

Kinetics of Methyl Methacrylate Grafting Polymerization onto Flaky Aluminum Powder

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ABSTRACT: With ammonium persulfate (APS) as the initiator, the kinetics of methyl methacrylate (MMA) grafting polymerization onto flaky aluminum powder (Al) was studied. It was found that the experimental apparent grafting polymerization rate, $R_g = K C_{Al}^{0.521} \times C_{APS}^{0.429} \times C_{MMA}^{0.978}$, was basically consistent with the theoretical result based on the theory of stable polymerization and equivalent activity, $R_g = K C_{Al}^{0.5} \times C_{APS}^{0.5} \times C_{MMA}$. The activation energy of grafting,

homogenous, and total polymerization rate was calculated as 65.1, 35.4, and 37.5 kJ mol⁻¹, respectively. It could be validated that the relationship among these activation energies accorded with the theoretical result of parallel reactions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3040–3044, 2010

Key words: kinetics; methyl methacrylate; grafting polymerization; flaky aluminum powder

INTRODUCTION

In our previous report,¹ poly(methyl methacrylate)/flaky aluminum composite particle (called PMMA/Al) had been successfully prepared by *in situ* grafting polymerization in the presence of 3-methacryloxypropyltrimethoxysilane (MPS). The process was divided into two steps: flaky aluminum (Al) powder was first coupled with MPS, and then encapsulated with PMMA by *in situ* emulsion grafting polymerization of methyl methacrylate (MMA). The mechanism of MPS coupling onto flaky Al was studied, and the effect of coupling percentage and emulsifier concentration on *in situ* polymerization was also investigated. The resulting PMMA/Al composite particle had been characterized by means of Fourier transformer (FTIR) spectroscopy, energy dispersive spectroscopic (EDS) analysis, and the evolved hydrogen detection.

It was noticeable that the kinetics of MMA grafting polymerization onto flaky Al had not been studied. Nevertheless, a tremendous research activity had been devoted to the kinetics of the homogenous polymerization of MMA. Murthy and coworkers^{2,3} had studied the kinetics of poly(styrene peroxide) initiated photopolymerization of MMA, and the resulting polymer was characterized by means of ultraviolet spectrum (UV), hydrogen nuclear magnetic resonance (H-NMR), and thermogravimetric analysis (TGA). Šebenik et al.⁴ investigated the effect of soft segment length on kinetics of seeded semi-batch-emulsion copolymerization of MMA and butyl acrylate. Suzuki et al.⁵ studied the effect of mixing ratio of anionic emulsifiers on the kinetic behavior of MMA emulsion polymerization.

In accordance, some research works about the kinetics of organic monomer grafting polymerization onto superfine particles had been gradually reported. The influence of different surface functional groups of nano-SiO₂ on nylon-6 *in situ* polymerization was investigated, and the kinetics of the grafting polymerization was systematically studied.⁶ The kinetics of *in situ* polymerization of isooctyl acrylate and butyl acrylate on cassava starch was also investigated.⁷ The kinetics of acrylic acid grafting polymerization onto maize starch using ammonium persulfate-sodium bisulfate as initiator was studied.⁸ Chern et al.⁹ investigated the kinetics of atom transfer radical polymerization (ATRP) of styrene in the presence of montmorillonite, and the effect of the pristine sodium montmorillonite on the styrene

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polymerizations with different concentrations of sodium dodecyl sulfate (SDS) was studied.

Based on the earlier discussions, it was well-known that there were few reports about the kinetics of MMA grafting polymerization onto flaky Al powder. Following our previous report,¹ we studied the kinetics of MMA grafting polymerization onto flaky Al powder in this work. The goal of this work was, therefore, to gain a better understanding of the process for the formation of PMMA/flaky aluminum composite particles.

EXPERIMENTAL

Materials

Flaky Al powder (Shanghai Weiye Co., China, $D_{50} = 15 \mu\text{m}$, aspect ratio is about 100–200) was dried in vacuum at 100°C for 24 h to remove the volatile organic compounds before use. MMA (Guangzhou Chemical factory, China) was washed with dilute alkali solution and distilled water, dried over calcium chloride, and distilled under reduced pressure. MPS (Wuhan University Silicone New Material Co., Hubei, China) as a coupling agent, cetytrimethylammonium bromide (CTAB, Shanghai Chemical Reagent Plant, China) as an emulsifier, and ammonium persulfate (APS, Tianjin Chemicals Co., China) as an initiator, were all analytical grade reagents and used as received.

