

# Tentative Study on Kinetics of Bulk Polymerization of Methyl Methacrylate in Presence of Montmorillonite

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Received 26 September 2002; accepted 7 April 2003

**ABSTRACT:** The kinetics of the bulk polymerization of methyl methacrylate (MMA) in the presence of montmorillonite (MMT) were studied. The effect of MMT on the radical polymerization of MMA was researched by determining the polymerization rate dilatometrically. It was assumed that there were both bimolecular and monomolecular termination processes involved in the termination of the radicals in the polymerization. It was found that a lower benzoyl peroxide (BPO) concentration promotes a higher fraction of monomolecular mode in chain termination. The results

show that there is an optimal ratio of MMT to initiator that increases the bulk polymerization rate of MMA. The X-ray results show that the layer structure of the formed PMMA–MMT composites was also affected by the BPO concentration. With lower initiator concentration, less pronounced layer structure will be observed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3690–3695, 2003

**Key words:** kinetics; radical polymerization; nanocomposites

## INTRODUCTION

In recent years, much attention has been paid to layered clay/polymer nanocomposites as advanced plastic materials prepared by *in situ* intercalative polymerization. The nanocomposite made of poly(methyl methacrylate) (PMMA)/clay has been the most widely studied, and montmorillonite is a widely used layer silicate.<sup>1–4</sup> Different methods of forming the so-called nanocomposites, such as bulk, solution, suspension and emulsion polymerization have been studied. The major studies have focused on the layer structure changes caused by the use of different intercalative agents and different polymerization conditions. Obviously, the polymerization of the monomers will also be affected by the silicates added to the system. This will in turn affect the layer structure and finally the properties of the nanocomposites formed.

Uskov reported that methyl methacrylate (MMA) can graft onto air-dried sodium bentonite under vibrodintegration.<sup>5</sup> At the same time, no homopolymer was found in the polymerization. This indicates that the bentonite has an initiation effect on the polymerization of vinyl monomers. Solomon systematically studied the effect of different minerals on the polymerization of styrene.<sup>6</sup> The results show that the polymerization has characteristics expected of both a radical and a cationic reaction. And it was found that

the aluminum atom in the octahedral coordination of the mineral surface was responsible for the catalyst activity. In the radical polymerization of MMA, it was found that aluminosilicates and magnesium silicates played an inhibitory role.<sup>7</sup> This was contrary to the styrene system.

It is necessary to conduct a systematic study of the effect of silicates on the polymerization kinetics of vinyl monomer, and we hope that this study will provide further information on this subject.

## EXPERIMENTAL

### Materials

Na-montmorillonite (MMT) was used in this study and was supplied by Zhejiang Huate Bentonite Corporation (Linan, China). MMA (Tianjin Chem. Co., Tianjin, China) was of analytical purity grade and washed free of inhibitor with an aqueous solution of sodium hydroxide; it was then washed with deionized water, dried, and distilled under reduced pressure before the middle fraction was collected. Benzoyl peroxide (BPO) was of analytical reagent grade and recrystallized twice in toluene. Cetyltrimethyl ammonium bromide (CTAB) was used as supplied. All water used in the experiment was deionized and distilled.

### Preparation of OMMT

The inorganic MMT was purified by dispersion of crude clay into distilled water and separation of non-

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**TABLE I**  
**Induction Periods at Different Concentrations of BPO**  
**and OMMT at 60°C (min)**

BPO Concentration (mol/L)	0.0025	0.005	0.01	0.02	0.04
0 wt % OMMT	26.5	16.7	12.9	9.8	7.6
0.1 wt % OMMT	19.7	15.6	10.7	8.9	6.5
0.2 wt % OMMT	17.7	14.4	10.6	8.4	6.9
0.4 wt % OMMT	17.6	13.5	11.2	8.6	6.5

colloidal impurities. To obtain cation exchange, the purified MMT was suspended in an aqueous solution of  $\text{Na}_2\text{SiO}_3$  for 24 h with agitation at room temperature, and then CTAB was added to the system to carry out the cation exchange reaction. The system was maintained at around 68°C for about 4 h and then filtered and repeatedly washed with distilled water. The filtrate was titrated with 0.1N  $\text{AgNO}_3$  until no  $\text{AgBr}$  precipitated to ensure the complete removal of bromide ions. The product was then dried, crushed and sieved with 325-mesh to obtain organo-montmorillonite (OMMT). The ion exchange capacity was determined with a TA-2000 component thermogravimeter (SDT2960) to be 82.4 meq/100g clay.

