIR spectra suffer



**Figure 6** FTIR spectra of the obtained polyacrolein at different  $[M]/[I]$  ratios with the initiator *tert*-BuLi.



**Figure 7** FTIR spectra for the low-molecular-weight polyacrolein obtained at different  $[M]/[I]$  ratios with the initiator *sec*-BuLi.

some changes. These variations were more visible in the spectral range between 1400 and 1700  $\text{cm}^{-1}$ .

For the oligomers synthesized with *sec*-BuLi as initiator, the presence of an absorption at 1588  $\text{cm}^{-1}$  was observed. The intensity of this band tended to decrease (Fig. 7) with the increase of the  $[M]/[I]$  ratio. On the other hand, two bands in the region of C=C absorption (around 1650  $\text{cm}^{-1}$ ) appeared in the spectra. Another important variation was observed for the band at 3080  $\text{cm}^{-1}$ . With the increase of the  $[M]/[I]$  molar ratio, this absorption became more defined.

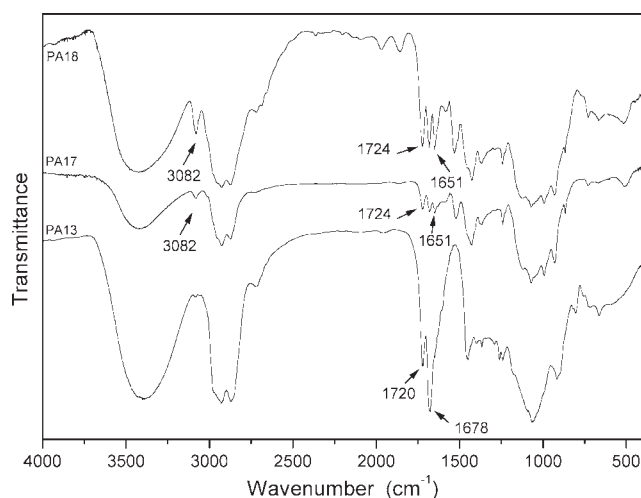
The band at 1588  $\text{cm}^{-1}$  could be attributed to cyclic structures (Fig. 1). These structures were

mainly observed for samples synthesized at a low  $[M]/[I]$  ratio, and initiated by *sec*-BuLi. Since the polymerization rate with *sec*-BuLi is lower than the *tert*-BuLi, specially at lower  $[M]/[I]$  ratios (samples PA28, PA29, and PA21), the molecular weight of the oligomers tends to be higher. Therefore, the formation of a higher content of cyclic structures may be explained as the result of the tendency for intramolecular transfer reactions, which are more likely to occur for reactions initiated by *sec*-BuLi, under conditions of low  $[M]/[I]$  ratios.

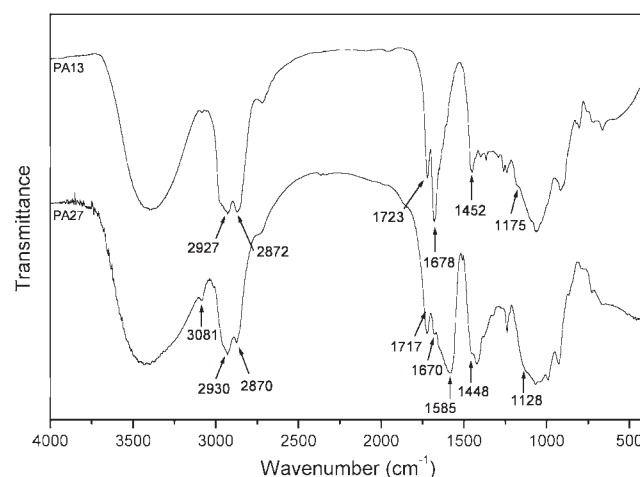
The absorption bands that appear at 1650 and 1670  $\text{cm}^{-1}$  in the spectra of Figure 7 can be attributed to unsaturated vinyl ether groups. The presence of these absorptions in FTIR spectra is more evident for samples PA21, PA22, PA23, PA24, PA25, and PA26. Nevertheless, they could be hidden in the spectra of the samples PA27, PA28, and PA29, since the high-intensity band at around 1100  $\text{cm}^{-1}$ , which corresponds to C—O—C asymmetric stretching, is present.