Determination of grafting polymerization rate

A certain amount of CTAB, 100 mL distilled water, 6 g MMA, and 0.5 mL acrylic acid were added into

a four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a guttate funnel. After complete emulsification through stirring for 30 min, 10 g MPS-coupled flaky Al was charged into the flask. When the mixture was heated to 65°C with 25 mL/min nitrogen flowing, 0.6 g APS aqueous solution was slowly added into flask by guttate funnel. Then, the mixture was heated to 85°C (To obtain the kinetic parameters, the experiments were carried out in 65, 75, 85, and 95°C , respectively). At the scheduled reactive time, diphenylpicrylhydrazyl (DPPH), a universal retarder, was added into the polymerizing system to terminate the reaction. The mixture was precipitated with methanol, demulsified with potassium chloride, and filtered. The resulting cake was dispersed in acetone with ultrasonic vibration and the nongrafted PMMA was dissolved in acetone. After centrifugation (10,000 rpm) for 1 h, nongrafted PMMA was obtained by precipitating the filtrate with methanol. The cake was dried in vacuum, and PMMA-grafted Al was obtained. Grafted PMMA in PMMA-grafted Al can be calculated from the content of coupled MPS through Si elemental analyses and the content of Al through evolved hydrogen detection in a reaction of aqua regia described in literature.¹⁰ Total PMMA was the sum of grafted PMMA and nongrafted PMMA. So the grafting polymerization rate (R_g), homogenous grafting polymerization rate (R_h), and total grafting polymerization rate (R_t) were calculated according to the following relationships:

$$R_g = \frac{\text{grafted PMMA(g)}}{\text{molecular weight of MMA(g/mol)} \times \text{reactive time(min)} \times \text{reactive volume(L)}} (\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1})$$

$$R_h = \frac{\text{nongrafted PMMA(g)}}{\text{molecular weight of MMA(g/mol)} \times \text{reactive time(min)} \times \text{reactive volume(L)}} (\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1})$$

$$R_t = R_g + R_h (\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1})$$

Therefore, the rate constants of grafting, homogenous, and total polymerization could be calculated according to the R_g , R_h , and R_t , respectively.

RESULTS AND DISCUSSION

The experimental kinetics of grafting polymerization

The existence of solid particles was the essential difference between grafting and homogenous polymerization.^{11,12} Figure 1 shows the logarithmic relationship between the grafting polymerization rate (R_g) and flaky Al concentration. As can be seen, $\text{Ln}(R_g)$

increased linearly with the increasing $\text{Ln}(C_{\text{Al}})$, which could be attributed to the augment of the probability of MMA *in situ* polymerization onto flaky Al. It was also found that slope of the simulated line was 0.521. So the relationship between grafting polymerization rate at the beginning and flaky Al concentration could be described as $R_g \propto C_{\text{Al}}^{0.521}$.

The effect of initiator concentration on the grafting polymerization rate was demonstrated in Figure 2. As was clearly observed, an approximate linear relationship was found between $\text{Ln}(R_g)$ and $\text{Ln}(C_{\text{APS}})$. The number of radicals increased with the increasing initiator concentration, which led to the increase of grafting polymerization rate at the beginning.^{13,14} As was apparent, $R_g \propto C_{\text{APS}}^{0.429}$ could be used to depict

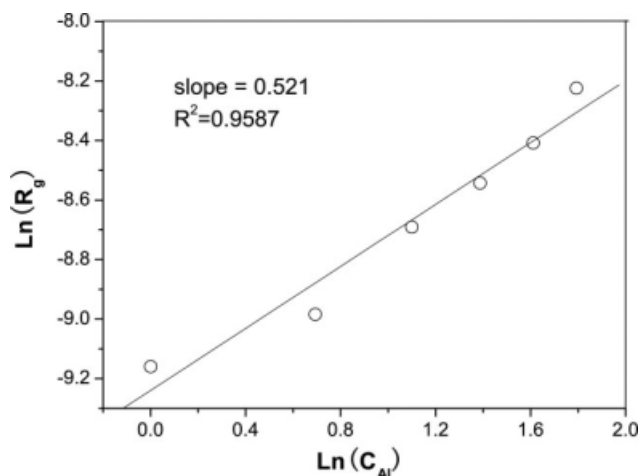


Figure 1 The relationship between $\text{Ln}(R_g)$ and $\text{Ln}(C_{\text{Al}})$.

the relationship between the grafting polymerization rate and initiator concentration.