#### Determination of Polymerization Rates

All glass vessels employed were washed before use with a potassium dichromate/concentrated sulfuric acid solution and distilled water and dried under vacuum at 100°C for 24 h.

Measured amounts of BPO and OMMT were dispersed in MMA via ultrasonication at 25°C for 10 min. Then the rates of polymerization were measured dilatometrically in a water bath fixed at  $60 \pm 0.1^\circ\text{C}$ . During the course of the reaction, no visible sediment was observed. The contents in the dilatometer were poured into a large amount of ethanol, and the products were isolated by filtration and then dried in an oven under reduced pressure to achieve a constant weight.

#### X-ray Characterization

X-ray diffraction (XRD) patterns were recorded by monitoring the diffraction angle,  $2\theta$ , from 1 to 15° on a

DMAX-RC X-ray crystallographic unit. 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  $0.03^\circ$  respectively.

## RESULTS AND DISCUSSION

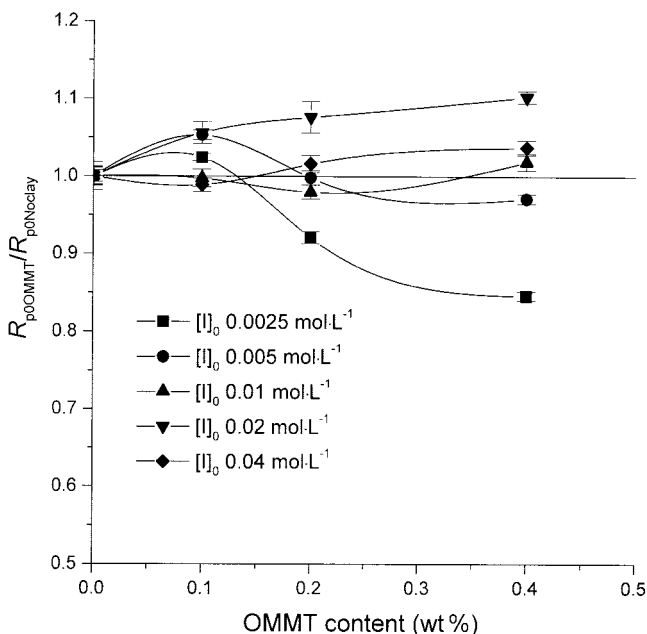
#### Polymerization Rates

Initially, to verify the nonexistence of the polymerization of MMA without initiator (BPO) and with only OMMT present, experiments were carried out. The results showed that the rate neared zero within 7 h. This indicates that there is no evident thermal polymerization or polymerization initiated by OMMT. In other words, polymerization is negligible. The polymerization behavior of MMA was then studied with different concentrations of BPO and OMMT. The obtained induction periods and initial polymerization rates ( $R_{p0}$ ) are summarized in Table I and Table II respectively.

