

# Copolymerization of Styrene with *N*-Phenyl Maleimide in the Presence of Montmorillonite

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**ABSTRACT:** The copolymerization of styrene with *N*-phenyl maleimide in the presence of organomodified montmorillonite or Na<sup>+</sup> montmorillonite was investigated. The conversion of the monomer was determined dilatometrically or gravimetrically. The copolymerization rate was accelerated and the polymerization activation energy in bulk and solution copolymerization decreased in the presence of montmorillonite. The tendency of alter-copolymerization was enhanced for bulk and solution polymerization, but not affected for emulsion polymerization, by the addition of

organomodified montmorillonite or Na<sup>+</sup> montmorillonite. X-ray diffraction studies showed that the methods of emulsion and bulk intercalative polymerization were more appropriate techniques for preparing nanocomposites with good dispersibility of clay. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1932–1937, 2005

**Key words:** clay; copolymerization; kinetics (polym.); nanocomposites

## INTRODUCTION

Polymer/layered silicate nanocomposites (PLSNs) have attracted considerable technological and scientific interest in recent years, especially after a nylon 6/montmorillonite (MMT) nanocomposite was reported by Okada et al. in 1987.<sup>1</sup> This technological interest has stemmed from the dramatic enhancements in the physical, thermal and mechanical properties of PLSN materials with a minimal increase in density as a result of a low inorganic loading.

MMT is the most widely used silicate; its crystal structure consists of two-dimensional layers formed by the fusion of two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Polymer intercalation and intercalative compounding by *in situ* bulk, solution, and emulsion polymerization have been studied widely.<sup>2–6</sup> Most studies have focused on the layer structure changes of MMT caused by the usage of intercalative agents with different structures and compounding by different intercalative polymerization techniques or polymer intercalative methods. It has been believed that the polymerization of the monomer is also affected by the addition of the clay, which in turn affects the structure and properties of the prepared nanocomposites.<sup>7–9</sup> However, reports

on this are still lacking, and this article presents a study of the effect of clay on the polymerization of a monomer and some results on this matter. In our previous articles,<sup>8,9</sup> the bulk polymerization of methyl methacrylate and styrene (St) initiated thermally by benzoyl peroxide (BPO) in the presence of MMT has been investigated. In both cases, MMT can accelerate the polymerization rate.

Studies on the effect of clay on copolymerization are much scarcer. Lee et al.<sup>10</sup> studied the emulsion copolymerization of St and acrylonitrile in the presence of MMT, and the acrylonitrile contents of the copolymer intercalated were lower than the input quantity. The authors ascribed this result to the solubility difference between the comonomers in water. However, this interpretation was too vague to illuminate how MMT affected the copolymerization.

This work involves the copolymerization of St and *N*-phenyl maleimide (PMI) in the presence of organomodified montmorillonite (OMMT) or Na<sup>+</sup> montmorillonite (NaMMT). The copolymerization rate, copolymerization activation energy, and comonomer composition have been determined, and the results are discussed.

## EXPERIMENTAL

### Materials

NaMMT was supplied by Huate Co. (Zhejiang, China). The clay was purified by its dispersion into deionized water and the separation of the noncolloidal

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impurities. Then,  $\text{Na}_2\text{SiO}_3$  was added to this suspension and agitated for about 24 h at room temperature. The obtained suspension was then centrifuged and washed several times with deionized water. The product was dried, crushed, and sieved with 400 mesh to obtain NaMMT.

Cetyltrimethyl ammonium bromide was added to the aforementioned suspension to carry out the cation-exchange reaction. The system was maintained around  $68^\circ\text{C}$  for about 4 h and then filtered and repeatedly washed with distilled water. The filtrate was titrated with  $0.1\text{N}$   $\text{AgNO}_3$  until no  $\text{AgBr}$  precipitated to ensure the complete removal of bromide ions. The product was then dried, crushed, and sieved with 400 mesh to obtain OMMT. The ion-exchange capacity was determined with a TA-2000 component thermogravimeter (SDT2960) (TA Instruments, New Castle, DE) to be  $82.4$  mequiv/100 g of clay.<sup>8</sup>

St (Tianjin Chem Co., Tianjin, China) was analytically pure and was distilled under reduced pressure after the removal of the inhibitor by two washings with a 5%  $\text{NaOH}$  solution and several washings with deionized water. PMI was supplied by Lanchou Chem Co. (Gansu Province, China) and recrystallized several times in a water/ethanol mixture (2 : 1 volume ratio). BPO was an analytical reagent and was recrystallized twice in toluene.

