

## Research Article

# Influence of Lauro lactam Content on the Clay Intercalation of Polyamide 6,12/Clay Nanocomposites Synthesized by Open Ring Anionic Polymerization

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*In situ* anionic homo- and copolymerization of caprolactam (CL) and lauro lactam (LL) with sodium montmorillonite clay (NaMMT) was carried out using two different initiators, sodium caprolactamate (CLNa) and caprolactam magnesium bromide (CLMgBr). Degree of conversion and final molecular weight were used to assess the advancement and efficiency of the polymerization reaction and X-ray diffraction and electron microscopy were used to evaluate the sodium montmorillonite clay intercalation/exfoliation. The use of CLNa as initiator produced a higher conversion degree and molecular weight than the use of CLMgBr. Through DSC, it was observed that CLNa and CLMgBr tended to produce random and block copolymer structures, respectively, and either random or block, this eventually has an effect on the clay dispersion within the polymer matrix. In all cases, increasing the LL content produced a decrease in the conversion degree and in the molecular weight of the resulting polymer.

## 1. Introduction

Fast-activated anionic polymerization has been successfully used for the polymerization of lactams. The intended high-polymerization rate of the anionic polymerization is achieved by introducing an activator, which is a compound containing an N-acyllactam structure. In this sense, sodium hydride in caprolactam [1] and sodium caprolactamate (CLNa) [2] have been used as initiators for the initiation stage.

The technology of the *in situ* polymerization with sodium montmorillonite clay (NaMMT) was first established at the Toyota laboratories via the hydrolytic polymerization of  $\epsilon$ -caprolactam intercalated in a complex of 12-aminododecanoic acid-NaMMT, in order to obtain a polyamide 6/clay nanocomposite (PA6/Clay) [3, 4]. Combination of the

*in situ* polymerization techniques with the anionic polymerization of lactams has been reported, where polyamide nanocomposites are readily obtained [5, 6]. Jung et al. [7] recently reported the obtaining of PA6/Clay nanocomposites via the *in situ* anionic polymerization of caprolactam (CL) with clay, using CLNa as initiator and N-acetyl-caprolactam (ACL) as activator. While studying the synthesis of PA6/clay nanocomposites, Liu et al. [8] reported that when using NaMMT, they obtained exfoliated nanocomposites whereas when using organomodified montmorillonite they obtained intercalated nanocomposites. Ahmed and Lee [9] studied the effect of clay concentration on the mechanical and viscoelastic properties of PA6/clay nanocomposites synthesized via anionic polymerization.

On the other hand, studies on the synthesis of composites based on the *in situ* anionic copolymerization of CL and

lauro lactam (LL) with NaMMT have not received so much attention. In this sense, Ricco et al. [10] studied the copolymerization of CL with LL, using CLNa and sodium lauro lactamate or a mix of both, as initiators, and found that the greatest conversion resulted when using CLNa. Budín et al. [11] studied the anionic copolymerization of CL with LL using either, CLNa or caprolactam magnesium bromide (CLMgBr) as initiators, and found that when using CLNa, there was a tendency to produce random copolymers, whereas when using CLMgBr, the tendency was to produce block copolymers. Although, the structure type of the copolymer was also dependant on the temperature of reaction and on the monomers molar ratio.

The purpose in this work, therefore, was to study the effect of the initiator type on the conversion degree and molecular weight of the final polymer, as well as the effect of the copolymer structure on the clay intercalation-exfoliation.

## 2. Experimental

**2.1. Material.** The materials used in this study were caprolactam (CL), from Univex; lauro lactam (LL), from Aldrich; sodium caprolactamate (CLNa) in Caprolactam at 18.5 wt% concentration from Brüggemann Chemicals; caprolactam magnesium bromide (CLMgBr) in caprolactam at 17 wt% concentration from Brüggemann Chemicals; N-acetyl caprolactam (ACL) from Aldrich; sodium montmorillonite clay (NaMMT) from Southern Clay Inc.