It was observed that the induction periods were shortened rather than lengthened by the addition of OMMT. The results show that the OMMT may accelerate the initiation of the polymerization. As can be seen from Table II,  $R_{p0}$  was affected not only by the BPO concentration but also by the OMMT content. It is reasonable that  $R_{p0}$  increases with increasing BPO concentration. The influence of OMMT is more complex. When the BPO concentration is small, with increasing OMMT content,  $R_{p0}$  rises to a maximum and then decreases, but when the BPO concentration is relatively large, the value increases continually. This indicates that the effect of OMMT content on  $R_{p0}$  is related to the BPO concentration, and  $R_{p0}$  is affected by the combination of BPO with OMMT. Also, the relative increase of  $R_{p0}$  (ratio of rate with OMMT,  $R_{p0\text{OMMT}}$  to rate without OMMT,  $R_{p0\text{NoClay}}$ ) is plotted in Figure 1. Figure 1 also indicates that when the OMMT content increases, the difference between the relative increase of  $R_{p0}$  at different BPO concentrations become larger. Obviously, it is difficult to draw the conclusion that the existence of OMMT will increase or decrease the rate of polymerization,  $R_{p0}$ .

**TABLE II**  
**Initial Polymerization Rates ( $R_{p0}$ ) at Different Concentrations of BPO and OMMT at 60°C ( $10^{-6}$  mol/L s)**

BPO Concentration (mol/L)	0.0025	0.005	0.01	0.02	0.04
0 wt % OMMT	$121.7 \pm 0.9$	$160.7 \pm 1.7$	$235.0 \pm 2.7$	$311.3 \pm 5.6$	$460.5 \pm 5.8$
0.1 wt % OMMT	$124.6 \pm 0.6$	$169.3 \pm 1.0$	$234.5 \pm 2.7$	$328.8 \pm 4.3$	$457.5 \pm 3.9$
0.2 wt % OMMT	$112.0 \pm 0.9$	$160.4 \pm 1.5$	$230.3 \pm 2.2$	$335.1 \pm 6.3$	$470.0 \pm 5.1$
0.4 wt % OMMT	$102.9 \pm 0.7$	$156.1 \pm 1.1$	$239.4 \pm 2.4$	$343.3 \pm 2.5$	$479.8 \pm 4.4$



**Figure 1** The effect of OMMT on  $R_{p0\text{OMMT}}/R_{p0\text{No clay}}$

### Chain Termination Process

The classic radical polymerization theory gives the following equation for rate of polymerization:<sup>8</sup>

$$R_p = k[M]^m[I]^n \quad (1)$$

where  $[M]$  and  $[I]$  represent the concentrations of monomer and initiator respectively,  $m$  and  $n$  represent the reaction orders with respect to monomer and initiator respectively, and  $k$  is a general rate constant. When the termination of the chain is a bimolecular process,  $n = 0.5$ . In the case of monomolecular termination,  $n = 1$ . For most cases,  $n = 0.5 \sim 1$ . The equation shown below can be used to calculate the value of  $n$ :

$$\ln R_p = n \ln[I] + \ln k + m \ln[M] \quad (2)$$

The slope of the plot of  $\ln R_{p0}$  versus  $\ln[I]_0$  will give the value of  $n$ , as well as information about the termination process. The plot of  $\ln R_{p0}$  versus  $\ln[I]_0$  for pure MMA is shown in Figure 2, and the obtained  $n$  values for different OMMT contents are listed in Table III.

From Table III, we can see that  $n$  increases with increasing OMMT content except in the case of 0.1 wt % OMMT, which requires further study. The results indicate that there is an increasing fraction of monomolecular mode in the chain termination.

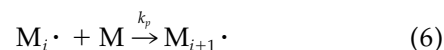
Combined with the increase of  $R_{p0}$  under some concentrations of BPO, we can also draw a conclusion that OMMT will increase the initiation rate of the reaction. The following mechanism has been proposed to interpret the experimental results:

### 1. Initiation:



where  $C^*$  represents the activity spots of montmorillonite.  $[C^*]$  was assumed to be in proportion to the concentration of OMMT.