Analogously, the influence of MMA concentration on the grafting polymerization rate was studied, and the result was given in Figure 3. A good linear relationship was observed between $\text{Ln}(R_g)$ and $\text{Ln}(C_{\text{MMA}})$. According to the principle of chemical reaction dynamics, grafting polymerization rate would increase with the reactant concentration. The slope of the line was 0.978, so the relationship between grafting polymerization rate and MMA concentration could be simulated as $R_g \propto C_{\text{MMA}}^{0.978}$.

According to the earlier investigations, the experimental apparent grafting polymerization rate onto flaky Al powder could be described as $R_g = KC_{\text{Al}}^{0.521} \times C_{\text{APS}}^{0.429} \times C_{\text{MMA}}^{0.978}$.

The theoretical kinetics of grafting polymerization

To clarify the mechanism of MMA grafting polymerization onto flaky Al powder, the theory of stable

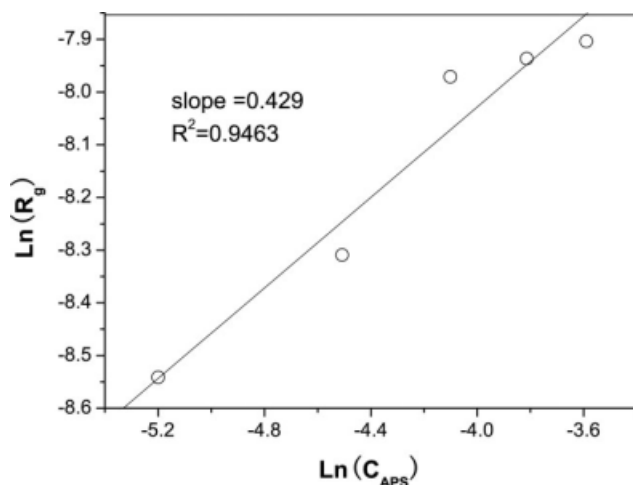


Figure 2 The relationship between $\text{Ln}(R_g)$ and $\text{Ln}(C_{\text{APS}})$.

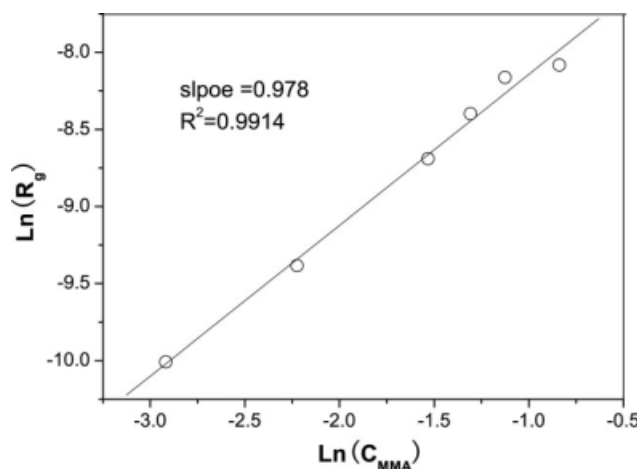
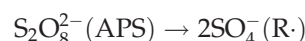


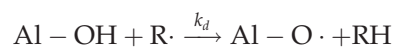
Figure 3 The relationship between $\text{Ln}(R_g)$ and $\text{Ln}(C_{\text{MMA}})$.

polymerization and equivalent activity could be used to simplify the reactive process. So the mechanism of grafting polymerization rate might be describes as follows:

1. The generation of primary radicals:



2. The formation of flaky Al skeleton radicals:



3. The initiating step:



4. The propagating step:



5. The terminating step: Combination would be dominant terminating way at low-initiator concentration, and then,



According to the theory of stable polymerization and equivalent activity, the following relationship could be established:

$$\frac{dC_{Al-O}}{dt} = k_d C_{Al} C_{APS} - k_i C_{Al-O} C_{MMA} = 0$$

Namely, $k_d C_{Al} C_{APS} = k_i C_{Al-O} C_{MMA}$

$$\frac{dC_{Al-OM}}{dt} = k_i C_{Al-O} C_{MMA} - k_t C_{Al-OMMA_n}^2 = 0$$

That is to say, $k_i C_{Al-O} \cdot C_{MMA} = k_t C_{Al-OMMA_n}^2$.