**2.2. Copolymerization.** The *in situ* anionic polymerization was carried out in test tubes, where CL, LL, or a mix of both were introduced and heated to 180°C. Thereafter, 0.5 mol% of CLNa or CLMgBr was added as initiator, then, 2 wt% of NaMMT was added, and finally, 0.5 mol% of N-acetyl caprolactam was added as activator, all percentages with respect to the total mols of CL + LL. The reaction was allowed to proceed for 30 min in a nitrogen atmosphere. The copolymerizations of CL with LL were carried out using 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 mol% of CL/LL, respectively. Nanocomposites obtained were then grounded, purified through Soxhlet extraction with methanol, and vacuum-dried at 110°C for 8 hours.

**2.3. Characterization.** Conversion was determined gravimetrically by Soxhlet extraction with methanol of the material from the test tubes, where the reaction took place, for 24 hours, using a 2:1 methanol-water mixture as the solvent, in order to extract the unreacted monomers and initiators. Thereafter, the remaining material in the Soxhlet tube was dried at 110°C until constant weight. The conversion was taken as the final weight in the Soxhlet divided by the initial weight and multiplied by 100.

An Alliance 2695 Gel Permeation Chromatograph, with a UV detector model 2487 (248 nm) and styragel columns, was used to determine the evolution of molecular weight of all samples. Samples were first dissolved in trifluoroacetic acid and run in the GPC at a flow rate of 1 mL/min.

X-ray diffraction (XRD) analyses were carried out in a Siemens D5000 using an anode of CuK $\alpha$  X-ray of 1.54 Å at

35 Kv and 25 mA. Samples were scanned at diffraction angles from 2 to 12° in  $2(\theta)$ . Runs were performed with a step size of 0.02° and step time of 1.0 s. Bragg's law ( $n\lambda = 2d \sin\theta$ ) was used to convert the data of diffraction angle ( $2\theta$ ) to distance ( $d$ ). Samples for X-ray analysis were obtained from the compression molded process.

Differential Scanning Calorimetry (DSC) analysis was performed on a TA Instruments 2920 Modulated DSC to establish the thermal transitions and structural characteristics of all samples. Samples of ca 10 mg were analyzed under a nitrogen atmosphere. Thermal analysis was carried out as follows: samples were first heated up to 250°C at a heating rate of 10°C/min and then cooled down to 0°C at -10°C/min. Finally, samples were heated again up to 250°C at 10°C/min.

The clay structural organization was studied through STEM observations using a Jeol-JSM7104F electron microscope equipped with STEM modulus and a field emission gun, at an accelerating voltage of 30 kV, using a LEI (low electron image) detector. Ultrathin sections for STEM analysis were previously cut from compression molded samples with a diamond knife at -30°C using a Leica cryogenic ultramicrotome.

## 3. Results and Discussion

**3.1. Physicochemical Properties.** Figure 1 shows the conversion and molecular weight of the *in situ* anionic homo- and copolymerizations of CL, LL, and CL with LL, respectively. The NaMMT content was kept at 2 wt%. All polymerizations were carried out for 30 min, using either CLNa or CLMgBr as initiators.

It can be observed in Figure 1(a), that the highest conversion was achieved during the homopolymerization of CL for obtaining polyamide 6/NaMMT (PA6/NaMMT), independently of the initiator used. Also, it was observed that conversion decreased as the LL/CL ratio increased in the nanocomposites of poly (caprolactam-co-lauro lactam)/NaMMT (PA6:12/NaMMT), but this seems to be dependent on the initiator used, since conversion was higher when using CLNa as initiator at all LL/CL ratios, except above ca. 90/10. This diminished catalytic activity of CLMgBr, as compared to CLNa, is attributed to the steric hindrance of the larger CLMgBr molecular size.

