

Rapid Synthesis of Poly(*p*-dioxanone)/Montmorillonite Nanocomposites under Microwave Irradiation

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ABSTRACT: A rapid and “green” synthesis of poly(*p*-dioxanone) (PPDO)/montmorillonite (MMT) nanocomposites was carried out smoothly and effectively under constant microwave powers of 30, 60, 90, and 120 W in a microwave oven at a frequency of 2.45 GHz. The temperature of polymerization was in the range 103–224°C. PPDO, with a viscosity-average molecular weight of 111,000 g/mol and a conversion of 85%, was obtained at 60 W for 10 min, in which the ratio of *p*-dioxanone to AlEt₃ was 300/1 (mol/mol). The intercalated structure of

PPDO/MMT nanocomposites was confirmed by X-ray diffraction and transmission electron microscopy. Thermogravimetry data showed that the thermal stability of the nanocomposites prepared under microwave irradiation was improved with respect to those prepared via conventional heating. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: clay; irradiation; nanocomposites; ring-opening polymerization

INTRODUCTION

During the past decade, polymer/layered-silicate nanocomposites have attracted a great deal of attention because of their improved mechanical properties and heat resistance^{1–3} and reduced gas permeability and flammability^{4,5} in comparison with those of pure polymers or conventional composites. However, the dispersion of clay in the polymer matrix is a crucial factor for the properties of the nanocomposites, and it is depended on the synthesis method, type of clay modifier, and clay concentration.⁶

Poly(*p*-dioxanone) or poly(1,4-dioxan-2-one) (PPDO), whose synthesis route is shown in Scheme 1, is a kind of biodegradable polyether ester with excellent biodegradability, bioabsorbability, and biocompatibility and good flexibility; it has applications in medical fields such as bone and tissue fixation devices.⁷ Because the

raw material, *p*-dioxanone or 1,4-dioxan-2-one (PDO), used to produce PPDO can be obtained by a simple production process from diethylene glycol,⁸ PPDO has been viewed as a candidate not only for medical use but also for general purposes such as films, molded products, laminates, foams, nonwoven materials, adhesives, and coatings.⁹ However, its blowing processing is very difficult because of its low melt strength and low crystallization rate. In our laboratory, Huang et al.¹⁰ synthesized PPDO/montmorillonite (MMT) nanocomposites via the *in situ* ring-opening polymerization (ROP) of PDO in the presence of MMT and found that the aforementioned situation was obviously improved. To obtain PPDO with a high molecular weight, several hours were needed. The shortening of the reaction time is of great importance in reducing the energy consumption and cost.

Microwave irradiation has a number of advantages over conventional heating, such as its noncontacting, instantaneous, rapid, and high specific heating nature.¹¹ Recently, our results showed that compared with that of PPDO synthesized under traditional heating, PPDO with a relatively high viscosity-average molecular weight (M_v) and yield could be obtained under microwave irradiation.¹² Yoo et al.¹³ prepared polycarbonate/MMT nanocomposites by microwave-aided solid-state polymerization, and found that microwave solid-state polymerized nanocomposite showed an exfoliated and/or intercalated structure, whereas conventional solid-state polymerization with oil heating only increased the gallery size of the MMT.

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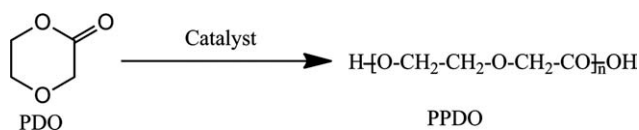
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Scheme 1 Synthesis route of PPDO.

In this study, the microwave-assisted *in situ* intercalation ROP of PDO with MMT with triethylaluminum as a catalyst was investigated. The polymerization conditions of the PPDO/MMT nanocomposites, including the catalyst content, temperature, and reaction time, were studied via microwave heating. The intercalated structure of the PPDO/MMT nanocomposites was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found the thermal stability of the PPDO/MMT nanocomposites prepared under microwave irradiation was better than that of nanocomposites prepared under traditional heating.

EXPERIMENTAL

Materials

PDO was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China). It was dried over calcium hydride (CaH_2) and distilled under reduced pressure before use. Triethylaluminum (AlEt_3) was provided by Nanjing Tonglian Chemical Corp. (Nanjing, China), and it was diluted with anhydrous toluene. CaH_2 , 1,1,2,2-tetrachloroethane, phenol, and toluene were purchased from Chengdu Kelong Reagent Corp. (Chengdu, China) and were used without further purification. MMT was modified by hydroxyethylhexadecyldimethyl ammonium bromine through cation exchange. Before polymerization, the MMT was dried *in vacuo* at 70°C for 1 night.

