Study of Microwave Irradiation Polymerization Mechanism in the Presence of Carriers

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ABSTRACT: Microwave irradiation polymerization was studied in the presence of a carrier. The influence of different carriers, such as Al_2O_3, SiO_2, and MgO on the microwave irradiation polymerization mechanism of acrylamide and 2-ethylhexyl acrylate was studied by adopting polymerization inhibitors such as an anionic inhibitor, cationic inhibitor, and radical inhibitor hydroquinone. When the system contains the carriers Al_2O_3 and SiO_2, the polymerization mechanism occurs according to a radical mechanism, but when the system contains MgO, the polymerization mechanism occurs according to not only a radical mechanism but also an anionic polymerization mechanism with superficial grafting occurring. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1519–1524, 2004

Key words: microwave irradiation; polymerization mechanism; carrier; graft; acrylamide

INTRODUCTION

Microwaves are a nonionized electromagnetic energy. They have received considerable attention since Gedye and coworkers first introduced them into organic synthesis in 1986.[1] In recent years, microwave irradiation has been widely used in the chemical field. In organic chemistry, the use of microwave heating results in short reaction times compared with conventional heating, ease of workup after a reaction, and reduction. Microwave ovens provide a clean and cheap alternative to conventional oil baths. Microwave irradiation is also used in polymerization.[2–21] The microwave irradiation polymerization mechanism needs to be studied, especially in many microwave irradiation polymerization systems, when carrier is added and the influence of its existence to the polymerization mechanism cannot be avoided. In this paper, high-active liquid monomer 2-ethylhexyl acrylate and solid-state monomer acrylamide (AM) were polymerized by microwave irradiation and the influence of different carriers, Al_2O_3, SiO_2, and MgO, to the microwave irradiation polymerization mechanism of acrylamide and 2-ethylhexyl acrylate was discussed.

EXPERIMENTAL

Materials

2-Ethylhexyl acrylate was distilled under reduced pressure. AM was recrystallized by $CHCl_3$. Al_2O_3 (d = 0.236 μm), SiO_2 (d = 0.208 μm), light MgO (d = 1.17 μm), common MgO (d = 1.67μm), ethanol, benzoic acid, hydroquinone are all analytical grade.

Procedure of polymerization

Liquid polymerization of 2-ethylhexyl acrylate

Quantities of monomer and solid carrier Al_2O_3, SiO_2, or MgO were weighed, placed in a small Erlenmeyer flask, and placed into the microwave oven (700 W, 2,450 MHz). After being degassed with nitrogen for 30 min, the irradiation time and intensity were set up to a prescribed value. After the microwave irradiation reaction, the resulting product was centrifuged. In the Al_2O_3 and SiO_2 carrier systems, the thick upper layer was polymer and the lower section was solid carrier Al_2O_3 or SiO_2. In the MgO system, the precipitated upper liquid layer was polymer, which can be used in the determination of intrinsic viscosity, and the lower solid phase was washed repeatedly with benzene, dried and weighed, and the graft rate was calculated. The substrate magnesium oxide was removed by washing the graft polymer with 6 mol/L hydrochloric acid. The grafted polymer poly-2-ethylhexyl acrylate was obtained.

Solid phase polymerization of acrylamide

Quantities of monomer and inorganic carrier Al_2O_3, SiO_2, or MgO were weighed and ground thoroughly,
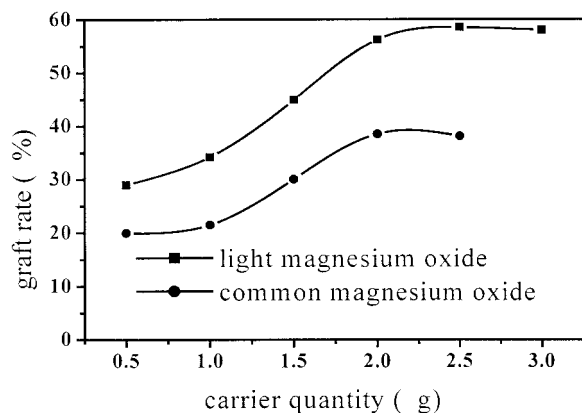
Figure 1 Relation between quantity of carrier MgO and graft rate.

