

# Study on the Polymerization of $\epsilon$ -Caprolactam in the Interlamellar Spaces of [TEACOOH]–Montmorillonite Intercalations Complex and Its Characterization

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Received 20 February 2002; accepted 13 July 2002

**ABSTRACT:** The polymerization of  $\epsilon$ -caprolactam between the interlamellar spaces of the [TEACOOH]–montmorillonite intercalations complex was attempted using Na–montmorillonite and 10-carboxy-*n*-decyltriethylammonium bromide to achieve [TEACOOH]–polycaprolactam–montmorillonite, in which montmorillonite (inorganic polymer) is chemically bonded with the polycaprolactam (organic polymer). The results of X-ray and IR analysis for the samples obtained after polymerization showed that the polymerization reaction has been successfully accomplished. For the purpose of studying the polymeric reaction product more precisely, we have isolated the polymerized product from

the silicate layers and analyzed it with X-ray diffractometer and IR spectrometer. Comparison of the results of X-ray and IR analysis between the isolated polymer and the polymer that was synthesized by the reaction of  $\epsilon$ -caprolactam only with the organic cation without montmorillonite showed that both obtained polymers are the same compounds. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1904–1910, 2003

**Key words:**  $\epsilon$ -caprolactam; interlamellar space; organic and inorganic polymers; montmorillonite intercalations complex; 10-carboxy-*n*-decyltriethylammonium bromide

## INTRODUCTION

Montmorillonite, which belongs to the smectite group,<sup>1,2</sup> is a layer silicate of mica type<sup>3,4</sup> and is used very widely in industry because of its good swelling property. Pure polymer materials that are not reinforced with reinforcement or filler have many poor mechanical properties, such as strength, elasticity, rigidity, toughness, and stiffness. Therefore, studies on the synthesis of clay–polymer nanocomposites using clay such as kaoline, talc, sand, and quartz as a reinforcement to improve the poor mechanical properties of such pure polymer materials are now very active.<sup>5–8</sup>

However, montmorillonite, which has the highest industrial use, has not been widely applied as a filler for polymer composites. Theoretically, it is possible that a composite in which inorganic and organic polymer are chemically bonded can be synthesized, and the studies on this area are now very active.<sup>9–17</sup> In this case, it is very important to select the appropriate organic cation that will replace the metal ion, i.e., sodium ion, between the layers of Na–montmorillo-

nite to ensure the reaction space in the silicate layers and be chemically bonded with the organic polymer, so that the clay (inorganic polymer) and the organic polymer eventually can be chemically linked. In this case, the organic polymer would not be separated from the clay under the solvent in which it is soluble. Otherwise, for instance, in case that clay and the organic polymer are not chemically bonded, the organic polymer will be separated from the clay under the solvent in which it is soluble. Then the resultant clay–polymer nanocomposites cannot play a role as a composite anymore.

The clay–polymer nanocomposites in which the organic polymer are chemically linked with the inorganic polymer (clay) can be used, for example, as an automobile bumper, and it will have excellent stability because of the absorbing effect of the impact, good economic efficiency because of the long durability, and environmental friendliness because of the reduction of the waste plastics.

In this research to achieve the montmorillonite–polymer nanocomposite, we have studied if it is possible to form a polymer composite in which the inorganic polymer is chemically linked with the organic polymer and analyzed it. For this purpose, we have replaced sodium ion in the interlayer space of Na–montmorillonite by an organic cation with a long alkyl chain, (10-carboxy-*n*-decyl)triethyl ammonium bromide (hereafter abbreviated as [TEACOOH] Br), to ensure enough space for chemical reaction between the silicate layers at first.

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Contract grant sponsor: Basic Research Program of the Korea Science and Engineering Foundation; contract grant number: 2001-1-30100-006-1.

Thereafter, we have tried to intercalate additionally the organic monomer  $\epsilon$ -caprolactam into the organophilic montmorillonite, [TEACOOH]-montmorillonite intercalations complex (hereafter abbreviated as [TEACOOH]-mont) and then to polymerize the intercalated monomer to have the desired montmorillonite-poly- $\epsilon$ -caprolactam nanocomposite. Finally, we have analyzed chemically the obtained products.