Microwave equipment

A 2.45-GHz multimode microwave oven (Whirlpool-J220, Shanghai, China) with a maximum output power of 850 W was applied in our study. The output power could be achieved at 10 different levels by a power on-off cycle. The temperature of the materials was measured by the insertion of a thermocouple into a self-made ampule.

Thermal effects of microwaves on PDO with MMT

The thermal effects of microwaves on PDO with MMT was measured according to our previous report.¹⁴ A certain amount of PDO with MMT was put into an ampule, which then was vacuum-sealed, and it was irradiated with pointed microwave power for 25 min. The temperature was recorded every minute.

Preparation of the PPDO/MMT nanocomposites

The desired amount of MMT was placed in a glass ampule, and the ampule was degassed *in vacuo*. A known amount of PDO was then added under nitrogen with a syringe, and the reaction medium was shaken for 3 h with an ultrasonic device. Then, the catalyst, a solution of AlEt_3 in dry toluene, was added, and the ampule was sealed *in vacuo*. The reaction mixture was then irradiated at selected microwave power levels. At the end of the reaction, the ampule was immediately removed from the microwave oven and immersed in ice water. The crude solid product was purified by precipitation from a phenol/1,1,2,2-tetrachloroethane (2 : 3, w/w) solution with methanol and dried *in vacuo* at 40°C to a constant weight. The monomer conversion of PDO was determined by the weight of the dried PPDO.

Synthesis of the PPDO/MMT nanocomposites under conventional heating

The conventional synthesis of PPDO with 3 wt % MMT was carried out in an oil bath. A certain amount of PDO (60.8 mmol) was placed in a glass ampule, and the ampule was degassed *in vacuo*. Then, a solution of AlEt_3 in dry toluene [monomer-to-catalyst molar ratio (M/C) = 300] was added with a syringe. Finally, the ampule was sealed *in vacuo* and put into a 60°C oil bath for 20 h. The other procedures were the same as those used for microwave-assisted synthesis. A PPDO/MMT nanocomposite with an M_v of 53,400 g/mol was obtained for thermogravimetry (TG) measurement.

Intrinsic viscosity ($[\eta]$) of the PPDO/MMT nanocomposites

As conventional solvents such as chloroform, tetrahydrofuran, and toluene used in gel permeation chromatography measurements cannot dissolve the resulting polymers with higher molecular weights, only the M_v value of the resulting polymers were measured in phenol/1,1,2,2-tetrachloroethane (2:3 w/w) solution with an Ubbelohde viscosimeter thermostated at 25°C . The molecular weights of PPDO were calculated from $[\eta]$ according to the Mark-Houwink equation:

$$[\eta] = K\bar{M}_v^\alpha$$

where α is 0.63 and K is equal to $79 \times 10^{-3} \text{ cm}^3/\text{g}^{-1.15}$.

XRD analysis

XRD analyses were performed on a DX-1000 X-ray diffractometer (Dandong Fangyuan Instrument Co.; Ltd, China) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 25 mA with a scanning rate of $0.3^\circ/\text{s}$.

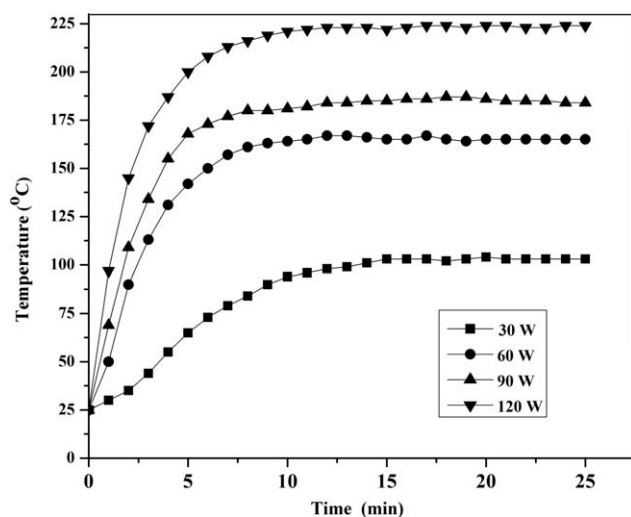


Figure 1 Temperature profile of the PDO (60.8 mmol) with 3 wt % MMT under microwave irradiation.