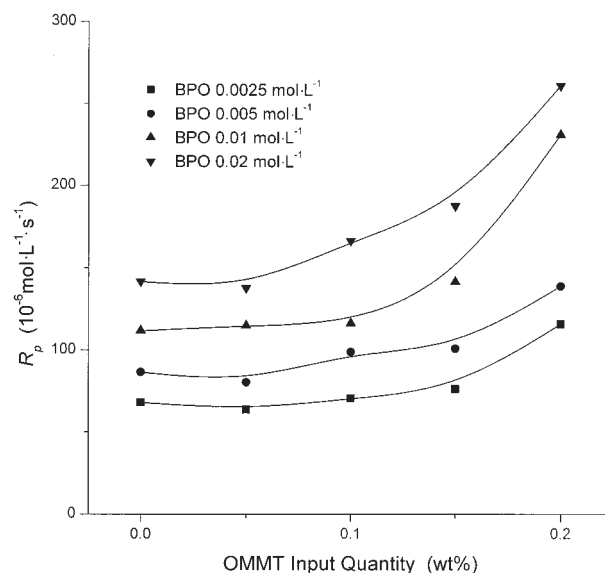
### Determination of the polymerization rates

All glass vessels were washed before use with a potassium dichromate/concentrated sulfuric acid solution and deionized water and then dried *in vacuo* at  $100^\circ\text{C}$  for 24 h.

Measured amounts of OMMT were dispersed in PMI/St (1 : 9 molar ratio) via ultrasonication at  $25^\circ\text{C}$  for 10 min. Then, BPO was added, and the rates of polymerization were measured dilatometrically in a water bath fixed at  $40 \pm 0.1^\circ\text{C}$ . During the course of the reaction, no visible sediment was observed in the studied MMT content range. The contents in the dilatometer were poured into a large amount of ethanol, and the products were isolated by filtration with ethanol and then dried in an oven under reduced pressure to achieve a constant weight.

For solution copolymerization, PMI and St in 1 : 9 molar ratio was dissolved in chloroform, and the polymerization was carried out at  $50 \pm 0.1^\circ\text{C}$  under a nitrogen atmosphere. A measured amount of the solution was taken out at predetermined time intervals and poured into a large amount of ethanol. The products were filtered and dried *in vacuo* to give a constant weight. The polymerization rate was calculated gravimetrically.

The emulsion polymerization was carried out at  $60 \pm 0.1^\circ\text{C}$ , and sodium lauryl sulfate was used as the emulsifier agent.



**Figure 1** Bulk polymerization rates of styrene with N-phenyl maleimide at different OMMT input quantities.

### Characterization and measurements

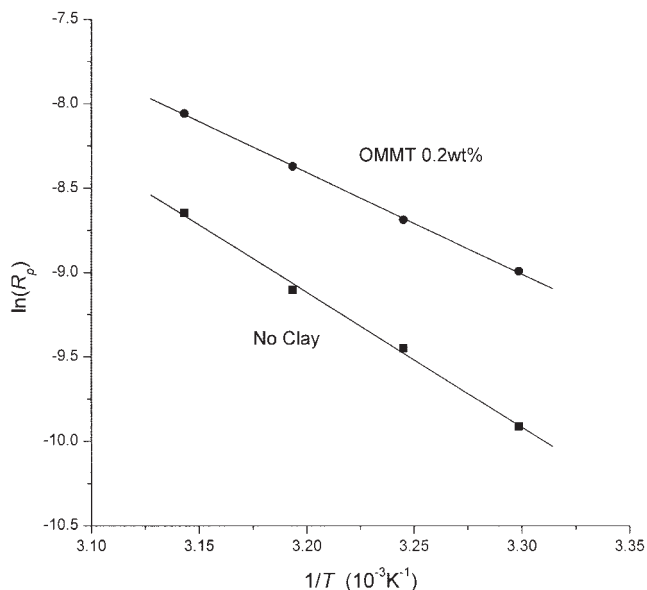
X-ray diffraction (XRD) patterns were recorded by the monitoring of the diffraction angle ( $2\theta$ ) from  $1$  to  $30^\circ$  on a DMAX-RC X-ray crystallographic unit (Rigaku Co., Tokyo, Japan). The unit was equipped with a Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm) source at a voltage of  $50$  kV and a current of  $180$  mA. The scanning speed and step size were  $1^\circ/\text{min}$  and  $0.02^\circ$ , respectively.