and then set into a special vial reactor and degassed with nitrogen for 30 min. The beginning temperature and weight of the mixture were determined. The mixture was radiated at the prescribed power and time. Afterward, the temperature and weight of the mixture were determined again. The mixture was poured into a quantity of methyl alcohol, the unreacted monomer was removed, filtered, dried at 120°C, and weighed accurately. The filter cake was added into deionized water, the homopolymer was dissolved in the water and centrifuged, the separated solid was washed with deionized water repeatedly, and then dried and weighed accurately. For the Al_2O_3 or SiO_2 system, there was only homopolymer and the percent conversion of polymerization was calculated. For the MgO system, not only was homopolymer formed but also the MgO graft. The graft rate and percent conversion was calculated. The substrate magnesium oxide was removed by washing the graft polymer with 6 mol/L hydrochloric acid.

Measurement

Determination of intrinsic viscosity

Intrinsic viscosity of 2-ethylhexyl acrylate was measured by the one-point method in the toluene solvent at 25 ± 0.1°C.

The infrared (IR) spectrum was determined by America Perkin–Elmer model-577 IR spectrum.

RESULTS AND DISCUSSION

2-Ethylhexyl acrylate polymerization

MgO adopted as carrier

Research shows that, when was MgO adopted as carrier, poly-2-ethylhexyl acrylate was formed and poly-2-ethylhexyl acrylate was grafted on the surface of MgO, which is shown in Figure 1.

In Figure 1, the quantity of solid monomer was fixed and the content of carrier MgO was changed and then the grafted curves were obtained. First, the organic monomer can be grafted not only on the light magnesium oxide but also on the common magnesium oxide. Furthermore, the graft rate increased along with the increase of carrier quantity in the case of light magnesium oxide, as well in the case of common magnesium oxide. Second, the efficiency of the light magnesium oxide is obviously greater than that of the common magnesium when the quantity is equal. This is because that the grain size of light magnesium is small and the surface area is larger, increasing the grafted monomer.

Silicon oxide or aluminum oxide adopted as carrier

In Figure 2, the quantity of monomer was fixed and the silicon oxide was adopted as carrier and then the 2-ethylhexyl acrylate that polymerized was irradiated with the microwave and the curves were obtained.

The results show that there is no graft polymer formed on the surface of silicon oxide, but the monomer can be initiated by silicon oxide. The percent conversion increased along with the increase of the quantity of carrier to a certain degree. As to aluminum oxide, the result is similar to that of silicon oxide on the whole. In Figure 3, it shows the influence of the quantity of carrier to the percent conversion. In the same way, the aluminum oxide can initiate polymerization, but not grafting.

To show the organic monomer can be grafted on the surface of the magnesium oxide but not on the surface of the silicon oxide or aluminum oxide, quantitative anionic inhibitor ethanol was added into the polymerization system in which MgO was adopted as carrier. The result is shown in Figure 4. The results shown in Figure 5 were obtained when the quantitative radical inhibitor hydroquinone was added into the system.
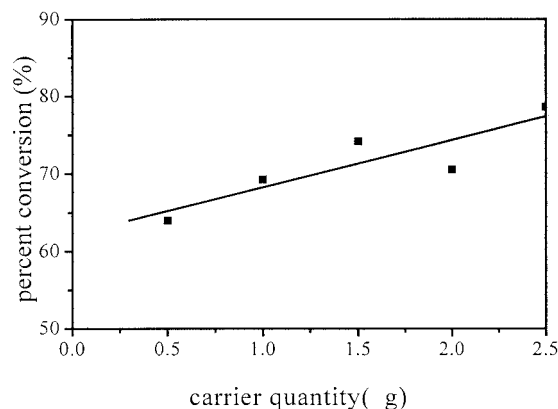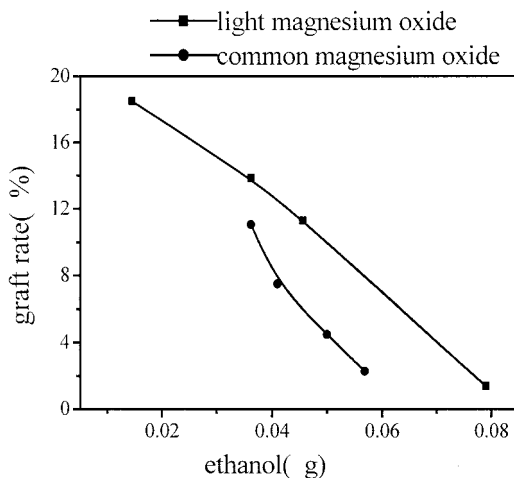