So, $C_{Al-OMMA_n} = (k_d/k_t)^{\frac{1}{2}} C_{Al}^{\frac{1}{2}} C_{APS}^{\frac{1}{2}}$

Consequently, $R_g = k_p C_{Al-OMMA_n} C_{MMA} = k_p (k_d/k_t)^{\frac{1}{2}} C_{Al}^{\frac{1}{2}} C_{APS}^{\frac{1}{2}} C_{MMA}$.

For sake of simplification, $k_p (k_d/k_t)^{\frac{1}{2}} = K$, the theoretical apparent grafting polymerization rate onto flaky Al could be described as: $R_g = K C_{Al}^{0.5} \times C_{APS}^{0.5} \times C_{MMA}$.

As was clearly observed, a basic agreement was obtained between experimental and theoretical apparent MMA grafting polymerization rate onto flaky Al powder. So the radical polymerization could be used to describe the mechanism. Of course, there were some small differences between experimental and theoretical grafting polymerization rate, and the reason could be possibly explained as follows. Firstly, a small quantity of primary radicals might take part in the terminating step. Secondly, gel effect would take place at high monomer conversion. Finally, there was discrepancy between the theory of stable polymerization (or equivalent activity) and actual experiments.

The activation energy of grafting, homogenous, and total polymerization

It was generally admitted that reactive temperature played an important role in the polymerization rate. As shown in Figure 4, a good linear relationship was observed between $\ln(k_g)$ and $(1/T)$, and the slope of the line was simulated as -7834.2 . According to the Arrhenius equation,¹⁵⁻¹⁷ the activation energy of MMA grafting polymerization (E_{ag}) onto flaky Al was calculated as:

$$E_{ag} = -8.314 \times (-7834.2) = 65.1 \text{ kJ mol}^{-1}.$$

As we know, the molecular structure was not taken into account in the Collisions Theory, so the activation energy of MMA grafting polymerization could possibly not be explained according the Collisions Theory.

Similarly, the activation energy of homogenous and total polymerization rate could be also calculated as 35.4 and 37.5 kJ mol^{-1} , respectively. It could be validated that the relationship among the activation energy of grafting, homogenous, and total polymerization accorded with the following equation:

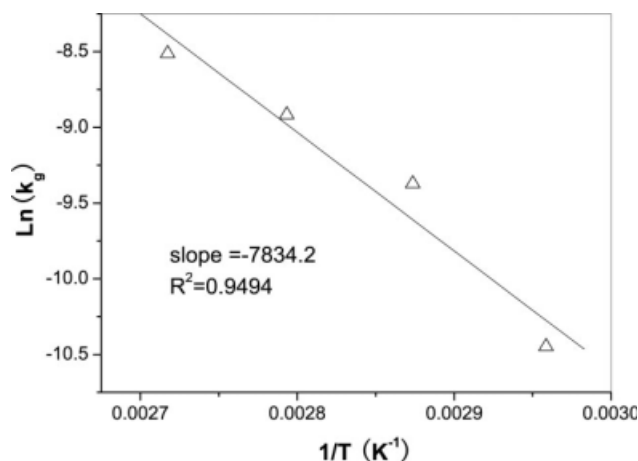


Figure 4 The relationship between $\ln(k_g)$ and $1/T$.

$$E_{at} = \frac{k_g E_{ag} + k_h E_{ah}}{k_g + k_h}$$

where, E_{at} was the activation energy of total polymerization;

E_{ag} was the activation energy of grafting polymerization;

E_{ah} was the activation energy of homogenous polymerization;

k_g was the rate constant of grafting polymerization; and

k_h was the rate constant of homogenous polymerization.

In fact, grafting and homogenous polymerization were a pair of parallel reactions. So the equation about the activation energy was exactly consistent with the theoretical result of parallel reactions.¹⁸

CONCLUSION

With APS as the initiator, the kinetics of MMA grafting polymerization onto flaky Al was studied. It was found that the experimental apparent polymerization rate equation, $R_g = K C_{Al}^{0.521} \cdot C_{APS}^{0.429} \cdot C_{MMA}^{0.978}$, was basically consistent with the theoretical result based on the theory of stable polymerization and equivalent activity, $R_g = K C_{Al}^{0.5} \cdot C_{APS}^{0.5} C_{MMA}$. The activation energy of grafting, homogenous, and total polymerization rate was calculated as 65.1, 35.4, and 37.5 kJ mol^{-1} , respectively. It could be validated that the relationship among these activation energies accorded with the theoretical result of parallel reactions: $E_{at} = \frac{k_g E_{ag} + k_h E_{ah}}{k_g + k_h}$.

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