Figure 1(b) shows that in all cases, the molecular weight of the resulting homo- or copolymer was greater when using CLNa as initiator. Additionally, with any of the two initiators, the molecular weight of the homopolymers was greater than that of the copolymers, showing a minimum when the LL content was ca. 60 mol%.

As expected, upon increasing the LL concentration, the molecular weight decreases. This is attributed to the much lower reactivity of the LL anions, as compared to those of CL [12]. These results coincide with those reported by Budín et al. [11], while studying the polymerization of CL or LL, without clay.

In all cases, CLNa produced a greater conversion and also a greater molecular weight, which coincides with Odian [13], who mentions that the ring opening anionic polymerization

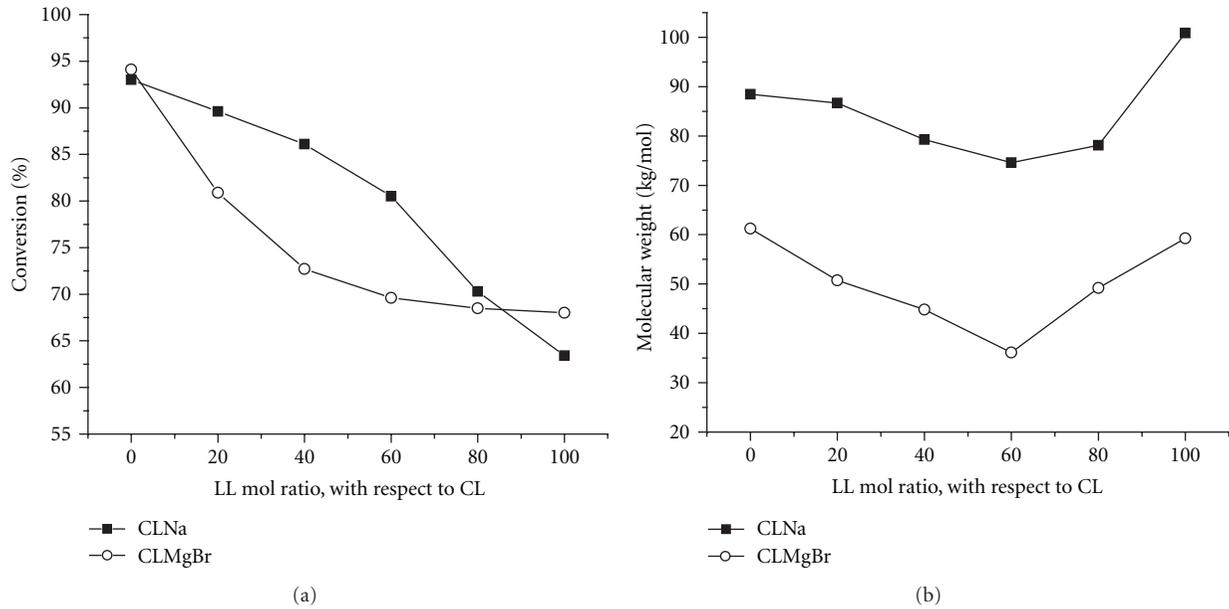


FIGURE 1: Effect of initiator type (CLNa or CLMgBr) and LL mol ratio on (a) conversion and (b) molecular weight during the *in situ* homo- and copolymerization of CL, LL, and CL/LL, with 2 wt% of NaMMT.