### 2. Propagation:

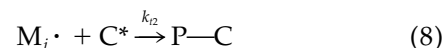


### 3. Termination:

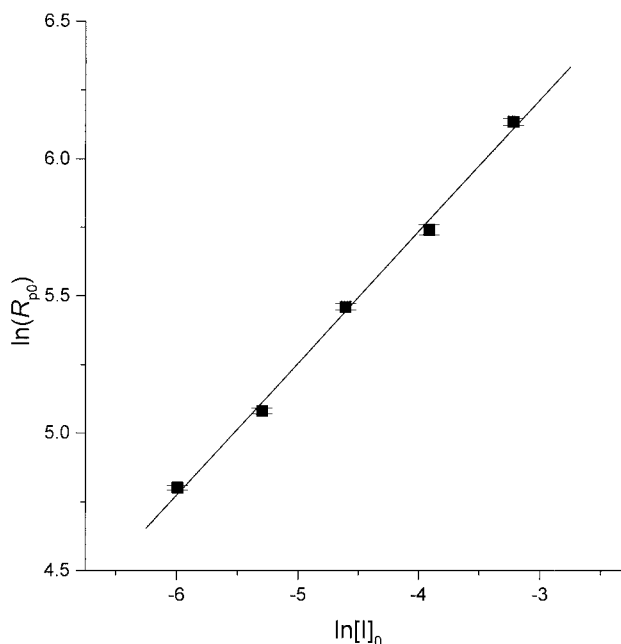
#### i. Bimolecular termination:



#### ii. Monomolecular termination:



$$R_p \equiv -\left(\frac{d[M]}{dt}\right) = k_p[M][M \cdot] \quad (9)$$



**Figure 2** Plot of  $\ln R_{p0}$  vs.  $\ln[I]_0$  of MMA without OMMT.

TABLE III  
Reaction Orders of Different OMMT Contents

OMMT Content (wt %)	0	0.1	0.2	0.4
$n$	$0.481 \pm 0.016$	$0.471 \pm 0.005$	$0.520 \pm 0.004$	$0.558 \pm 0.017$

Then we obtain:

$$2f_1k_{d1}[I] + f_2k_{d2}[C^*][I] = 2k_{t1}\left(\frac{R_p}{k_p[M]}\right)^2 + k_{t2}\frac{R_p}{k_p[M]}[C^*] \quad (10)$$

Suppose that  $f_1$ ,  $f_2$ ,  $k_{d1}$ ,  $k_{d2}$ ,  $k_p$ ,  $k_{t1}$ , and  $k_{t2}$  remain unchanged when the OMMT content changes.  $C^*$  has significantly lower activity than BPO, with a  $t_{1/2}$  around 96 h in benzene at 60°C.<sup>8</sup> So  $[C^*]$  decreases very slowly. And because the conversions are very low (smaller than 2%),  $[C^*]$  and  $[M]$  can both be considered to be constant, especially if initial polymerization rates obtained by the extrapolated method are considered. Let  $A = 2f_1k_{d1}$ ,  $B = f_2k_{d2}$ ,  $D = 2k_{t1}(1/k_p[M])^2$  and  $E = k_{t2}/k_p[M]$ , then eq. (10) can be simplified to

$$[I]_0(A + B[C^*]_0) = DR_{p0}^2 + E[C^*]_0R_{p0} \quad (11)$$

Rearranging it:

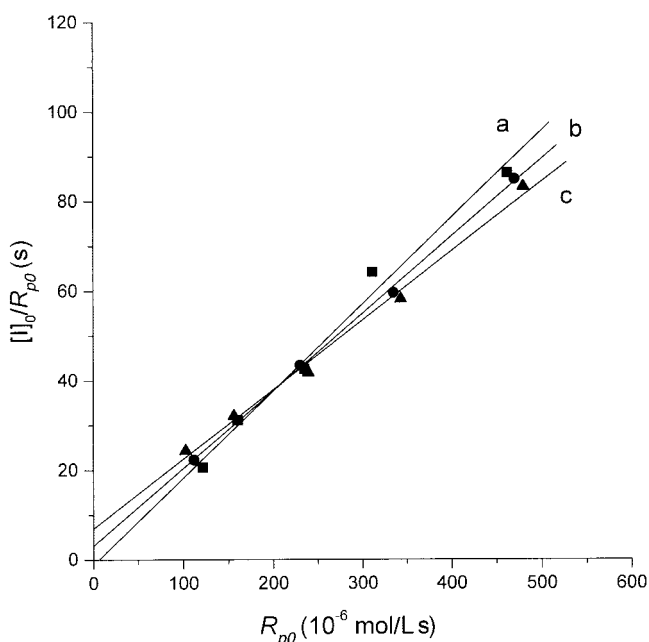


Figure 3 Plots of  $[I]_0/R_{p0}$  vs.  $R_{p0}$  with varying OMMT content: (a) 0 wt %, (b) 0.2 wt %, (c) 0.4 wt %.

$$\frac{[I]_0}{R_{p0}} = \frac{D}{(A + B[C^*]_0)} R_{p0} + \frac{E[C^*]_0}{(A + B[C^*]_0)} \quad (12)$$

So when the MMT content is fixed, the plot of  $[I]_0/R_{p0}$  vs.  $R_{p0}$  will be a line with a slope of  $D/(A + B[C^*]_0)$  and an intercept of  $E[C^*]_0/(A + B[C^*]_0)$ . Then the fraction of monomolecular termination can be calculated using the equation below:

$$f_m = \frac{\text{intercept}}{\text{intercept} + \text{slope } R_{p0}} \quad (13)$$

The plots of  $[I]_0/R_{p0}$  versus  $R_{p0}$  are shown in Figure 3. The obtained intercepts and slopes are listed in Table IV. The results show that the intercept increases but the slope decreases with increasing OMMT content. This is strongly related to the parameters in eq. (12) and indicates an increasing fraction of monomolecular termination process with increasing OMMT content. The calculated fractions of monomolecular mode in the chain termination are shown in Figure 4.

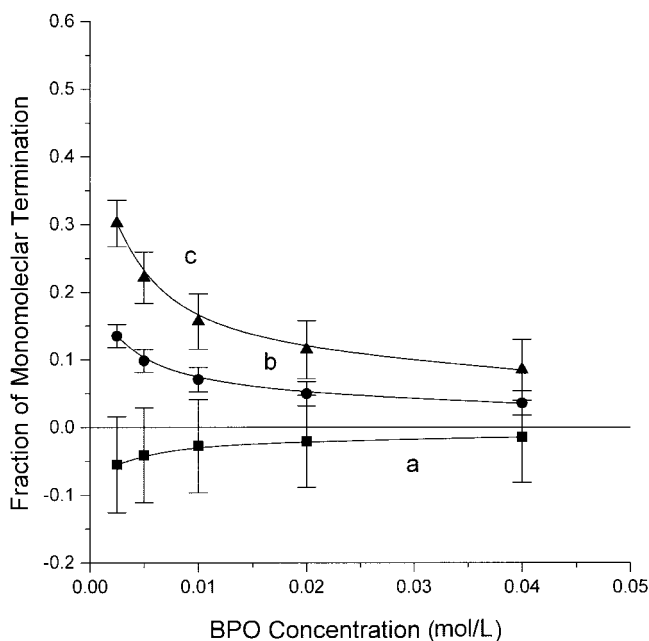
It is reasonable to observe that the fraction of monomolecular mode in the chain termination is zero within the range of deviation, although the slope of  $\ln R_{p0}$  versus  $\ln[I]_0$  is somewhat smaller than 0.5. This indicates a bimolecular termination process. The fractions of monomolecular termination are observed to increase with increasing OMMT content and decreasing BPO concentration. This is strongly related to eq. (12) in that the ratio of activity spots of OMMT to radicals is affected by the ratio of OMMT to BPO.