TEM

TEM was performed on a Tecnai20 TEM instrument (FEI, Eindhoven, Netherlands) with a 120-kV accelerating voltage. The pressed sheets were sectioned into thin sections roughly 50–100 nm at -30°C with an ultramicrotome (Leica Mikrosysteme GmbH, Vienna, Austria) equipped with a diamond knife and without staining.

Thermal stability of the nanocomposites

The thermal stability of the PPDO nanocomposite with 3 wt % MMT was measured with a thermogravimetric analyzer (PerkinElmer TGA7, Waltham, MA) in the temperature range from room temperature to 450°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ in an N_2 atmosphere.

RESULTS AND DISCUSSION

Thermal effects of microwave energy on PDO with MMT

The heating characteristics of the PDO/MMT mixture under microwave irradiation (MI) were investigated at four levels of microwave power (30, 60, 90, and 120 W), and the amounts used were 12.2, 36.5, 60.8, and 85.1 mmol, respectively. The temperature profiles of PDO (5 mL, 60.8 mmol) with 3 wt % MMT under different microwave powers are shown in Figure 1. As indicated in Figure 1, a rapid increase in the temperature occurred within 5 min; 5 min later, the temperature increased slowly and steadily. No temperature increase was measured from 20 to 25 min at any power level; this indicated that a constant temperature would be obtained under a given microwave power. This constant temperature was called the *balanceable temperature*. Also,

in the case of constant amounts of monomer, the temperature would increase with the increase of power level. This could be ascribed to the fact that the higher power microwaves had higher energy that was absorbed by the sample and induced the sample with a higher balanceable temperature.

The temperature profiles of PDO (with amounts of 12.2, 36.5, 60.8, and 85.1 mmol) with 3 wt % MMT under 90 W are shown in Figure 2. The effect of the PDO amount on the temperature profiles was the same as that of the microwave power. In the first 5 min, the temperature increased greatly, and then, the temperature increased slowly and steadily. Finally, an invariable temperature (the balanceable temperature) of the mixture was obtained. The temperature change trend was similar for a given PDO amount. It could be seen clearly that with increasing monomer amount, the temperature at a given time also increased. This result could have been due to the fact that a larger amount of PDO absorbed more energy, and at the same time, the absorbed more energy was difficult to lose.

Polymerization of PDO with MMT under microwave power

In this study, the balanceable temperatures of PDO (60.8 mmol) with 3% MMT were 103, 165, 184, and 224°C under the irradiations of four microwave power levels by which the ROP of PDO occurred. Thus, the four microwave power levels were applied to examine the ROP of PDO in the presence of MMT. The influence of the microwave power level on the conversion of the monomer and the molecular weight of the resulting polymers is illustrated in Table I.

The M_v values of PPDO were 87,000, 111,000, and 59,000 g/mol at microwave powers of 30, 60, and

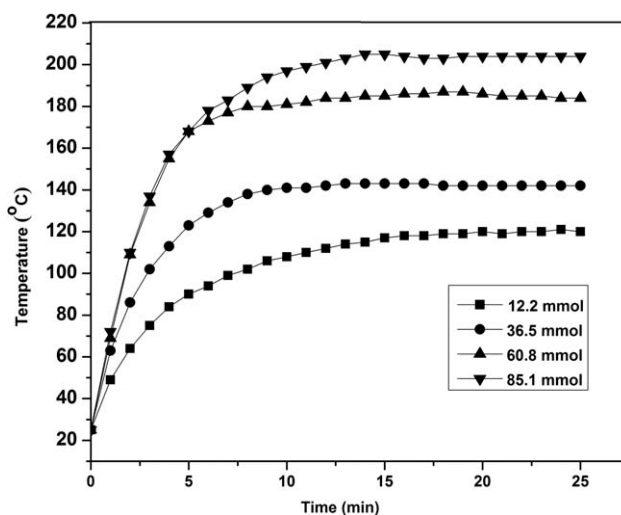


Figure 2 Temperature profile of the PDO with 3 wt % MMT under microwave (90 W) irradiation.

TABLE I
Monomer Conversion and M_v of PPDO at Various Microwave Powers

Power (W)	Time (min)	M/C (mol/mol) ^a	M_v (10^4 g/mol)	Conversion (%)	Color
30	10	300	8.7	79	White
60	10	300	11.1	85	White
90	10	300	5.9	77	Yellow
120	10	300	—	—	Yellow

90 W, respectively. When the power was 120 W, we could not obtain PPDO with a certain M_v , and the product became yellow. From Figure 1, we know that when the power levels were 30, 60, 90, and 120 W, the balanceable temperatures of the PDO/MMT mixtures (60.8 mmol) were 103, 165, 184, and 224°C, respectively. Therefore, it was deduced that when power level was 120 W, the decomposition of PPDO occurred.