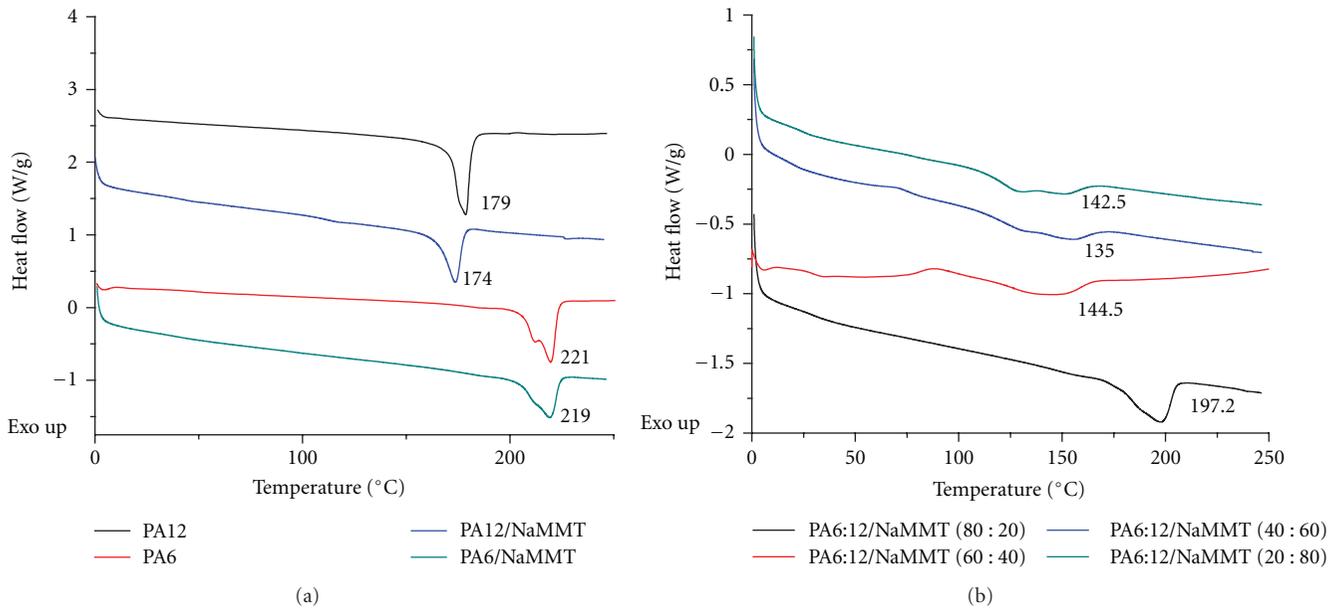


FIGURE 2: DSC curves for (a) homopolymers with and without MMT and (b) nanostructured copolymers of PA6:12 (at with 2 wt% of nanoclay). The initiator used in this case was CLNa.

proceeds in a way that the attained molecular weight varies linearly with conversion.

In addition, the greater molecular weights, when using CLNa, were indirectly assumed, as it was observed that during the copolymerization (CL/LL), the magnetic stirrer ceased turning after just 20 s of reaction when using CLNa, due to the viscosity increase, as a result of a greater molecular weight; whereas it took 35 s when using CLMgBr.

**3.2. Thermal Properties.** Figure 2 presents the effect of composition of the nanostructured polymeric compounds on the fusion temperature  $T_m$ . First, from Figure 2(a), it can be observed that the  $T_m$  of the homopolymer compounds is not altered significantly, by the inclusion of the NaMMT, it remains at 221°C ( $\pm 1^\circ\text{C}$ ) for PA6/NaMMT and 179°C for Polyamide 12/NaMMT (PA12/NaMMT), in agreement with that reported elsewhere [14]. Second, from Figure 2(b),

TABLE 1: Fusion temperature ( $T_m$ ) and enthalpy of fusion ( $\Delta H_m$ ) of the obtained homo- and copolymer compounds of CL and LL with NaMMT, using CLNa and CLMgBr.