## EXPERIMENTAL

### Materials

Ca-bentonite from Schwaiba, Germany, was chemically refined to achieve Na-montmorillonite.  $\epsilon$ -Caprolactam as starting material for the organic polymer triethylammonium bromide and *n*-undecanoic acid bromide for the preparation for the organic cation were commercially obtained from Fluka and/or Aldrich.

### Preparation of [TEACOOH]-mont

A suspension from Na-montmorillonite and distilled water was prepared, and a water solution of [TEACOOH] Br was added to the suspension under stirring. The whole mixture was then left at 65°C for 48 h under occasional stirring and thereafter centrifuged so that the swelling solution can be isolated from the product, [TEACOOH]-mont intercalations complex. This [TEACOOH]-mont was dried at 100°C in oven at first and continuously at 65°C in vacuum of  $10^{-3}$  torr for 24 h.

### Preparation of [TEACOOH]- $\epsilon$ -caprolactam-montmorillonite

The stoichiometric accounts of [TEACOOH]-mont and  $\epsilon$ -caprolactam were well mixed with mortar. The mixture was put into a 100 mL round flask and then left under  $N_2$  atmosphere for 30 min under occasional stirring. Thereafter, the round flask with the mixture was heated at 75°C for 30 min, cooled slowly up to 37°C, and well mixed with mortar. Then the sample was put into the reaction flask again, left under  $N_2$  atmosphere for 30 min with occasional stirring, heated at 75°C for 30 min, cooled slowly up to 37°C, and left at this temperature for 2 days.

### Polymerization of $\epsilon$ -caprolactam in silicate layers

[TEACOOH]- $\epsilon$ -caprolactam-montmorillonite was put into the thick horosilicate ampule, which was preheated with heat gun to remove the moisture, and then the ampule (including sample) was evacuated, sealed, and heated at 250°C for 24, 36, and 48 h to

polymerize the  $\epsilon$ -caprolactam in the layers of [TEACOOH]-mont.

### Polymerization of $\epsilon$ -caprolactam and [TEACOOH] Br without montmorillonite

In order to compare with the polymer obtained from the above procedure, the organic monomer  $\epsilon$ -caprolactam alone was polymerized with the organic cation [TEACOOH] Br without montmorillonite at 250°C for 36 h. The product was purified by washing with water and drying at 65°C for 24 h in high vacuum of  $10^{-3}$  torr.

### Separation of poly- $\epsilon$ -caprolactam from [TEACOOH]-mont

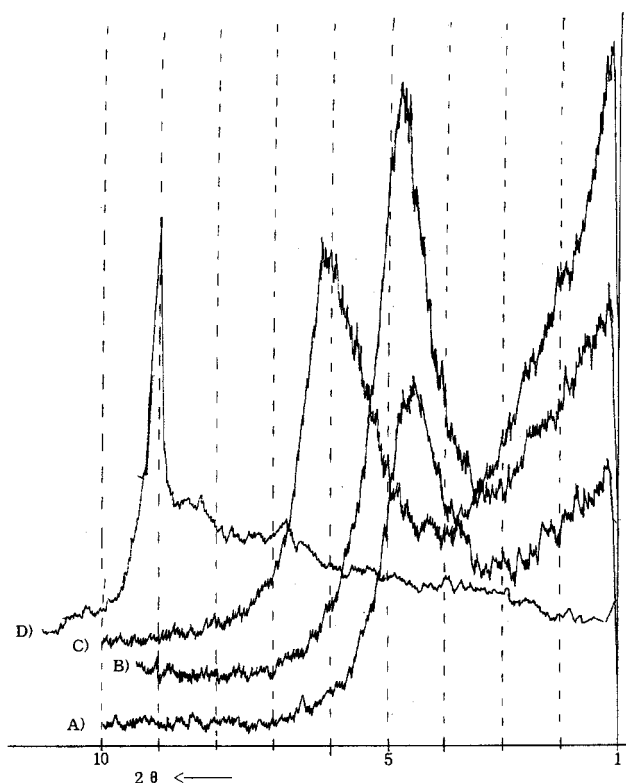
The poly- $\epsilon$ -caprolactam polymerized in the layers of [TEACOOH]-mont was separated by the decomposition of silicate lattice using an ammonium hydrogen fluoride ( $NH_4[HF_2]$ ) solution. For the purpose of comparison, the pure Na-montmorillonite, which was not polymerized, that is, does not include any organic compound, was also decomposed in the same way.