The band near 1660  $\text{cm}^{-1}$ , which is related to (1,4) monomer addition, is more intense in the spectra of the samples polymerized with *sec*-BuLi, but is also present in the spectra of oligomers obtained by *tert*-BuLi initiation. Figure 8 shows the effect of the decrease of polymer molecular weight in the FTIR spectra with the increase of  $[M]/[I]$  ratio for the samples obtained with the system *tert*-BuLi.

Comparing the polymers synthesized with *sec*-BuLi and *tert*-BuLi at the same  $[M]/[I]$  molar ratio, for example  $[M]/[I] = 10$ , substantial microstructural differences can be noticed, as shown in Figure 9. The absorption at 3080  $\text{cm}^{-1}$  is observed for the sample PA27, which was obtained with *sec*-BuLi; although it is not noticed for the sample PA13,

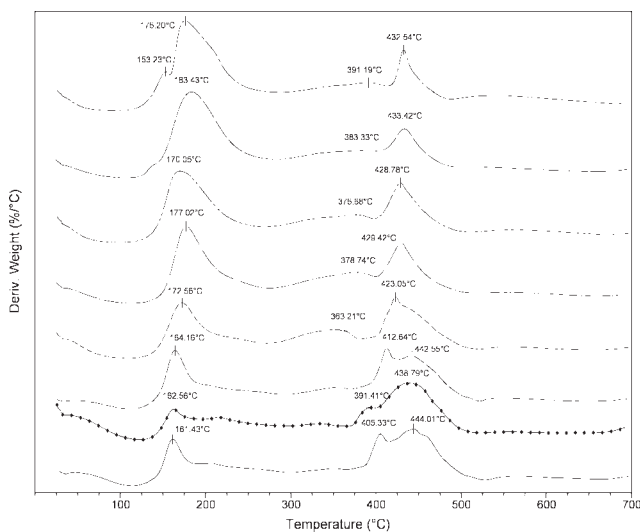


**Figure 8** Polyacrolein microstructure varying with the increase of  $[M]/[I]$  ratio for the samples obtained with *tert*-BuLi.



**Figure 9** FTIR spectra for the acrolein oligomers obtained at  $[M]/[I] = 10$  with the initiators *sec*-BuLi (PA27) and *tert*-BuLi (PA13).





**Figure 10** Thermal degradation curves for the low-molecular-weight polyacrolein obtained at different  $[M]/[I]$  ratios with the initiator *sec*-BuLi.

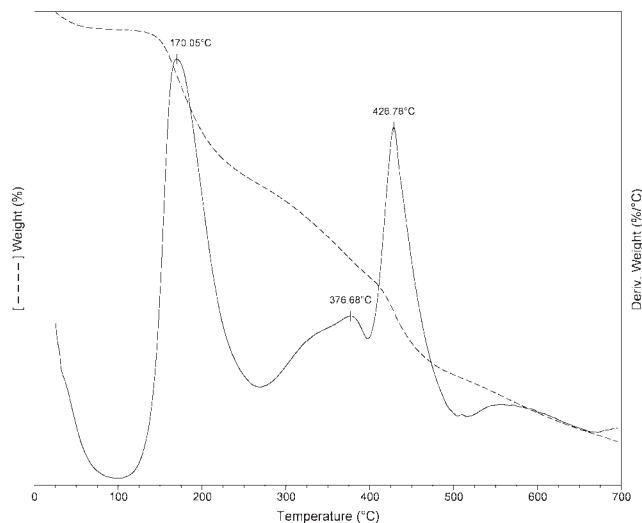
which was obtained with *terc*-BuLi. Another important factor is that the absorption bands related to ether groups (at  $1128\text{ cm}^{-1}$ ) are more intense in the spectrum for sample PA27 than in the spectrum for PA13. This indicates that, in the polymerization of acrolein with *sec*-BuLi as initiator, 3,4-addition occurs. The absorption band at  $1580\text{ cm}^{-1}$  appears only for the sample PA27, which reveals that the formation of cyclic structures is associated with the nature of the initiator and also with the  $[M]/[I]$  ratio.