Using CLNa as initiator	LL concentration (% mol)	$T_m$ ( $^{\circ}\text{C}$ )		$\Delta H_m$ (J/g)	
PA6/NaMMT	0	219.3		42.2	
	20	197.2		35.1	
	40	144.5		19.9	
PA6 : 12/NaMMT	60	135.0		22.1	
	80	142.5		21.7	
	100	174.0		35.1	
Using CLMgBr as initiator	LL concentration (% mol)	$T_{m1}$ ( $^{\circ}\text{C}$ )	$T_{m2}$ ( $^{\circ}\text{C}$ )	$\Delta H_{m1}$ (J/g)	$\Delta H_{m2}$ (J/g)
PA6/NaMMT	0	219.5	—	44.8	—
	20	201.8	183.5	7.3	26.5
PA6 : 12/NaMMT	40	175.2	154.3	4.1	15.8
	60	152.6	131.4	—	21.7
	80	149.9	145.6	11.3	21.2
PA12/NaMMT	100	—	172.3	—	31.5

the  $T_m$  of the copolymer PA6 : 12/NaMMT compounds, on the other hand, decreased as the concentration of LL increased, reaching a minimum (135 $^{\circ}\text{C}$ ) at a LL content of 60 mol%.

It is also observed that the fusion temperature of the copolymers is below that of the two homopolymers. This abatement is attributed to alpha and gamma crystalline phases of Polyamide 6 (PA6) and Polyamide 12 (PA12), respectively, trying to coexist in the copolymers, as reported by Budín et al. [11]. As the LL concentration increases, the alpha crystalline phase of PA6 tends to coexist with the gamma crystalline phase of PA12, generating many crystallite imperfections. On the other hand, upon increasing the LL content in the copolymers, the crystal size and the crystalline content decrease, decreasing the fusion temperature, as reported by Kubota and Nowell [15].

Finally, it can also be observed in Figure 2(b) that the crystallinity (associated with the fusion enthalpy  $\Delta H_m$ ) of the copolymer compounds is less than that of the homopolymers and it decreases with the concentration of LL, as can be determined from the enthalpies of fusion (Table 1).

Figure 3 shows the thermograms of the copolymers obtained using a CL/LL composition equal to 40/60. An important difference observed in the copolymers, when comparing that obtained with CLNa versus that obtained with CLMgBr initiator, is that, when using CLNa, the copolymer shows just one fusion peak, at 144.5 $^{\circ}\text{C}$ . This is indicative of a random copolymer. When using CLMgBr, on the other hand, the copolymer shows two fusion peaks, at 154.2 and 175.2 $^{\circ}\text{C}$ . This, on the other hand, is indicative of a block copolymer. These present a fair agreement with results reported by Budín et al. [11].

With respect to the fusion temperatures of the synthesized block copolymers, when using CLMgBr, it can be assumed that one block is a random block of CL (PA6) and LL (PA12) units. This randomness would hinder the formation of regular-perfect crystals, resulting in a diminished crystalline fusion temperature. The other block, on

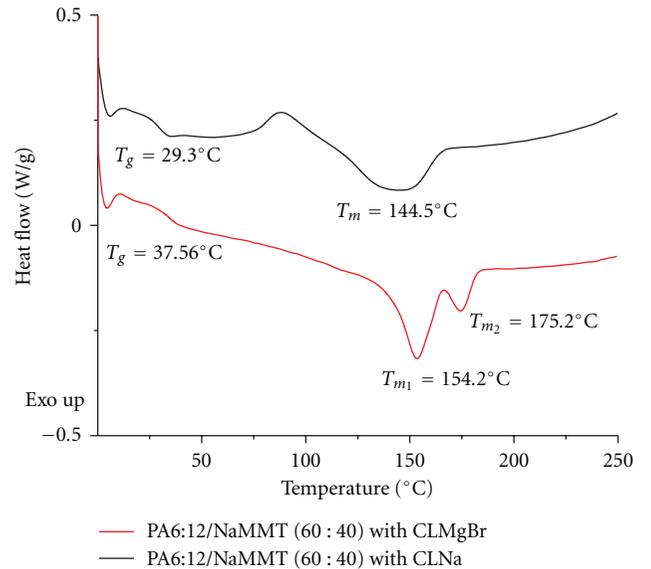


FIGURE 3: DSC curves of the two nanostructured polymer compounds of PA6 : 12, with CL/LL ratio of 60/40, obtained with CLNa and with CLMgBr as initiators.

the other hand, would be composed mostly of CL units, though not sufficiently long as to show the  $T_m$  of the PA6 homopolymer, but sufficiently long as to permit the formation of more regular-perfect crystals, with higher crystalline fusion temperature.