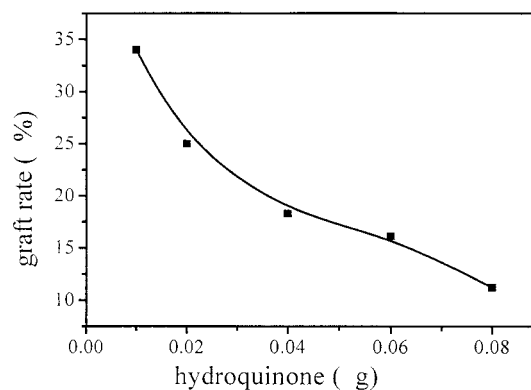**Figure 2** Influence of quantity of carrier SiO_2 to percent conversion.
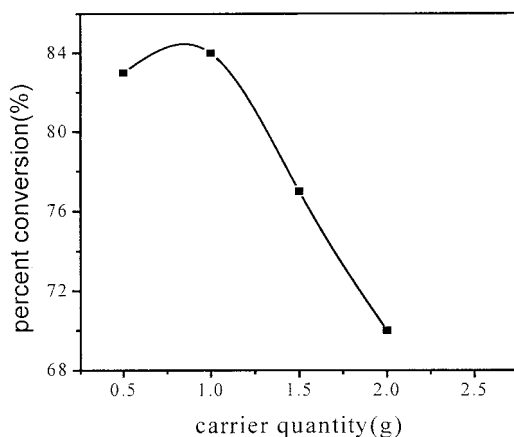
Figure 3 Relation between quantity of carrier Al_2O_3 and percent conversion.

Figure 5 Relation between amount of hydroquinone and graft rate.

As can be seen in Figures 4 and 5, when the ethanol was added to the MgO reaction system, the graft rate decreased with the increase of the quantity of ethanol, showing anionic polymerization in the polymerization. When the hydroquinone was added into the system, the graft rate decreased along with the increase of the quantity of the hydroquinone, showing radical polymerization in the polymerization, while when 0.083 g ethanol anionic inhibitor was added into the Al_2O_3 and SiO_2 systems, examination of the polymerization shows that the graft rate and the productive rate were equal approximately to those of the system that had no inhibitor. When 0.08 g radical inhibitor hydroquinone was added into the system, the productive rate decreased, showing that radical initiating occurs only when Al_2O_3 and SiO_2 initiate the organic monomer. The conclusion of this kind of negative approach is identical to that obtained by way of capturing with the radical capture agent 1,1-diphenyl-

2-trinitrop-henylhydrazine (DPPH). To the mechanism of inorganic solid surface irradiation grafting, many researchers explain it with the viewpoint of crystal quality of the inorganic solid itself and the irradiation impairment. According to Yanova and Kolloidnzh,[22] solid impairment occurred after the energetic irradiation and longer lifespan charge was formed, by which radicals came into being. Eifler[23] thought that the monomer graft occurred on the dissociation surface of the solid. Most authors thought that the grafting of the solid surface was initiated by the free radical.[24,25] Brailsford and Morton[26] showed that O-anion radical existed on the surface of the MgO crystal lattice; Wong and Lunsford[27] thought that the O-anion exists on the surface of the MgO crystal lattice where it was irradiated. Because of the existence of O-anion radical on the surface of the MgO crystal, the active site of grafting that can initiate the grafting polymerization of organic monomer is formed, and the reaction then can be initiated not only according to the radical initiation mode but also according to the anionic mode. Because the anion formed on the surface of the MgO under microwave irradiation (it should be O-anion), the grafting occurred on the surface of the MgO. While the carrier Al_2O_3 or SiO_2 existed, there is no graft polymer formed, but the monomer was initiated by the radical.