Without microwave irradiation, the ROP of PDO with MMT took place slowly at 50°C, and it took 20 h to obtain PPDO/MMT with an M_v of 69,300 g/mol with AlEt_3 as the catalyst.¹⁰ Obviously, the ROP of PDO with MMT was greatly accelerated by a constant microwave power.

The influence of the irradiation time on ROP of PDO with 3 wt % MMT could also not be neglected. As indicated in Figure 3, catalyzed by AlEt_3 and irradiated at 30 W for only 5 min, the polymerization took place rapidly and resulted in a PPDO/MMT nanocomposite with an M_v of 121,000 g/mol. When the polymerization lasted for 10 min, the M_v increased to 140,000 g/mol. For these samples, the monomer conversions were approximately 80%. When the time was even longer, the M_v became lower. The decrease in M_v was due to intermolecular esterification (trans-esterification). Therefore, it was deduced that within 20 min, there were maybe two kinds of reactions: the ROP of PDO and the trans-

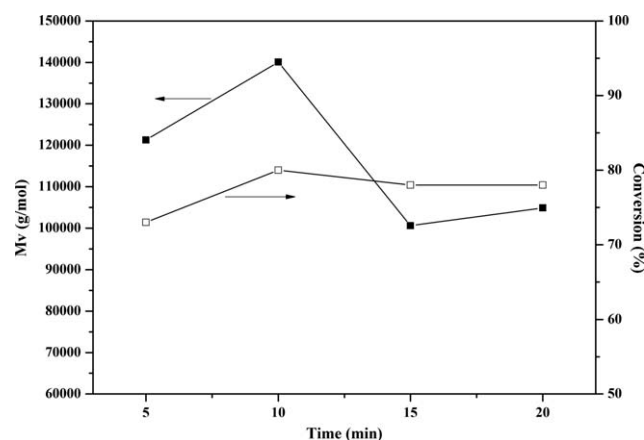


Figure 3 Effect of the irradiation time on the PDO polymerization with 3 wt % MMT [30 W, M/C (mol/mol) = 300].

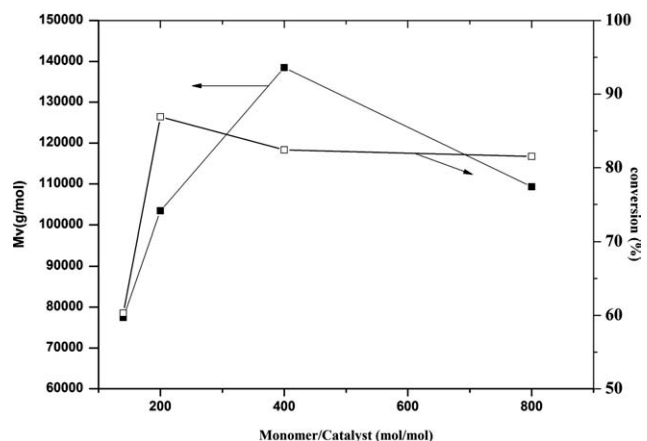


Figure 4 Effect of the catalyst concentration on the PDO polymerization with 3 wt % MMT (time = 10 min, 30 W).

esterification of the resulting PPDO macromolecules. The dominant reaction was ROP in the presence of the monomers, but transesterification became obvious after most of the monomer was consumed.

The influence of the catalyst concentration on the ROP of PDO with 3 wt % MMT was investigated at 30 W; the results are shown in Figure 4. In the case of AlEt_3 as the catalyst, M/Cs were selected as 140, 200, 400, and 800, and the reaction mixtures were irradiated for 5 min. An increase in M_v of PPDO/MMT was observed when the ratio of PDO to AlEt_3 was increased from 140 to 400, and the highest M_v value was 138,000 g/mol at a molar ratio of PDO to AlEt_3 of 400. However, a lower concentration of AlEt_3 (M/C = 800) led to a lower M_v (110,000 g/mol, shown in Fig. 4). This result may have been caused by the absence of stirring, and the catalyst was not dispersed well in the PDO monomer, especially at a lower concentration. From the figure, one can also see that the monomer conversion increased sharply from 60.3 to 86.9% when M/C was increased from 140 to 200 and then decreased slightly with further increases in M/C.