In addition, the insertion of the long aliphatic chains of PA12 into the structure of the PA6 in the growing PA6/PA12 copolymer chains, would give rise to a change in the crystalline type, from alpha, typical of PA6, to gamma, typical of PA12. These changes in the crystalline structure of PA would also tend to abate the fusion temperature, as has been reported elsewhere [16]. Table 1 presents the fusion temperature ( $T_m$ ) and the enthalpy of fusion ( $\Delta H_m$ ) for all the nanostructured polymer compounds studied, using

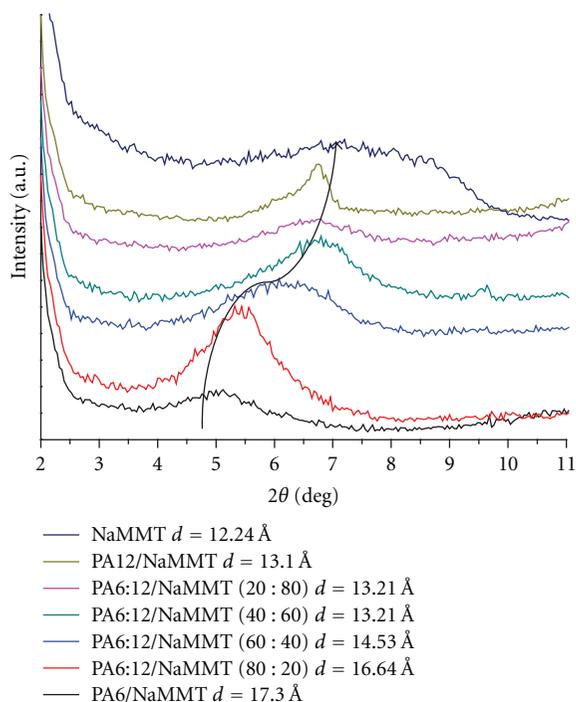


FIGURE 4: X-Ray diffraction curves of the homo- and copolymers of CL and LL, with 2 wt% of nanoclay, obtained using CLNa as initiator.

either CLNa or CLMgBr as initiators. It can be observed that the fusion temperature and the enthalpy of fusion of the copolymers are clearly affected by the increasing concentration of LL, as reported by Ricco et al. [10].

As an outcome, it can be said that the initiator type is the one that determines if the result is going to be a random or a block copolymer. In addition, the effect of LL content upon the fusion temperature of the copolymer is the same, no matter if the initiator is CLNa or CLMgBr. Finally, the addition of NaMMT has no apparent effect on the homopolymers fusion temperature (PA6 221°C; PA12 179°C) as shown in Figure 2(a).

**3.3. Exfoliation and Dispersion of the Nanoclay.** For the case of the polyamide/clay nanocompounds obtained using CLNa as initiator, Figure 4 shows that all the nanocompounds present a progressive shift of the X-Ray diffraction peak to lower  $2\theta$ , with respect to that of the pure NaMMT. This indicates an increase in the gallery spacing, producing an intercalated structure, attributed primarily to the insertion of the CL and LL monomeric units into the clay galleries prior to the *in situ* polymerization. It is important to bear in mind that when using CLNa as initiator, there is a tendency to produce random type copolymers.