### Extraction Results

Extraction experiments are widely used in the study of the interaction between clay and polymer macromolecules. The obtained composites with 0.4 wt % OMMT

TABLE IV  
Intercepts and Slopes of  $[I]_0/R_{p0}$  vs.  $R_{p0}$  at Different OMMT Contents

OMMT Content (wt %)	Intercept ( $10^{-2}$ s)	Slope ( $10^4$ L s <sup>2</sup> /mol)
0	$-123.0 \pm 373.7$	$19.45 \pm 1.31$
0.2	$302.5 \pm 96.9$	$17.32 \pm 0.33$
0.4	$690.1 \pm 226.0$	$15.53 \pm 0.76$



**Figure 4** Fractions of monomolecular termination with varying OMMT content: (a) 0 wt %, (b) 0.2 wt %, (c) 0.4 wt %.

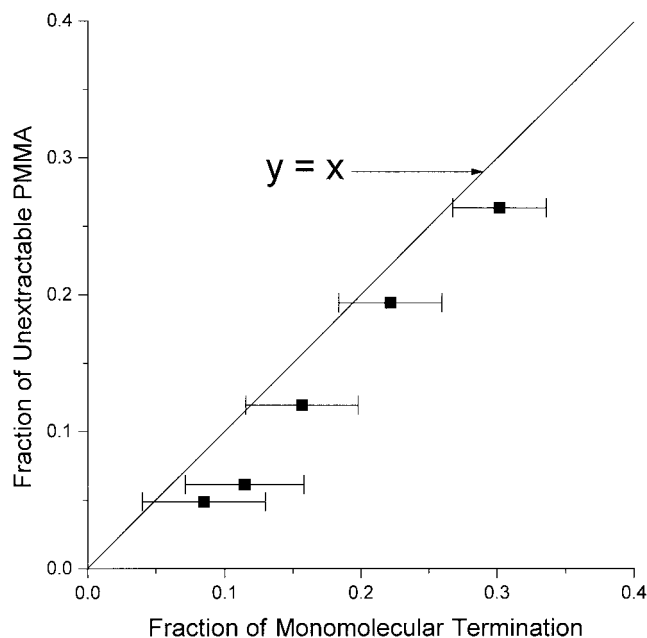
fed in this study were exposed to boiling toluene using a Soxhlet extractor for 48 h to remove non-bonded macromolecules.<sup>9</sup> As shown in Table V the products held unextractable organic materials, which can be regarded as bonded PMMA. It is interesting to find that the fraction of unextractable PMMA varies greatly, although the OMMT content is fixed. To investigate the relationship between the extraction properties and the polymerization, a plot of the fraction of unextractable PMMA versus the fraction of monomolecular termination process is shown in Figure 5. The solid line is a theoretical line, which comes from the assumption that only the PMMA terminated on, or grafted onto, the OMMT is unextractable.

As seen in Figure 5, the fraction of unextractable PMMA is strongly related to the fraction of the monomolecular termination process. This indicates that the reason the unextractable PMMA cannot be dissolved in hot toluene is the PMMA has bonded onto the MMT, but not merely due to the small quantity of PMMA intercalated into the MMT layers. Although

**TABLE V**  
Fraction of Unextractable PMMA at Different BPO Concentrations

BPO Concentration (mol/L)	0.0025	0.005	0.01	0.02	0.04
OMMT content in product (%)	17.1	18.2	14.0	11.3	11.9
Fraction of unextractable PMMA (%)	48.2	19.4	11.9	6.1	4.9