As mentioned before, the polymerization rate of acrolein was expected to be lower for the system initiated with *sec*-BuLi. Therefore, in this case, cyclization reactions were more likely to occur, producing cyclic ether linkages, and also increasing the absorption of the band at  $1580\text{ cm}^{-1}$ . Following this, the samples of polyacrolein obtained with *sec*-BuLi at low  $[M]/[I]$  ratios (6, 8, 10, and 20) contained higher amounts of cyclic structures in the oligomer.

Accordingly, the increase of the polymerization rate with the use of *terc*-BuLi and higher  $[M]/[I]$  ratios led to the linear polymerization of acrolein. On the other hand, the increase of the  $[M]/[I]$  ratio caused the decrease of oligomers molecular weights because of the chain-transfer reactions with the polar monomer.

#### Thermal analysis: Microstructure study for polyacrolein samples obtained with *sec*-BuLi as initiator

Figure 10 shows first-derivative plots corresponding to the thermal degradation of the polyacrolein samples synthesized with *sec*-BuLi. Three main degradation temperatures were noticed, around 170, 370, and  $430^\circ\text{C}$ . Samples PA27, PA28, and PA29,

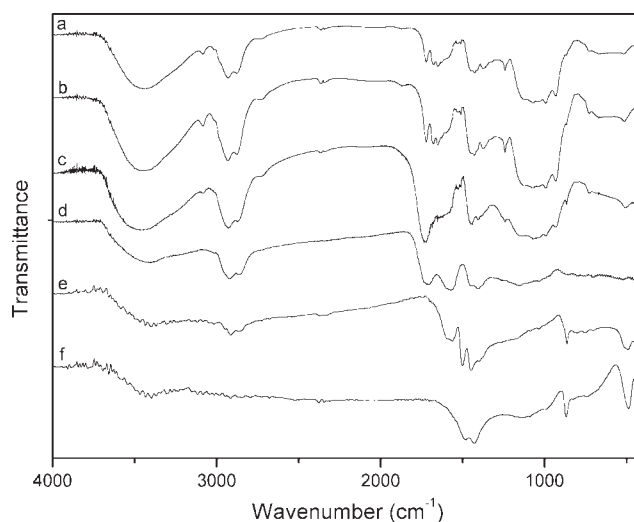


**Figure 11** Thermal degradation profile and the derivative curve for sample PA23.

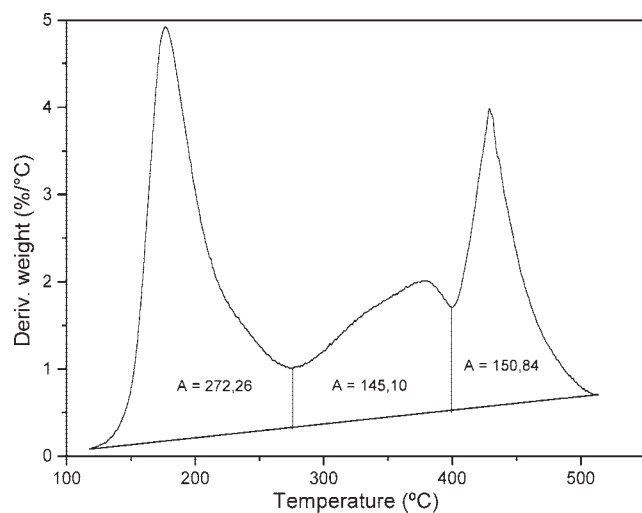
obtained at lower  $[M]/[I]$  ratios, also presented thermal degradation near  $400^\circ\text{C}$ . The degradation profile around  $370^\circ\text{C}$  is very broad, and it is also different from the other peaks at 170 and  $430^\circ\text{C}$ , which have a sharp and well-defined shape.