The IR spectrum and analysis (Figure 6)

Spectrum 1: microwave polymer. The maximum spectrum line around 1,736.1 cm^{-1} is the stretching vibration of carbonyl. In spectrum 5, the line 1,639.6 cm^{-1} of magnesium is broken into two peaks, the line around 1,736.1 cm^{-1} is the stretching vibration absorption spectrum. The position, shape, and relative intensity of each absorption band of magnesium oxide and the poly-2-ethylhexyl acrylate have a certain inhomogeneous change, this is different from the ordinary lamellar insertion and surface coating; the organic

Figure 4 Relation between quantity of ethanol and graft rate.
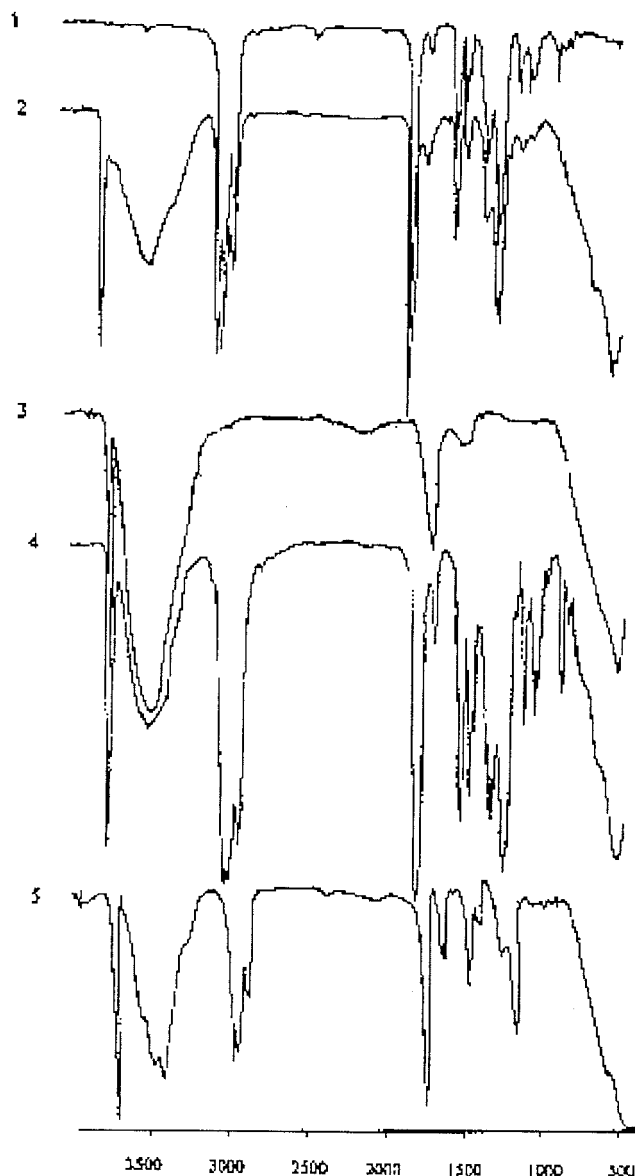
Figure 6 IR spectrum of polymer. (1) Poly-2-ethylhexyl acrylate with irradiation; (2) grafting poly-2-ethylhexyl acrylate; (3) magnesium oxide; (4) magnesium + 30% poly-2-ethylhexyl acrylate; (5) graft polymer of magnesium oxide.

monomer is grafted on the surface of the solid magnesium oxide.

Spectrum 2. In Figure 6, 2 is the spectrum of the polymer chain and magnesium oxide was removed by hydrochloric acid. Compared to the irradiation polymer, the grafting chain has a stronger absorption band around 3,100–3,700 cm^{-1}, because the grafting chain has an end hydroxy formed while getting rid of the substrate in the acid solution and an endo-hydrogen bond formed between the hydroxy and the ester of the grafting chain; this is a powerful proof that the surface of the magnesium is initiated by oxygen after the grafting reaction.

According to the analysis above, it could be concluded that graft reaction of monomer to the carrier's

surface easily occurred when MgO was used as a carrier. At the same time, the polymerization was initiated in a radical as well as anion mechanism. There is no graft polymer formed on the carrier Al_2O_3 or SiO_2, only the radical initiates the monomer.

Solid phase polymerization of acrylamide

Demonstration of the mechanism of the solid surface graft polymerization of MgO

Free radical inhibitor (hydroquinone), anionic inhibitor (benzoic acid), and cationic inhibitor (benzoguanamine) were added into the reaction system containing the carrier MgO, Al_2O_3, or SiO_2, and the percent conversion of polymerization and the change of graft rate were examined.

The reaction with carrier SiO_2 and Al_2O_3

The reaction had no graft polymer after treatment with carrier SiO_2 and Al_2O_3. No characteristic peak of grafting poly(acrylamide) (PAM) was found in their IR spectrums. It was proven that the monomer was not grafted on the surface of the SiO_2 or Al_2O_3.