Na- and poly- $\epsilon$ -caprolactam-montmorillonite were mixed with excess amount of 1 n  $NH_4[HF_2]$  solution, respectively. Each mixture solution was then left at room temperature for 2 days under stirring, and thereafter concentrated  $NH_4OH$  solution was added to each one, which had a pH 3.5 at the beginning, so that it will be neutral or weak alkalic. The precipitate was separated from the solution by the filtration, dried at 65°C for a short time in oven at first, and then continuously in high vacuum of  $10^{-3}$  torr for 24 h. The dried sample was mixed with the excess amount of 100% glacial acetic acid, and the mixture was filtered at 60–70°C. The separated solution phase for glacial acetic acid was then treated with an excess of diethyl ether. The polymer precipitate was isolated and dried at 65°C for 24 h in high vacuum ( $10^{-3}$  torr).

### Characterization

[TEACOOH]-mont intercalations complex, [TEACOOH]- $\epsilon$ -caprolactam-montmorillonite, [TEACOOH]-polycaprolactam-montmorillonite, and the separated samples treated with the  $NH_4[HF_2]$  solution were characterized by X-ray diffractometer (Philips Novelco) using  $Cu K_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with a scan speed of 1.00 deg/min.

Infrared spectroscopic measurements on the Na-montmorillonite, [TEACOOH]-mont, [TEACOOH]-polycaprolactam-montmorillonite, the polymer material separated from this inorganic-organic hybrid, and the pure polymer synthesized without montmorillonite were also performed using a Prekin Elmer 325 spectrometer.



**Figure 1** X-ray diffraction patterns of [TEACOOH]-mont. A, after 48-h exchange time, under exchange solution; B, after eight times washing, under water; C, after 24-h drying in high vacuum at 65°C; D, Na-montmorillonite dried in high vacuum at 65°C 24 h.

## RESULTS AND DISCUSSION

### Results of intercalation complexes

The organophilic [TEACOOH]-mont obtained from the reaction of Na-montmorillonite with [TEACOOH] Br was characterized with an X-ray diffractometer under the following conditions. The equilibrium solution after exchange reaction was centrifuged; the solid residue was analyzed with X-ray diffractometer under still wet condition with the adherent equilibrium solution (Fig. 1, graph A). Thereafter, the centrifuged solid sample was washed eight times with distilled water until it was free from halide and characterized with X-ray diffractometer under still wet condition with water (Fig. 1, graph B). The washed sample was dried at 65°C for 24 h in high vacuum ( $10^{-3}$  torr) and

analyzed with X-ray diffractometer under dried condition in high vacuum (Fig. 1, graph C).