Figure 11 shows the thermal degradation and its respective derivative curve for the sample PA23 ( $[M]/[I] = 40$ ). Three main degradation temperatures appeared for this sample, with maxima at 170, 377, and  $429^\circ\text{C}$ .

To follow the degradation and investigate the structure of the remaining products, sample PA23 was heated up to 100, 260, 400, 500, and  $670^\circ\text{C}$ , and the residual products at each degradation



**Figure 12** FTIR spectra of degradation products of sample PA23 at different temperatures.



**Figure 13** Area under the first-derivative curve of mass loss of the sample PA22, considering the baseline.

temperature were analyzed by FTIR spectrometry. Figure 12 shows the FTIR spectra for each degradation product of this sample. The spectrum of PA23 after heating up to 100°C did not undergo any modification when compared with the nonheated sample. This means that by heating this sample up to 100°C, no thermal degradation of the low-molecular-weight polyacrolein occurred. On the other hand, heating to 260°C caused mostly the degradation of double bonds, as can be visualized by the spectral change in the 1400–1600  $\text{cm}^{-1}$  range, as well as by the absorption band at 3080  $\text{cm}^{-1}$ , which has also changed. The thermal treatment at 400°C induced specially the degradation of ether bonds, whose spectral modifications appear in the 900–1100  $\text{cm}^{-1}$  range. The degradation profile of the ether bonds is very broad and this behavior can be attributed to the possible different environment for the ether bonds in the polymer backbone. Moreover, the degradation product obtained after heating to 500°C led mainly to the degradation of the aldehyde carbonyl groups, which can be noticed by the disappearance of the absorption band at 1700  $\text{cm}^{-1}$  and also through the change

in the spectra at the 2800  $\text{cm}^{-1}$  doublet. The carbonyl degradation seems to occur with the formation of new structures, which can be observed by the appearance of absorption bands at around 1500  $\text{cm}^{-1}$  and 500  $\text{cm}^{-1}$ . The FTIR spectrum for the product obtained after heating sample PA23 at 670°C presented few bands, and it is the most different from the spectrum of the original sample.

After determining the thermal degradation temperatures for the main functional groups in the synthesized polyacroleins, and considering the baseline as presented in Figure 13, it was possible to estimate the amount of each repetitive unit obtained at different  $[M]/[I]$  molar ratios. These results can be seen in Table II.

It can be observed that the main reaction path followed by these polymerizations is through  $\text{C}=\text{O}$  bonds, which represents (3,4) monomer addition, and results in pendant vinyl groups, as expected for anionic polymerization of acrolein. Similarly, the amount of pendant aldehyde groups resulting from 1,2-polymerization has decreased with the increase of  $[M]/[I]$  ratio. Therefore, the higher the  $[M]/[I]$  ratio in the polymerization medium (and consequently, at higher polymerization rates), the higher is the probability for the monomer insertion to occur through (3,4) addition, in detriment to the (1,2) addition, leading to the increase of the amount of pendant  $\text{C}=\text{C}$  groups.

The amount of  $\text{C}-\text{O}-\text{C}$  units (1,4-addition) did not vary appreciably at  $[M]/[I]$  between 20 and 100, remaining around 20%, except in the range of low  $[M]/[I]$  ratios. Apart from samples PA29, PA28, and PA27, a degradation peak near 400°C was observed, which could be associated with the degradation of the previously mentioned cyclic structures present in these oligomers.

### Solubility analysis of the low-molecular-weight polyacrolein samples

The solubility of the oligomers was qualitatively evaluated, and the results are shown in Table III.