In Figure 4, it can also be observed that the diffraction peak of the PA6/NaMMT nanocompound occurs at the lowest  $2\theta$  angle, which would correspond to the largest intergallery spacing (17.3 Å). On the contrary, the peak of the PA12/NaMMT nanocompound occurs at the highest

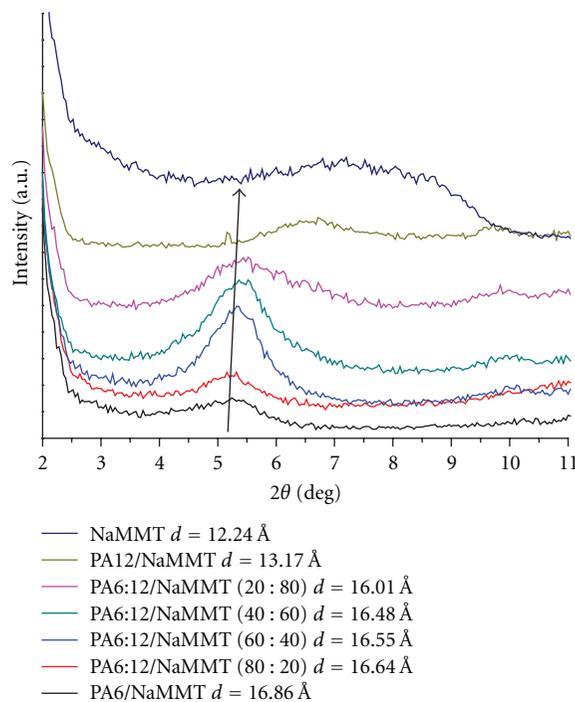


FIGURE 5: X-Ray diffraction curves of the homo- and copolymers of CL and LL, with 2 wt% of nanoclay, obtained using CLMgBr as initiator.

$2\theta$  angle, corresponding to the smallest intergallery spacing (13.1 Å).

In all the PA6:12/NaMMT nanocompounds, the peak occurs at higher  $2\theta$  angles as the LL content increases. That is, the intergallery spacing diminishes with the concentration of LL. These differences can be attributed to the lower polarity of PA12, compared to that of PA6, due to the longer aliphatic, nonpolar segments (12 C atoms) along its chains, as compared to the shorter aliphatic segments (6 C atoms) in the PA6 chains. That is, for a given polymer chain length, the PA12 shows a smaller content of the polar amide groups than the PA6. This diminished polarity of the PA12 chains makes them less compatible to the highly polar NaMMT. Thus, the decreasing intergallery spacing with increasing LL content, up to the smallest spacing for the PA12/NaMMT nanocompound.

For the case of the polyamide/clay nanocompounds obtained using CLMgBr as initiator, Figure 5 shows that all the nanocompounds present the same shift of the X-Ray diffraction peak to lower  $2\theta$ , which would correspond to an intergallery spacing of ca. 16.5 Å, with the exception of the PA12/NaMMT nanocompound, which presents an intergallery spacing of 13 Å.

When using CLMgBr as initiators, there is no effect of the LL content on the  $2\theta$  angle of the X-ray diffraction peak, as observed in Figure 4. This no-effect is assumed to be due to the block copolymer structure formed when using CLMgBr as initiator, in which case, the CL short blocks act as the highly polar PA6 homopolymer does and shows the