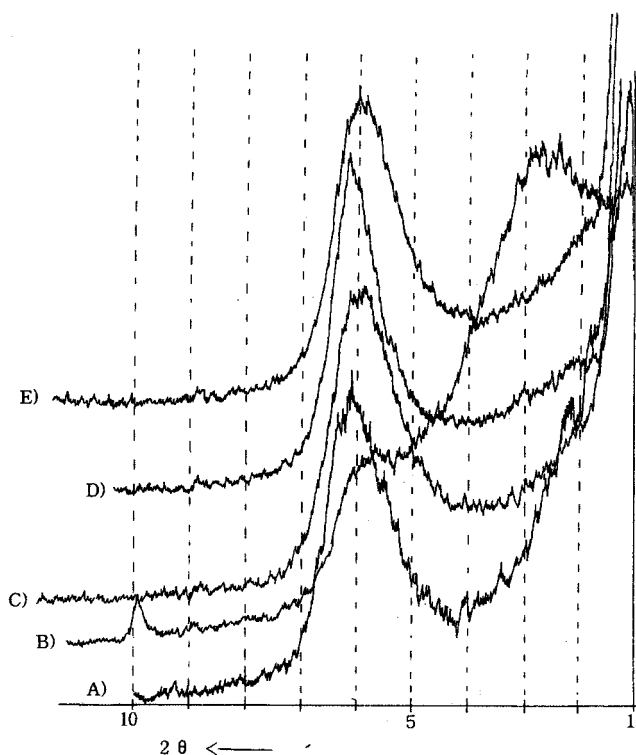
The results measured with X-ray diffractometer are summarized in Table I, which shows that the basal spacing values between the reaction products [TEACOOH]-mont and the starting material Na-montmorillonite are quite different. In case of [TEACOOH]-mont, the basal spacing of 19.64 Å is obtained under the exchange solution, but it lies on 18.52 Å with the reduction of 1.12 Å after washing eight times with water until it was free from halide. Under this condition, it is obvious that the sample has still much water between the layer of the intercalations complex. Therefore, the sample was dried at 65°C in high vacuum ( $10^{-3}$  torr) for 24 h, whereafter the closed packing was obtained and the basal spacing also decreased up to 14.50 Å with the reduction of 4 Å. It is a comprehensible value, because the density of charge of montmorillonite used in this research is very small. Under such density of charge, the alkyl ammonium ions with up to at least 12 C atom numbers form a flat lying monolayer, as we know from many other researches.

The Na-montmorillonite used as a starting material swells toward infinity under distilled water, that is, the layers of the crystals separate to the individual layers. So the attractive interactions between the adjacent layers will be reduced. After drying under high vacuum, its basal spacing falls to 9.8–10.1 Å. The X-ray diffraction patterns for the summarized data in Table I are demonstrated in Figure 1.

Figure 2 shows the x-ray diffraction (XRD) patterns for the [TEACOOH]- $\epsilon$ -caprolactam-montmorillonite synthesized by the reaction of [TEACOOH]-mont with  $\epsilon$ -caprolactam. As showed in Figure 2, the X-ray pattern of the [TEACOOH]- $\epsilon$ -caprolactam-montmorillonite is quite different from that of the starting material, [TEACOOH]-mont. This suggests that the caprolactam is successfully intercalated into the layer of [TEACOOH]-mont. But from Figure 2, we can observe that the X-ray patterns obtained after drying in high vacuum directly after the exchange reaction and after extraction with methanol and following drying in high vacuum are almost the same as that of the starting material, [TEACOOH]-mont. This suggests that the intercalated  $\epsilon$ -caprolactam between the layers

**TABLE I**  
Basal Spacings Measured after the Cation Exchange Reaction

Sample treatment	Basal spacing (Å) of	
	Reaction product	Na-montmorillonite
After more than 48-h exchange time under exchange solution	19.64	-
After eight times washing measured under water	18.52	Toward infinitely
After 24-h drying in high vacuum at 65°C	14.52	9.8–10.1



**Figure 2** X-ray diffraction patterns of [TEACOOH]-mont with  $\epsilon$ -caprolactam. A, [TEACOOH]-mont as a starting material; B, after intercalation of  $\epsilon$ -caprolactam into [TEACOOH]-mont; C, after drying of B in high vacuum right after the exchange reaction; D, after extraction with methanol and following drying in high vacuum of B; E, after extraction with ethanol and following drying in high vacuum of B.

of [TEACOOH]-mont are extensively removed again from the layers.

### Results of polymerization

In order to know if the polymerization of  $\epsilon$ -caprolactam in the layers of [TEACOOH]-mont has been successful, the sample was treated in high vacuum at 65°C for 24 h. Under these conditions, the unreacted  $\epsilon$ -caprolactam intercalated into the silicate layers will

be removed from the layers again, and the basal spacing will be falling to ca. 14.5 Å, which was the value for the starting material, [TEACOOH]-mont, dried in high vacuum. Independent of this procedure, extraction analyses of samples were performed with the solvents in which only the monomer or small oligomers are soluble, but not the polymer. The results measured with X-ray diffractometer are showed in Table II and Figure 3.