The composition of the copolymer in the composites was determined by elemental analysis. A Heraeus CHN-O rapid elemental analyzer (Foss Heraeus, Hanau, Germany) was employed, and the content of element N was used to calculate the PMI content in the copolymer.

## RESULTS AND DISCUSSION

### Copolymerization rates

Figure 1 shows the rates of bulk copolymerization of St with PMI at different OMMT input quantities with BPO concentrations at  $0.0025$ ,  $0.005$ ,  $0.01$ , and  $0.02$  mol/L. The polymerization rates increased with the addition of OMMT in the studied range of BPO concentrations, and this is consistent with our study on the homopolymerization of St. Al-Esaimi<sup>7</sup> attributed the catalytic effect of clay to the formation of a clay/initiator complex. However, the article gave no further evidence, and a clear mechanism still needs further and thorough studies. As discussed in previous articles,<sup>8,9</sup> the acceleration of the polymerization rate in the presence of clay may be attributed to the promotion of the clay on the chain initiation.



**Figure 2** Bulk polymerization rates of styrene with N-phenyl maleimide under different temperatures.

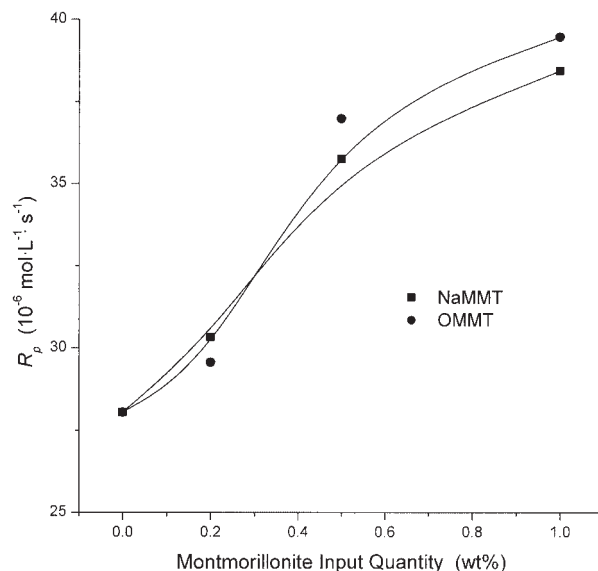
Also, the bulk copolymerization of St with PMI at different temperatures was carried out to obtain the copolymerization activation energy with an Arrhenius equation as follows:

$$\ln R_p = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (1)$$

where  $R_p$  is the initial polymerization rate at temperature  $T$ ,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy, and  $R$  is the gas constant. The BPO concentration was fixed at 0.01 mol/L. Figure 2 shows the results of that in the presence of 0.2 wt % clay and without clay. The copolymerization activation energy in the presence of clay was determined to be 50.07 kJ/mol. In comparison with the value of 66.45 kJ/mol of that without clay, the great decrease in the activation energy also confirmed the promotion effect of the clay on the copolymerization.

For solution copolymerization, the situations in the presence of either OMMT or NaMMT have been investigated. As shown in Figure 3, the addition of clay can also increase the copolymerization rate greatly for solution copolymerization. When the clay input content was 0.5 wt %, the copolymerization rates increased more than 35%. Also, the remarkable increase in  $R_p$  can be attributed to the catalytic effect of the clay.