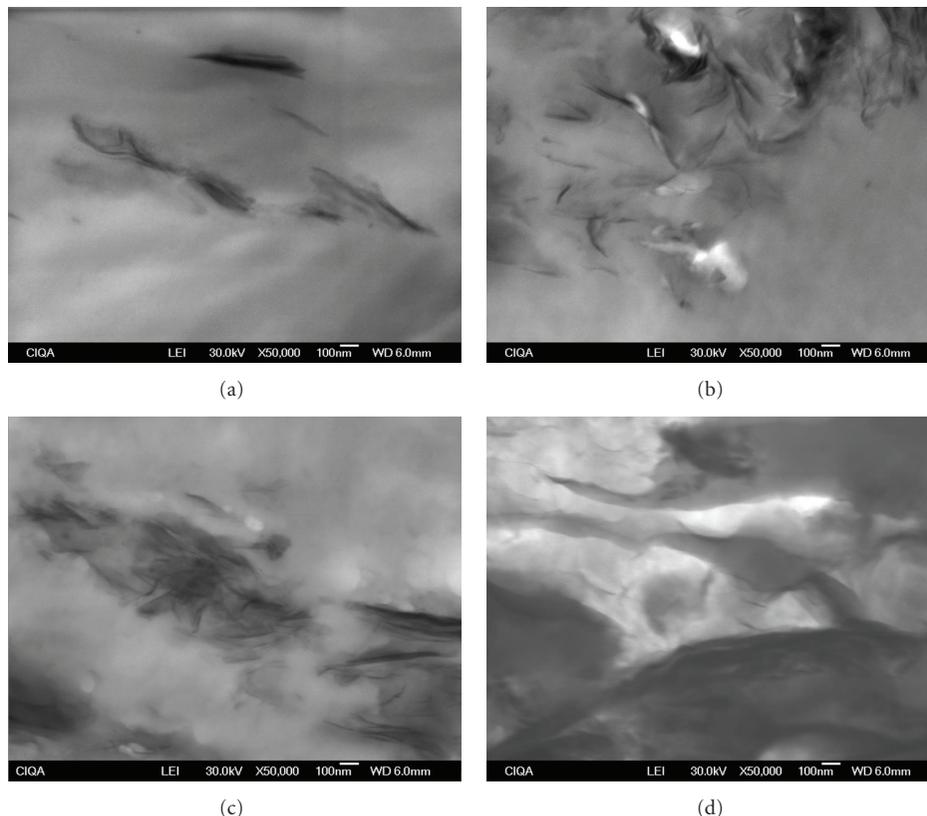


FIGURE 6: Electron micrographs of (a)  $\text{PA6/NaMMT}$ , (b)  $\text{PA6:12/NaMMT}$  (80 : 20), (c)  $\text{PA6:12/NaMMT}$  (60 : 40), and (d)  $\text{PA12/NaMMT}$  obtained with CLMgBr (scale bar at 100 nm).

capability to intercalate into the clay galleries, as the highly polar PA6 homopolymer does.

The micrographs in Figures 6(a), 6(b), and 6(c) show similar levels of exfoliation/intercalation, but not that in Figure 6(d), which corresponds to the PA12/NaMMT homopolymer compound, where very little or no exfoliation/intercalation is obtained. These results agree with those obtained via the XRD analysis, where the PA6/NaMMT as well as all the PA6:12/NaMMT copolymers prepared in the presence of CLMgBr initiator, present the same intergallery spacing of ca. 16.5 Å, with the exception of the PA12/NaMMT homopolymer.

The incomplete clay exfoliation, even though the high affinity between the highly polar PA6 and NaMMT, can be attributed to the lack of application of any shear stresses during the preparation of the nanostructured PA compounds. It might be expected that the preparation of the same PA compounds, via reactive extrusion, could render a much higher level of clay exfoliation.

#### 4. Conclusions

Homo- and copolyamide type nanocompounds were obtained, via *in situ* anionic polymerization of caprolactam and lauro lactam with NaMMT, using two initiator types.

The use of CLNa as initiator tended to produce a random-type copolymer, whereas the use of CLMgBr tended to produce a block-type structure, which affected both the crystallinity of the copolymers and the intercalation/exfoliation of the nanoclay. In the random type copolymers, the intergallery spacing decreased with the LL content, whereas in the block type copolymer, the intergallery spacing remained the same (as that for PA6) for all the copolymers. The intergallery spacing of the PA12/NaMMT remained the lowest in all cases. The use of CLNa as initiator produced a higher conversion degree and higher molecular weight than the use of CLMgBr.

In all cases, increasing the LL content produced a decrease in the conversion degree and in the molecular weight of the resulting polymer compound.

Crystallinity of the copolymer compounds was found to be less than that of the homopolymers. Also, crystallinity was greatly affected by the LL concentration; as the LL concentration increased, crystallinity decreased, as observed from the enthalpies of fusion.

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