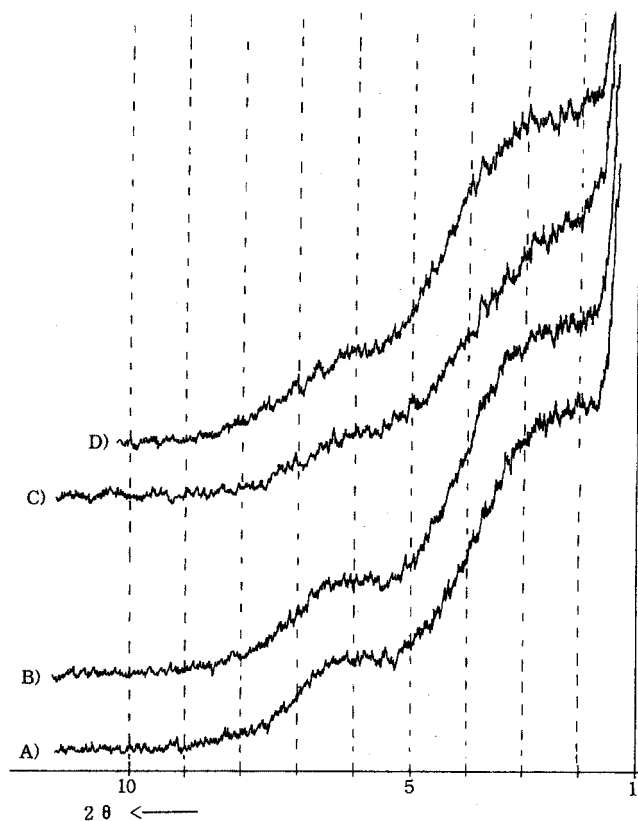
From the results of Table II and X-ray diffraction patterns in Figure 2, we can see that  $\epsilon$ -caprolactam was almost fully removed from the layers of [TEACOOH]-mont, if the caprolactam was not polymerized in the layers, dried at 65°C for 24 h in high vacuum directly after intercalation reaction (Fig. 2, graph C) and after extraction with solvent (here methanol, for example; Fig. 2, graph D). But the results of Table II and Figure 3 show that the  $\epsilon$ -caprolactam was not removed from the layers after the polymerization. This suggests that the polymerization of  $\epsilon$ -caprolactam is successfully performed between the layers of [TEACOOH]-mont.

In Table II, the basal spacings of the reaction products [TEACOOH]-caprolactam-montmorillonites, which were synthesized by the intercalations reaction of  $\epsilon$ -caprolactam into [TEACOOH]-mont and will be used as a starting material for the polymerization of the organic monomer, are summarized. The basal spacing of [TEACOOH]-caprolactam-montmorillonite before polymerization was 36.42 Å, but it was reduced to 15.32 Å after intercalation reaction and drying at 65°C for 24 h in high vacuum. This is caused by the removal of almost all  $\epsilon$ -caprolactam from the layers in high vacuum by vaporization. Table II and Figure 3 show us also that in case of the extraction with the solvents methanol and ethanol, in which the monomer is soluble and following drying in high vacuum at 65°C for 24 h, the monomer  $\epsilon$ -caprolactam was also removed from the layers and the basal spacings fell to 14.54 and 14.86 Å, respectively.