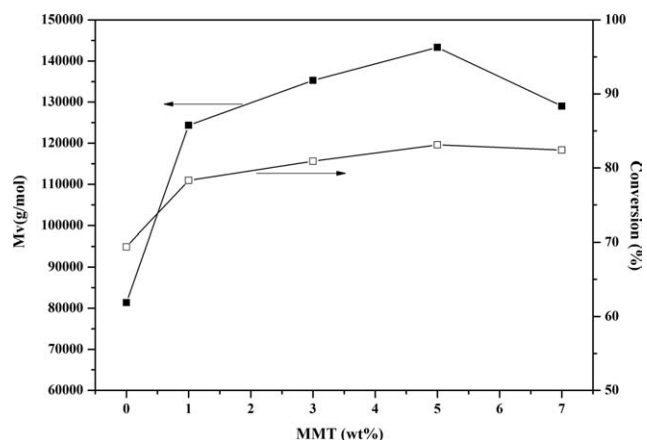


Figure 5 Effect of the MMT concentration on the polymerization [time = 10 min, 30 W, M/C (mol/mol) = 300].

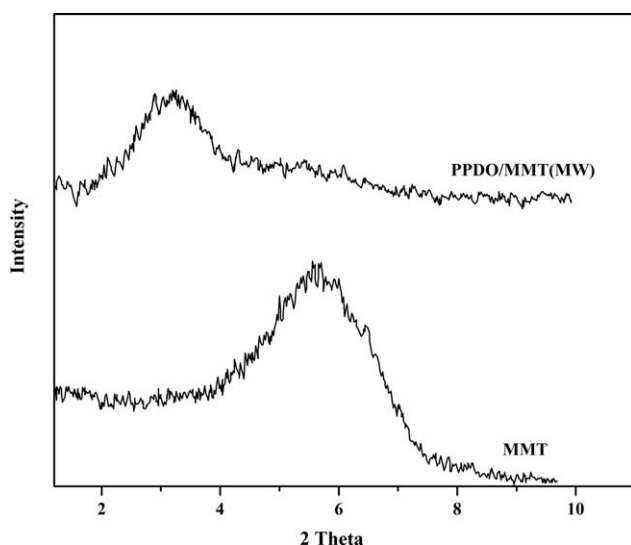


Figure 6 XRD patterns of the MMT and PPDO/MMT nanocomposites (MW-microwave).

As we know, with a lower concentration of $AlEt_3$, there were fewer active centers. As a result, the conversion of PDO was low.

The MMT concentration also had effect on the polymerization, as indicated in Figure 5. When 1 wt % MMT was added, the M_v value of PPDO increased from 81,000 (without MMT) to 124,000 g/mol. With a further increase in the MMT content from 3 to 5 wt %, the M_v value ranged from 135,000 to 143,000 g/mol; however, M_v decreased when the MMT content was increased to 7%. Also, a small amount of MMT improved the conversion of monomer. For example, the conversions of PPDO without MMT and PPDO/1%MMT were 69.4 and 78.3%, respectively. When the MMT content was further increased, however, the conversion of monomer remained at approximately 80%. These results indicate that the hydroxyl groups attached to the alkylammonium cations in the clay interlayer acted as potential initiators for the ROP of PDO.^{16,17} There-

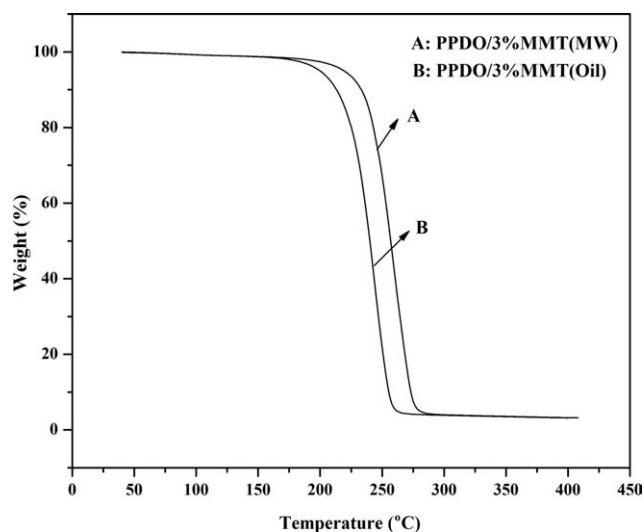


Figure 8 TG curves of the PPDO/MMT nanocomposites (MW-microwave).