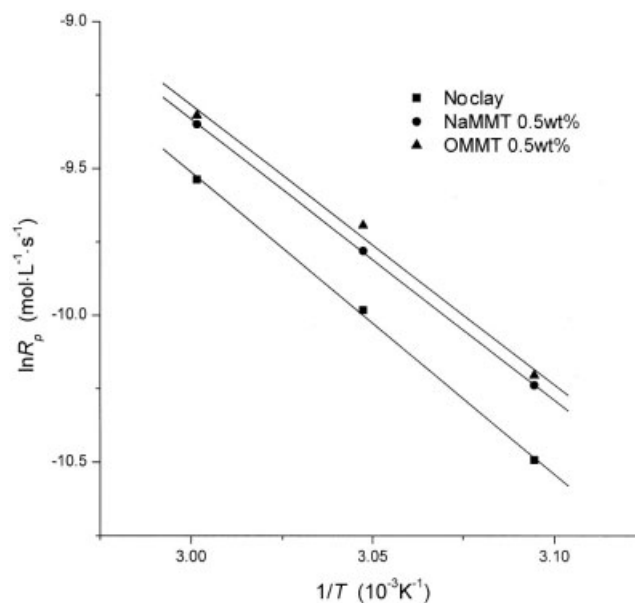
There was almost no difference whether OMMT or NaMMT was introduced into the system. The activation energies of the two cases were also found with no perceptible difference. When 0.5 wt % clay was introduced into the system, the activation energy decreased from 85.58 to 70.95 and 72.92 kJ/mol for NaMMT and



**Figure 3** The initial polymerization rates at different montmorillonite input quantities.

OMMT, as shown in Figure 4. This result shows that the catalytic effect of the clay on the polymerization may be mostly caused by the small-size effect of the clay layers, and the activity spots are on the surface of the clay particles rather than between the layers. The existence and structure of the intercalative agents have no effect on the catalytic effect on the polymerization.

A different result was found for emulsion polymerization, as shown in Figure 5(a,b). With NaMMT or OMMT introduced, the polymerization was depressed instead of promoted. This is believed to be



**Figure 4** Solution polymerization rates of styrene with N-phenyl maleimide under different temperatures.

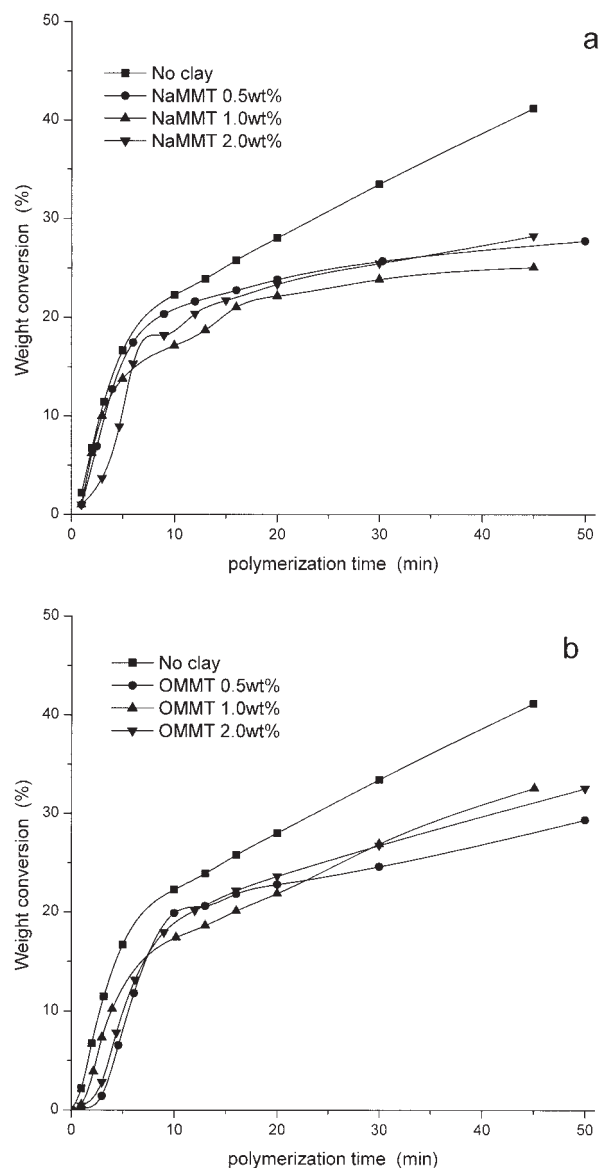


Figure 5 Weight conversion of St/PMI at different montmorillonite input quantities.