In Table II, the basal spacings of the products that were obtained after polymerization at 250°C for 24, 36,

**TABLE II**  
Results of Polymerization of  $\epsilon$ -Caprolactam in [TEACOOH]-Mont

Sample treatment	Basal spacings (Å) after reaction of [TEACOOH]-mont with monomer before polymerization	Basal spacings (Å) at 250°C for		
		24 h	36 h	48 h
Starting material for polymerization	36.42			
After polymerization		33.85	39.34	43.44
Dried in high vacuum at 65°C, for 24 h	15.32	29.64	35.46	41.54
After extraction with methanol wet with methanol	37.33	36.45	37.16	43.42
Dried in high vacuum at 65°C for 24 h	14.54	27.14	42.56	39.53
After extraction with ethanol wet with ethanol	37.12	35.21	37.15	43.42
Dried in high vacuum at 65°C for 24 h	14.86	26.94	31.92	40.16



**Figure 3** X-ray diffraction patterns of [TEACOOH]-mont with  $\epsilon$ -caprolactam after polymerization. A, after polymerization for 36 h at 250°C; B, after drying in high vacuum at 65°C for 24 h; C, after extraction with methanol and following drying in high vacuum of A; D, after extraction with ethanol and following drying in high vacuum of A.

and 48 h are summarized. From the results of Table II, we can see that in every case the basal spacing increased with the reaction time. After polymerization for 24 h, the basal spacing is 33.85 Å, while the basal spacings obtained after polymerization for 36 and 48 h are 39.34 Å and 43.44 Å, respectively. From these results, it is obvious that the polymerization has been successfully proceeded and the reaction proceeds more rapidly in the higher reaction temperature.

We can observe more precisely the polymerizations state by checking the basal spacings measured directly after drying at 65°C for 24 h in high vacuum. The basal spacing of the sample synthesized after polymerization for 24 h is 33.85 Å, but it fell to 29.64 Å after drying at 65°C for 24 h in high vacuum. Therefore, a large difference exists between the basal spacing between the two cases, from which we can know that large amounts of the monomer  $\epsilon$ -caprolactam intercalated between the interlamellar space have been removed from the layers. The results obtained after polymerization for the reaction time of 36 and 48 h are different from those for 24 h. For example, the basal spacings measured after polymerization for 36 and 48 h and directly after drying of these polymerized

products at 65°C for 24 h in high vacuum are 35.46 and 41.54 Å, respectively. In this case, the difference of the basal spacings is very small, which means that quite small amounts of the monomer in the layers are evaporable in high vacuum.

While the basal spacings obtained before polymerization lay between 14.54 and 15.86 Å because almost all amounts of the monomer were removed from the layers, those measured after extraction of the polymerized sample with solvents (here methanol and ethanol) in which the monomer is soluble and following drying at 65°C for 24 h in high vacuum are more than 25 Å in all cases, which means that the polymerization proceeded successfully. In general, we can see from the results of Table II that the less the basal spacing reduces, the longer the reaction time is.

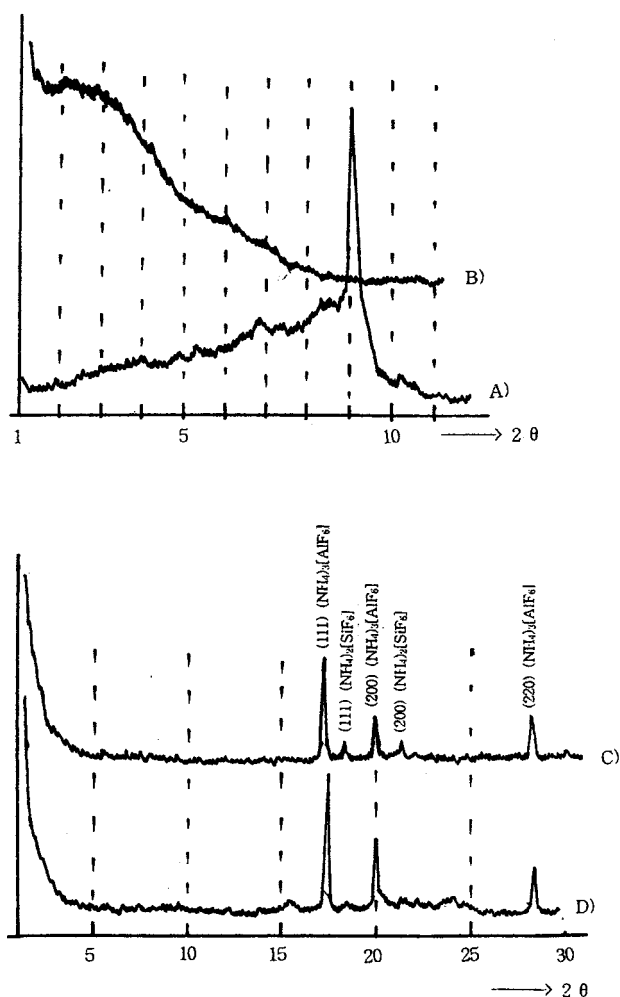
Comparing Figures 2 and 3, it is obvious that the X-ray peaks obtained after polymerization are not sharp and far broader than those measured before polymerization. For this reason, the basal spacings for the X-ray patterns after polymerization are much less precise than those obtained before polymerization. Therefore, due to the difficulty in measuring the exact basal spacings from the X-ray peaks after polymerization, it has to be considered that only the rough basal spacings could be taken in Table II and that the limit of error is 3 Å or more.