**TABLE II**  
Amount of the Chemical Groups in the Synthesized Low-Molecular-Weight Polyacrolein Microstructure

Sample	$[M]/[I]$ ratio	$M_w$	$\text{C}=\text{C}$ ( $\approx 170^\circ\text{C}$ ) (%)	$\text{C}-\text{O}-\text{C}$ ( $\approx 370^\circ\text{C}$ ) (%)	Other groups ( $\approx 400^\circ\text{C}$ ) (%)	$\text{C}=\text{O}$ ( $\approx 430^\circ\text{C}$ ) (%)
PA28	6	1,481	38.50	9.34	35.92	52.16
PA29	8	–	36.83	9.44	45.65	8.10
PA27	10	–	40.51	12.59	26.41	20.49
PA21	20	1,057	40.53	22.24	–	37.23
PA22	30	743	47.92	25.54	–	26.55
PA23	40	670	51.59	23.18	–	25.23
PA24	60	605	61.13	20.83	–	18.04
PA26	100	361	64.95	20.16	–	14.89

**TABLE III**  
**Relative Solubility of the Synthesized Acrolein Oligomers in Several Solvents**

Sample	Initiator	[M]/[I]	$M_w$	H <sub>2</sub> O	EtOH	DMSO	DMF	DMF/LiCl 0.01M
PA14	<i>tert</i> -BuLi	20	983	5	7	10	10	10
PA16		40	650	7	7	10	10	9
PA17		50	473	7	7	10	10	5
PA18		80	408	7	10	10	10	10
PA28	<i>sec</i> -BuLi	6	1,481	9	9	10	7	9
PA27		10	nd	9	9	10	10	10
PA21		20	1,057	7	5	1	1	5
PA23		40	670	7	5	1	5	5
PA24		60	605	7	5	1	1	5
PA26		100	361	7	9	10	10	10

Mass of the oligomer = 10 mg in 1 mL of solvent; values attributed from 0 to 10, where 10 is totally soluble; DMSO, dimethyl sulfoxide; DMF, dimethyl formamide.

It can be pointed out that the samples synthesized with *tert*-BuLi as initiator presented a higher solubility in aprotic polar solvents, as DMSO and DMF, than those obtained using *sec*-BuLi. This result indicates important differences in the chain microstructure of the low-molecular-weight polyacrolein samples, according to the type of initiator system. This fact can be related to the decrease in the amount of polar aldehyde groups and also to the increase of C=C side groups in the oligomer backbone, which agrees with the estimated amounts for main groups presented in the materials synthesized with *sec*-BuLi (Table II).

The introduction of LiCl salt to DMF caused an increase in solubility for the less polar oligomers, synthesized with *sec*-BuLi in DMF.

Chromatography for diluted solutions of oligomers in the DMF/LiCl system eliminates intramolecular interactions in acrolein oligomers, ensuring that realistic values for molecular mass averages were obtained. It is suggested that the oligomers interact with LiCl by hindering their intermolecular polar bonding, and so becoming more disaggregated, and adopting extended "coil-like" conformations. As a result, LiCl disentangles chains, which became better solvated.

An opposite behavior was observed for the samples obtained with *tert*-BuLi. The addition of the salt has decreased the oligomer solubility. In this case, for the more polar molecules, the interaction with the solvent alone promotes the solubility of the material, and the addition of LiCl competes with the oligomer-solvent interaction.

The water solubility is approximately as high as in ethanol for all samples, including those that possess low solubility in DMSO and DMF. Hydrogen interactions between aldehyde groups and protic solvents may be present.

## CONCLUSION

The three possible monomer insertions were observed for all synthesized samples. The molecular weights of polyacrolein obtained in this work decreased with the increase of monomer/initiator molar ratio for the both initiators, *tert*-BuLi and *sec*-BuLi.

The low-molecular-weight polyacroleins obtained in this work presented enough thermal stability to allow its use in bioconjugates, and the beginning of their degradation was found to be at temperatures higher than 100°C. The thermal degradation analysis of a polyacrolein sample at 170, 370, and 430°C revealed the association with the degradation of double bonds, ether linkage, and carbonyl groups, respectively.

The nature of the polymerization initiator has affected the polymer microstructure. Its highest influence was observed for samples obtained at lower [M]/[I] molar ratios. The lower the polymerization rate, when using the less basic initiator (*sec*-BuLi) and at low [M]/[I] ratios, the higher is the amount of cyclic structures formed in the polymer backbone.

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