fore, at first, with the increase in the initiation core, both M_v and the conversion were increased. If the initiation core was further increased, correspondingly, the chains of PPDO were shortened. This phenomenon was also found during the synthesis of poly(ϵ -caprolactone)/clay nanocomposites.¹⁸

XRD and TEM analysis of the PPDO/MMT nanocomposites

To obtain some insight into the morphological structures of the resulting composites, we performed XRD and TEM analysis on the PPDO/MMT nanocomposite. Figure 6 presents the XRD patterns for the composite that contained 3 wt % MMT and pure MMT. The diffractive 001 peak of MMT shifted from $2\theta = 5.52$ to 3.04° ; this indicated that the PPDO chains intercalated into the MMT interlayer successfully. The TEM images of the PPDO/MMT nanocomposite in Figure 7 also demonstrated the

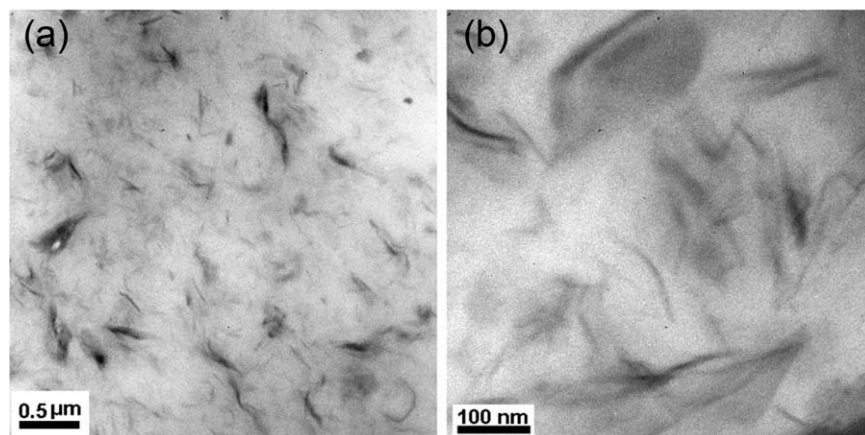


Figure 7 TEM images of the PPDO/MMT nanocomposite with 3 wt % MMT at (a) low and (b) high magnification.

TABLE II
TG Data of the PPDO/MMT Nanocomposites

Sample	M_v (g/mol)	$T_{5\%}$ (°C)	T_{max} (°C)	$T_{70\%}$ (°C)
PPDO/3% MMT (MW*)	49,200	220	259	264
PPDO/3% MMT (oil)	53,400	200	244	247

* Microwave.

intercalated structure clearly, in which the gray areas represent the MMT layers and the bright areas are the PPDO matrix. From the images, we can easily see that the MMT layers were dispersed homogeneously in the PPDO matrix, and most of them were intercalated into the PPDO matrix.

Thermal stability of the PPDO/MMT nanocomposites

To eliminate the influence of the molecular weight on the thermal stability of polymers, a PPDO/3% MMT nanocomposite with an M_v of 49,200 g/mol was synthesized under microwave irradiation [90 W, M/C (mol/mol) = 140] for 5 min. The thermal stability of the PPDO/MMT nanocomposites prepared by microwave irradiation and conventional heating were investigated by TG, as shown in Figure 8. The various decomposition temperatures based on the TG curves are given in Table II. From the table, we found that the 5% weight loss temperature ($T_{5\%}$), 70% weight loss temperature ($T_{70\%}$), and the maximum decomposition temperature (T_{max}) of the PPDO/MMT nanocomposites prepared by microwave irradiation were higher than those of the nanocomposites prepared by conventional heating; this indicated that the thermal stability of the nanocomposites was improved by microwave irradiation. This may have been due to the fact that the PDO monomer was easily polymerized in the interlayer of MMT under microwave irradiation, and the MMT layer obstructed thermal conduction.

CONCLUSIONS

The mixture of PDO and MMT was heated when it was irradiated with constant microwave power. Its

temperature increased rapidly within 5 min; however, it changed slightly 5 min later, and finally, a balanceable temperature was obtained. The ROP of PDO with MMT catalyzed by $AlEt_3$ proceeded smoothly with constant microwave power. The polymer with an M_v of 111,000 g/mol and a conversion of 85% was obtained when the ROP of PDO with MMT was carried out at 60 W for 10 min. An intercalated structure in the PPDO/MMT nanocomposites was obtained. With microwave irradiation, the thermal stability of the PPDO/MMT nanocomposites was further improved.

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