due to the fact that different polymerization methods have different mechanisms. For bulk and solution polymerizations, the clay and initiator are both dispersed uniformly in the system, and they have the maximum probability to act with each other to achieve the catalytic effect on the radical initiation. However, in emulsion polymerization, this is not the case. The initiator is dissolved, whereas the clay layers are suspended in the water. Meanwhile, as the polymerization kinetics described, the most important factors for determining the polymerization rate are the presentation rate of the radical and the concentration of the micelles, but not the chain initiation rate.<sup>11</sup> It is believed that the emulsifier agent may be absorbed onto the surface of the clay particles; this will decrease the concentration of the

emulsifier agent in water.  $R_p$  is proportional to  $S^{0.6}$  in emulsion polymerization, where  $S$  is the concentration of the emulsifier agents, so  $R_p$  decreased with the addition of clay to the system in the case of emulsion polymerization.

### Copolymer composition

The obtained composite at a monomer conversion around 5 wt % was used in the elemental analysis. The clay contents in the composite were estimated by the clay input quantities and the monomer conversion. The content of element N was used to calculate the PMI content in the copolymer. Table I tabulates the results of the copolymer compositions in the composites.

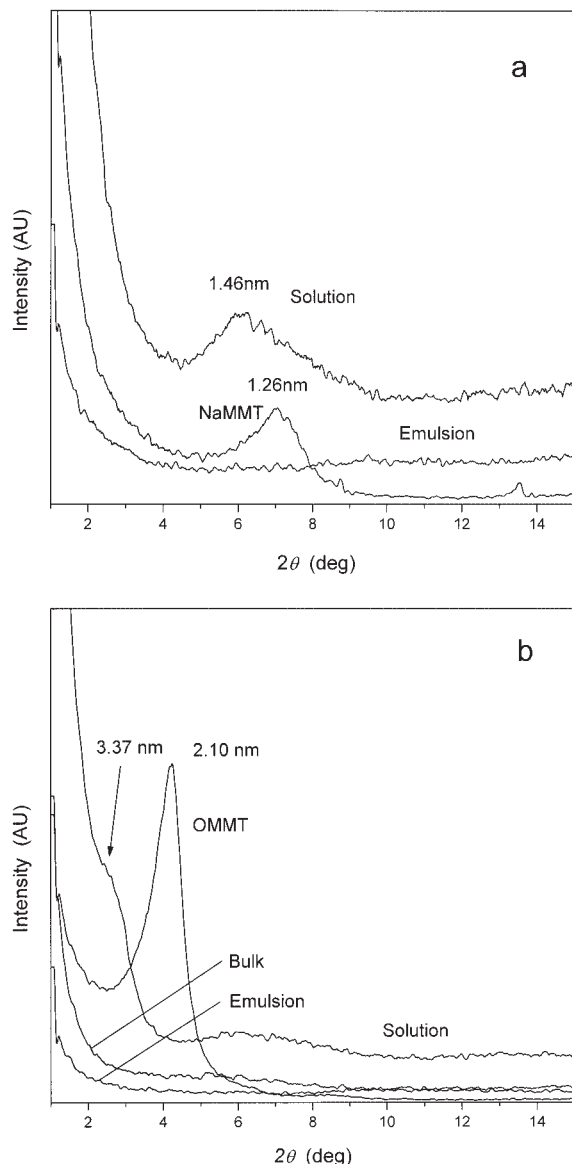
Table I shows that St and PMI have extensive tendencies to form an alternative copolymer in all three cases.<sup>12</sup> Similarly to the results for the polymerization rates, the tendency of alter-copolymerization was greatly enhanced in the case of bulk copolymerization. For solution copolymerization, the alternative tendency also increased to some extent. However, for emulsion copolymerization, the PMI contents in the copolymer showed no visible change. This result is consistent with the situation of  $R_p$ , but different from a study on the copolymerization of St and acrylonitrile in the presence of MMT.<sup>10</sup>

Previous studies have shown that the carbonyl groups interact with the clay layers and help with the dispersion of the clay layers in the matrices.<sup>13–15</sup> PMI has a stronger affinity to the clay layer and may be absorbed on the surface of clay particles. Therefore, PMI was not dissolved homogeneously in the solvent

TABLE I  
Copolymer Compositions at Different Clay Input Quantities

	Clay addition content (wt %)	$F_{\text{PMI}}$	
		NaMMT	OMMT
Bulk copolymerization	0		0.344
	0.05		0.418
	0.1	—	0.460
	0.15		0.438
	0.2		0.457
Solution copolymerization	0	0.408	0.408
	0.2	0.425	0.427
	0.5	0.427	0.420
	1.0	0.432	0.431
Emulsion copolymerization	0	0.377	0.377
	0.5	0.375	0.376
	1.0	0.377	0.377
	2.0	0.376	0.375

$F_{\text{PMI}}$  is the mole fraction of PMI in the copolymer.