The reaction with carrier MgO

The reaction situation adopting carrier MgO was obviously different from that adopting carrier SiO_2 and Al_2O_3. That is to say the monomer was grafted on the surface of MgO under microwave irradiation, and the existence of graft reaction also was verified by IR spectrum.
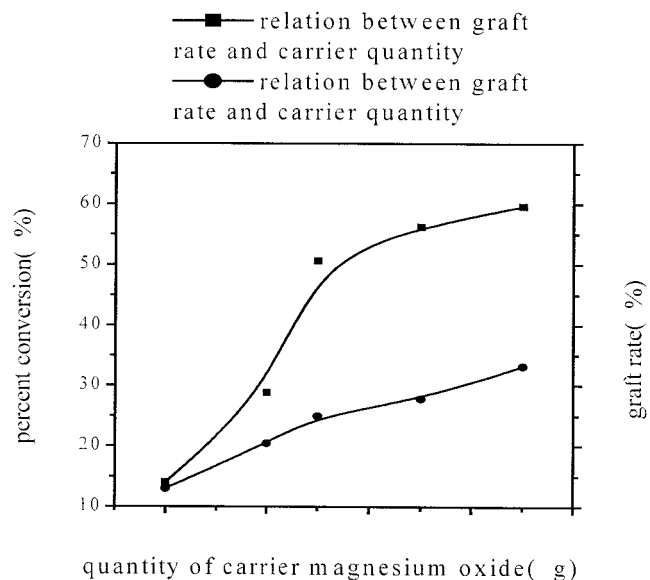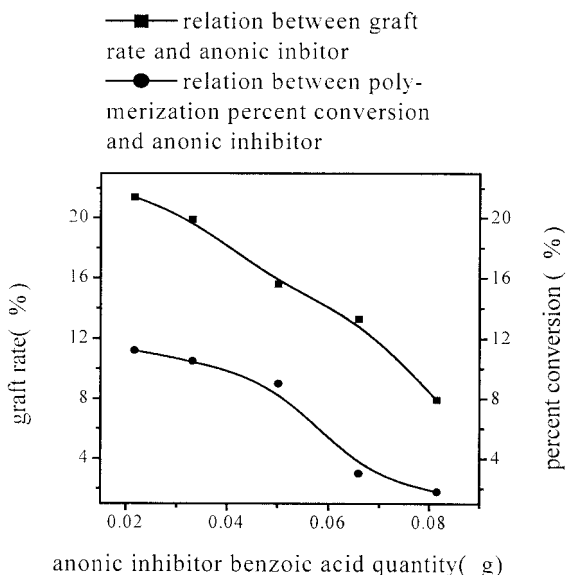

Figure 7 Relation between quantity of carrier MgO and percent conversion and graft rate.
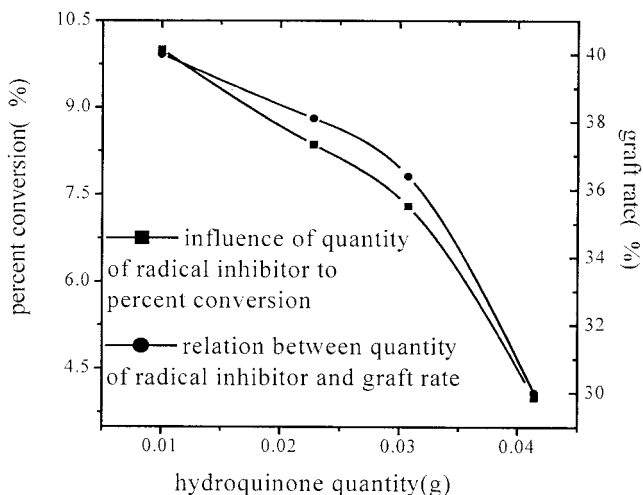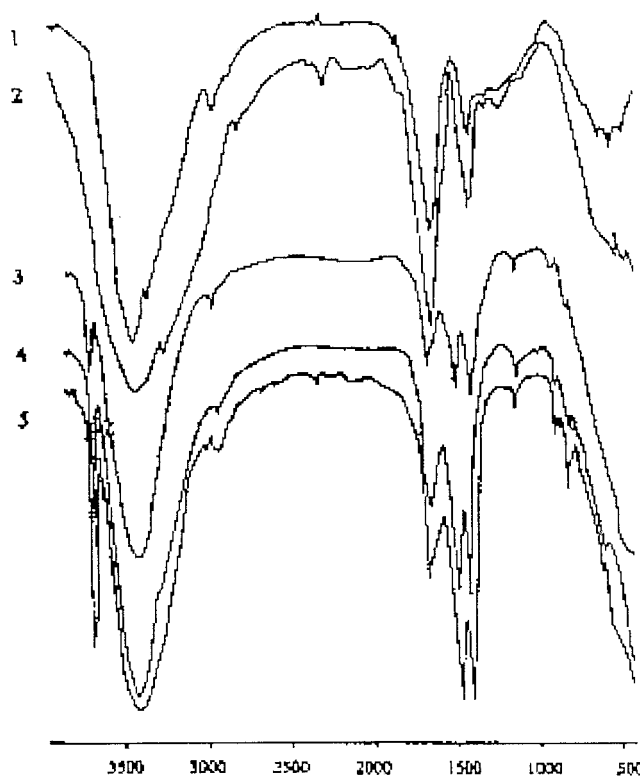
Figure 8 Influence of quantity of hydroquinone inhibitor to percent conversion and graft rate.