### Results of analysis of polymer isolated from layers

In order to investigate and analyze more precisely the polymer products, the polymerized sample was separated from the layers of montmorillonite. But as we know from the results of the extraction with solvents, it was not possible to isolate the polymerized product from the interlamellar space by extraction with solvents. It was also not possible to separate the polymer ion existing between the layers by cation exchange reaction because the ion with high molecular weight is linked more strongly with montmorillonite in the interlamellar space than the ion with low molecular weight. Therefore, in order to isolate it, we had to decompose the silicate lattice with the  $\text{NH}_4[\text{HF}_2]$  solution. The separated sample was then analyzed with X-ray diffractometer and IR spectrometer, and the results are demonstrated in Figures 4 and 5.

### Results of analysis with X-ray diffractometer

The X-ray diffraction patterns before and after the decomposition reaction of Na-montmorillonite and [TEACOOH]-polycaprolactam-montmorillonite are demonstrated in Figure 4, from which we can observe that the decomposition reaction has been proceeded successfully, that is, montmorillonite is decomposed by the chemical reaction with  $\text{NH}_4[\text{HF}_2]$ . From Figure 4, we can see that the typical (001) peaks for montmo-



**Figure 4** X-ray diffraction patterns of (A) Na-montmorillonite, dried in high vacuum at 65°C for 24 h; (B) [TEACOOH]-polycaprolactam-montmorillonite, polymerized for 36 h at 250°C, extraction with methanol, and dried in high vacuum at 65°C for 24 h; (C) insoluble residue in water and  $\text{NH}_4[\text{HF}_2]$ -water solution of Na-montmorillonite after decomposition reaction; (D) insoluble residue in water and  $\text{NH}_4[\text{HF}_2]$ -water solution of [TEACOOH]-polycaprolactam-montmorillonite after decomposition reaction.

rillonite disappeared, while those peaks for the precipitates that are not soluble in  $\text{NH}_4[\text{HF}_2]$  solution appeared: (111), (200), and (220) peaks, which are very sharp, are related to the  $(\text{NH}_4)_3[\text{AlF}_6]$  precipitate, while (111) and (200) peaks to the  $(\text{NH}_4)_2[\text{SiF}_6]$  precipitate. Here Al and Si from  $[\text{AlF}_6]^{3-}$  anion and  $[\text{SiF}_6]^{2-}$  anion, respectively, can be derived only from montmorillonite lattice layers.

### Results of IR analysis

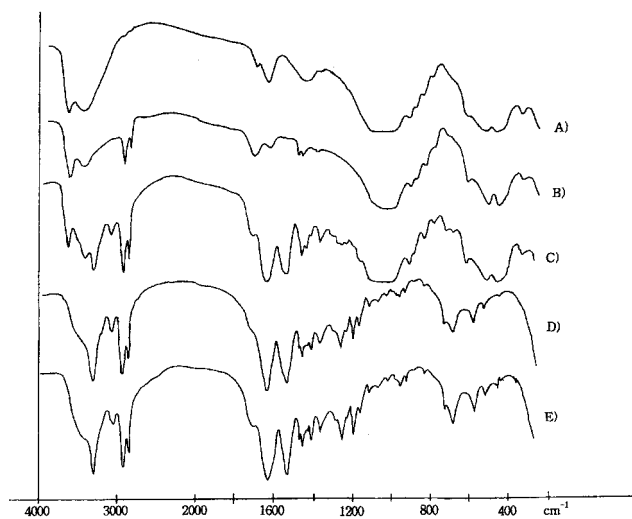
The results of IR analyses for each sample are shown in Figure 5. The IR spectrum for Na-montmorillonite is showed in Figure 5, graph A. This spectrum includes somewhat characteristic broad peaks. Graph B in Figure 5 shows the IR spectrum for [TEACOOH]-