**Figure 6** XRD patterns of montmorillonite and (a) St-PMI/NaMMT and (b) St-PMI/OMMT nanocomposites.

St in the case of bulk polymerization or in the solvent chloroform in the case of solution polymerization, but it had a higher concentration close to the clay particles. As discussed previously, clay has a catalytic effect on the polymerization reaction, so  $R_p$  near the clay particles was much higher and more PMI monomer was incorporated into the copolymer than in the case with no clay added. As a result, the copolymer had a higher PMI content. For emulsion polymerization, the relative incorporation rate of the two monomers into the chain was determined by the concentrations of the monomers in the micelles and the diffusion rates of the monomers in water. The addition of clay to the system may affect the two factors of St and PMI monomers with no apparent difference, so there is little difference in the copolymer compositions.

## XRD results

The XRD patterns of the obtained St-PMI/clay nanocomposites at low monomer conversions are shown in Figure 6. The clay contents estimated from the clay input quantities and the total weights of the composites are tabulated in Table II. As shown, although all the composites had similar clay contents, they showed prominent differences in the XRD patterns, which indicated different structures.

For the composites prepared via bulk and emulsion intercalative copolymerizations, no 001 peak was found, and this indicated a higher dispersibility of clay in the copolymer matrix. The absorptions of  $d_{001}$  were found for both St-PMI/NaMMT and St-PMI/OMMT composites prepared via solution polymerization, although the intercalation of the copolymer into the clay galleries was confirmed by the decrease in  $2\theta$  of the absorption peak.  $d_{001}$  increased from 1.26 to 1.46 nm for NaMMT and from 2.10 to 3.37 nm for OMMT.

The results show that emulsion polymerization is the better method for preparing a polymer/NaMMT nanocomposite, whereas bulk and emulsion polymerizations are both appropriate ways of preparing polymer/OMMT nanocomposites in comparison with solution polymerization. Solution polymerization is not suitable for preparing polymer/clay nanocomposites with higher dispersibility of the clay, not to mention its discommodiousness of solvent recycling. The result is consistent with the study of Noh and Lee<sup>16</sup> on the preparation of styrene-acrylonitrile (SAN)/clay nanocomposites. It has been reported that an SAN/NaMMT composite prepared via emulsion polymerization with unmodified MMT has even better properties than SAN/OMMT prepared via solution polymerization, although the clay has been modified to have hydrophobicity. In the case of solution intercalative polymerization, the salvation of solvent is very important. As is well known, in the solution intercalative polymerization technique, the role of the solvent is to improve the inclusion of monomers between the layers of clay. However, when we consider that the driving force for polymer intercalation by the solution method is the entropy gained by the desorption of solvent molecules due to the gain in translational freedom of many desorbed molecules from the

**TABLE II**  
Clay Contents in the Composites

Composite		Clay content (wt %)
Bulk polymerization	St-PMI/OMMT	4.78
	St-PMI/NaMMT	4.56
Solution polymerization	St-PMI/OMMT	4.64
	St-PMI/NaMMT	8.93
Emulsion polymerization	St-PMI/NaMMT	8.93
	St-PMI/OMMT	7.85

clay galleries, strong polar interactions between the solvent and the clay layers may cause less entropy gain and disadvantage the intercalation.

### CONCLUSIONS

The copolymerization of St with PMI was greatly promoted with the addition of clay in bulk and solution polymerizations but depressed in the case of emulsion polymerization. Also, the tendency of alter-copolymerization was enhanced for bulk and solution polymerizations, and there was no visible change in emulsion polymerization. XRD results show that the techniques of bulk and emulsion intercalative polymerizations are more appropriate for preparing nanocomposites with good dispersibility than the method of solution intercalative polymerization.

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