Figure 10 IR spectrum of polymer. (1) Irradiation polymerization PAM; (2) grafting chain PAM; (3) magnesium oxide; (4) magnesium oxide + PAM; (5) magnesium oxide grafted with PAM.

The relationship between the percent conversion of polymerization or the graft rate and the quantity of carrier MgO is shown in Figure 7. In Figure 7, the percent conversion of polymerization and graft rate increased along with the increase of the quantity of MgO. It can be seen from the mechanism that the O-anionic radical generated on the surface of MgO under irradiation increases with the increase of the quantity of MgO, and the active site of graft reaction increased also, which resulted in the increase of percent conversion of polymerization and graft rate to a certain degree.

Figure 9 Influence of anionic inhibitor benzoic acid to polymerization percent conversion and graft rate.

The mechanism of superficial graft polymerization of MgO under irradiation

The research result of acrylamide solid polymerization is completely identical to the one of the 2-ethylhexyl acrylate, namely, there are radical mechanisms and anionic mechanisms in the reaction. Figure 8 shows that the more radical the inhibitor to the hydroquinone, the less the percent conversion and graft rate of polymerization. It was proven that there is a radical mechanism of polymerization in the acrylamide solid phase reaction.

In Figure 9, the anionic inhibitor to percent conversion of polymerization and graft rate is shown. We find that the percent conversion of polymerization and graft rate decrease along with the increase of the anionic inhibitor quantity. It was proven that there is anionic mechanism in the reaction, and the percent conversion of polymerization and graft rate were invariable on the whole when cationic inhibitor is added. It was proven that the mechanism of graft polymerization on the surface of the MgO with irradiation not only has radical polymerization but also anionic polymerization, and it is identical to the result of 2-ethylhexyl acrylate.

The token of acrylamide's graft polymerization under irradiation on the surface of MgO (IR spectrum analysis as below)

In Figure 10, spectrum 1 is the IR spectrum of the irradiation polymerization of PAM. The maximum apex around $3{,}448.3$ cm^{-1} is the stretching vibration of $-NH_2$ and the $1{,}655$ cm^{-1} apex is the characteristic apex of $-C-NH_2$. $29{,}246$ cm^{-1} is the stretching vibration of C–H. Spectrum 2 is the IR spectrum of the graft polymer of MgO after removing the substrate with hydrochloric acid and being grafted with PAM. It is similar to spectrum 1 on the whole except that the characteristic frequency around $3{,}400$ cm^{-1} moves to lower wave number and the apex shape widens. It may be the hydroxyl of the graft polymer is formed in the acid solution, and the intermolecular hydrogen bond is formed between the hydroxyl and the intermolecular carbonyl. Spectrum 3 is the IR spectrum of magnesium oxide. Spectrum 5 is the IR spectrum of magnesium oxide grafted with PAM. Spectrum 4 is the IR spectrum of the simple mixture of the magnesium oxide and PAM. Spectrum 4 is similar to the spectrum 5 on the whole, but compared to spectrum 3 and 4, the position of the absorption band, shape, and relative intensity of spectrum 5 has inhomogeneous change. The before change shows sufficiently that the acrylamide was grafted on the surface of the magnesium oxide.

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