mont with the cation in the interlamellar space. In this spectrum, we can observe the sharp peaks in the region from 2,828 to 2,915  $\text{cm}^{-1}$  and from 1,468 to 1,490  $\text{cm}^{-1}$ , which did not exist in the spectrum for Na-montmorillonite and are derived from the organic cation intercalated between the layers.

Graph C in Figure 5 shows the IR spectrum for [TEACOOH]-polycaprolactam-montmorillonite sample synthesized by the polymerization of  $\epsilon$ -caprolactam in the interlamellar space of [TEACOOH]-mont intercalations complex, extracted with methanol solvent to remove the caprolactam, which was not polymerized, and then dried at 65°C for 24 h in high vacuum. In this case, we can observe additional sharp peaks.

In Figure 5, graph D, the IR spectrum for the sample separated from the interlayer spaces of montmorillonite after decomposition of [TEACOOH]-polycaprolactam-montmorillonite with  $\text{NH}_4[\text{HF}_2]$  was demonstrated. In order to compare it, the spectrum for the polymer that was synthesized by the reaction of  $\epsilon$ -caprolactam with [TEACOOH]-mont without montmorillonite is shown in Figure 5, graph E. Comparing graphs D and E in Figure 5, we can observe that the two polymers synthesized under different reaction conditions are the same compounds.

It is obvious from the polymerization experiments and the results of IR spectrums (Fig. 5, graphs C-E) that a chemical reaction (polymerization) in the interlamellar space of [TEACOOH]-mont appeared.



**Figure 5** IR spectrums for (A) Na-montmorillonite; (B) [TEACOOH]-montmorillonite; (C) [TEACOOH]-polycaprolactam-montmorillonite, polymerized for 36 h at 250°C, extraction with methanol, and dried in high vacuum at 65°C for 24 h; (D) polymer, isolated from the interlayer space of montmorillonite (original polymerization in interlayer space at 250°C for 36 h, extraction with methanol, then isolated by  $\text{NH}_4[\text{HF}_2]$  process); (E) polycaprolactam, synthesized without montmorillonite, after extraction with water, and dried in high vacuum at 65°C for 24 h.

## CONCLUSIONS

In this research, we have tried to polymerize  $\epsilon$ -caprolactam in the interlamellar space of [TEACOOH]-mont to achieve the [TEACOOH]-polycaprolactam-montmorillonite in which the montmorillonite (inorganic polymer) is chemically bonded with the organic polymer (polycaprolactam) and have found the following results.

The basal spacings for the samples obtained after polymerization lie from 26.94 to 41.54 Å under dried condition in high vacuum, while those for the samples before polymerization lie between 14.54 and 15.32 Å under the same condition. We can also observe that the less the basal spacing reduces, the longer the reaction time is.

By comparing the IR spectrum of the starting material before polymerization with that of the product obtained after polymerization, we can see that polymerization appeared in the interlamellar space of the intercalations complex.

Comparing the IR spectrum for the sample isolated from the layers of [TEACOOH]-mont after polymerization of  $\epsilon$ -caprolactam in the interlamellar space of [TEACOOH]-mont with that for the polymer synthesized by the reaction of  $\epsilon$ -caprolactam only with the organic cation [TEACOOH] Br without montmorillonite, it is obvious that the two polymers, synthesized under different reaction conditions, are the same compounds.

From all these results, it appears that the polymerization was successfully accomplished in the interlamellar space of the [TEACOOH]-mont intercalations complex.

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