OMMT feed content is fixed at 0.4 wt %



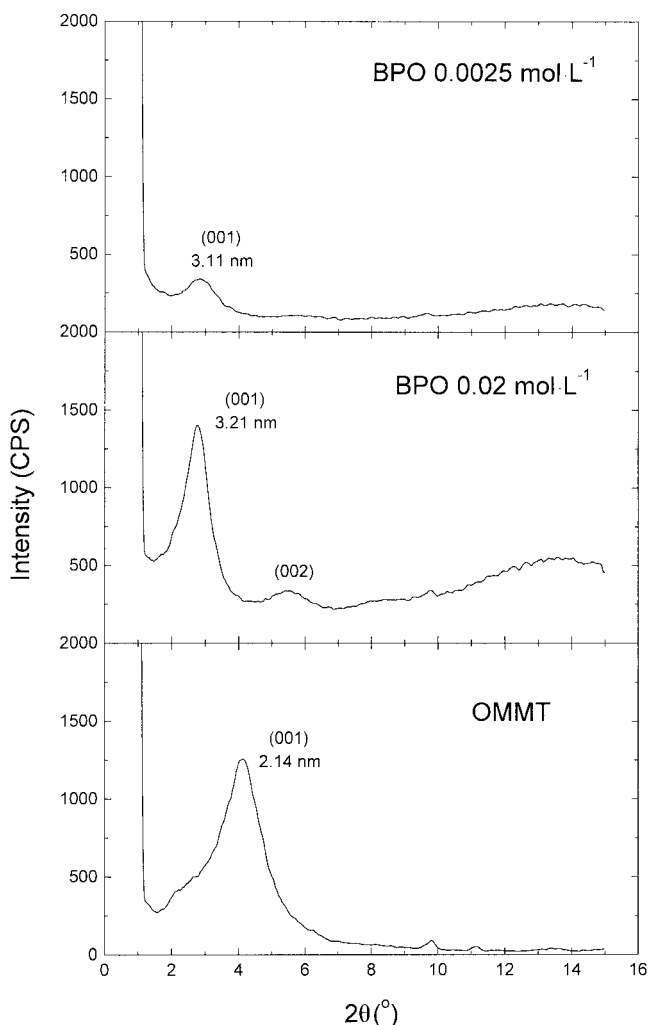
**Figure 5** Fraction of unextractable PMMA vs. fraction of monomolecular termination.

there is a little deviation between the fraction of unextractable PMMA and the fraction of monomolecular termination process, it can prove the credibility of the mechanism proposed earlier in this article.

### Structure Characterization

The X-ray diffraction patterns of OMMT used in this paper and two unextracted samples in the range of  $2\theta = 1 - 15^\circ$  are shown in Figure 6. When the BPO concentration is 0.02 mol/L, a strong diffraction peak at 3.21 nm corresponding to the  $d_{(001)}$  plane is observed. The fact that the interlayer spacing is larger than that of the OMMT, at 2.14 nm, indicates an intercalative reaction of MMA in the OMMT layers. The higher-order peak corresponding to  $d_{(002)}$  is also clearly observed, suggesting that the layer structure is maintained. In the case of 0.0025 mol/L BPO, although the interlayer spacing is 3.11 nm, a little smaller than that of the composites with 0.02 mol/L BPO, it is interesting to note that the diffraction peak of  $d_{(001)}$  is extremely weakened, although the OMMT feed content is the same as that of the former. And as can be seen in Table V, the OMMT content in the formed composites with 0.0025 mol/L BPO is more than that of the composites with 0.02 mol/L BPO. This suggests that the layer structure has largely been destroyed.

The results indicate that the layer structure is not by any means the same when the OMMT content and the polymerization conditions are fixed. It is also affected by the concentration of the initiator. From the mech-



**Figure 6** X-ray patterns of OMMT and composites.

anism proposed in this article, a lower initiator concentration will cause a lower radical concentration, and finally a larger fraction of monomolecular mode

in the chain termination. When the OMMT feed content is fixed and the content of PMMA formed in the polymerization is approximately equivalent, the OMMT will have more chance to react with the radicals when the initiator concentration is low. So it is reasonable to assume that the layer structure has more possibility of being destroyed.

## CONCLUSIONS

The polymerization rate of MMA is affected by OMMT content. The effect is determined not only by the OMMT content but also by the initiator concentration. When the OMMT content increases, the influence of the initiator concentration on the  $R_{p0}$  becomes greater.

According to the mechanism proposed in this paper, higher OMMT content and lower BPO concentration will result in higher monomolecular mode in the chain termination process, and will yield composites with less pronounced layer structures.

This work was supported by the National Science Foundation of Hebei Province (No. 202018 and 201006).

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