

Study on the self-polymerization and co-polymerization properties of gadolinium methacrylate

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Abstract

Gadolinium methacrylate (Gd(MAA)₃) was synthesized through the reaction of gadolinium oxide and methacrylic acid and characterized by FT-IR spectroscopy, DSC and TGA. The non-isothermal and isothermal analysis were used to study the kinetics of self-polymerization of Gd(MAA)₃. The monomer reactivity ratios of MMA/Gd(MMA)₃ were calculated by K-T method. The results showed that Gd(MAA)₃ could be induced to self-polymerization initiated by thermal and free radical and the activation energy of polymerization was 103.35kJ/mol in solid state and 58.55kJ/mol in aqueous solution. The rate of polymerization under low conversion was governed by the expression at 65 °C: $R_p = K[M]^{1.05}[I]^{0.60}$. The values of r_1 (MMA) and r_2 (Gd(MAA)₃) were 0.225 and 1.340.

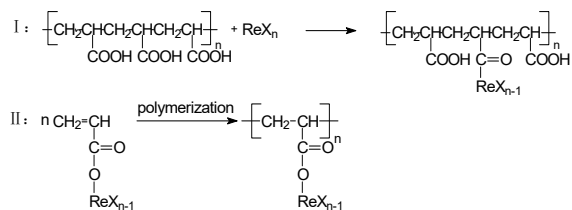
Keywords: gadolinium methacrylate; thermal analysis; kinetics of the polymerization; monomer ratios.

1. Introduction

Rare earth elements called “industrial monosodium glutamate” with the special 4f electronic structures have widely applications in the field of fluorescence [1], magnetism [2], hydrogen storage [3], and catalysis [4]. Recently rare earth-containing polymer as a kind of functional material has been received more and more attention, because it combines with the unique properties of the rare earth and the special properties of the polymer, such as light weight, excellent mechanical behavior and varied preparation method [5-6].

Generally rare earth can be induced into the polymer matrix by physical blending or chemical attachment [7]. Physical blending is a simple way to produce rare earth-containing polymer, but most rare earth compounds

have a bad compatibility with polymer and uneven dispersion which will cause poor mechanical properties. The chemical attachment method consists of two parts: (I) the interaction of rare earth ion with linear functionalized(such as carboxyl-containing) polymers; (II) the polymerization and copolymerization of rare earth monomers. Okamoto had produced a lot of rare earth containing polymers through method (I) as the first time in 1980 [8]. They found that the fluorescence intensities of the rare earth containing polymers were increase linearly with the rare earth ion content. However the disadvantage of method (I) is reflected in the low rare earth content and hard to quantify. The advantage of Method (II) is that high rare earth content can be get and easy to quantify. But the rare earth monomer should be synthesized first. Until now few papers have studied the self-polymerization and co-polymerization properties of the rare earth monomers.



In this paper, gadolinium methacrylate (Gd(MAA)₃) as an example of rare earth monomers was synthesized and its polymerization kinetics was studied through the thermal analysis. The reactivity ratio of Gd(MAA)₃ and methyl methacrylate was investigated and calculated by K-T method.

2. Experimentation

2.1 Materials

Gadolinium oxide (Gd₂O₃, 99.99%) was purchased from Shanghai Yuelong Chemical Factory, methacrylic acid (MAA, CP), ethanol (AR), N,N-dimethylformamide

(DMF,AR), methyl methacrylate (MMA, CP), azodiisobutyronitrile (AIBN, CP), and ammonium persulphate (APS, AR) were obtained from Sinpharm Chemical Reagent Co., Ltd. MMA was washed by sodium hydroxide solution and distilled water to eliminate the inhibitor and AIBN was recrystallization before used.

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2.2 Synthesis of gadolinium methacrylate (Gd(MAA)₃)

Gd(MAA)₃ was prepared by adding Gd₂O₃, MAA and H₂O with the molar ratio of 1:10:20 into a 100-mL three-necked flask. The reaction was carried out at 90°C for 1h until all the powders had been dissolved and the solution became transparent. The solution was filtered while still hot, and the filtrate was concentrated by distilling water. A white precipitate was obtained by adding ethyl alcohol in excess to the filtrate and leaving it overnight. The solid was filtered off, washed with ethyl alcohol and dried under vacuum. The final product was obtained in about 80% yield.

2.3 Polymerization

Self-polymerization of Gd(MMA)₃ was carried out in a 5ml vessel using water as a reaction medium and APS as a initiator and the exothermic process of polymerization was directly detected by the micro-DSC.

Copolymerization of MMA and Gd(MMA)₃ was carried out in a three-necked flask at 70°C under nitrogen atmosphere using DMF as a reaction medium and AIBN as a initiator. In the reaction system, the total monomer concentration was 20 wt%, and the initiator concentration was 2 wt% (on the basis of total monomers). Good agitation was used in the polymerization process to throw off the reaction heat instantaneously. The copolymerization was terminated at a low conversion of ≤10% to keep the copolymerization at a steady reaction stage. Then the precipitate mixture was isolated by filtration, washed successively with water and ethyl alcohol, and dried under vacuum at 60°C. The low conversions were measured by weighing method.

2.4 Characterizations

The Fourier transform infrared (FT-IR) spectra of samples were recorded at a resolution of 1 cm⁻¹ on a Varian Cary 5000 spectrometer. The thermal characteristics of Gd(MAA)₃ was obtained by DSC (PerkinElmer, DSC 8500) and TGA(PerkinElmer, Pyris 1 TGA). The analyses were performed at a heating rate of 10°C/min in nitrogen atmosphere.

Non-isothermal analysis by DSC (PerkinElmer, DSC 8500) was used as an alternative way of calculating the self-polymerization activation energy of Gd(MAA)₃ in the solid state known as the Kissinger method [9]. Kissinger method is based on a linear relationship between the logarithmβ/Tp² with the inverse of the endothermic peak through the following expression:

$$\ln \left[\frac{\beta}{T_p^2} \right] = \ln \left[\frac{RA}{E} \right] - \frac{E}{RT_p} \quad (1)$$

where β is the heating rate(°C/K), Tp is the endothermic peak temperature(K), R is ideal gas constant.

Isothermal analysis by micro-DSC (Setaram, C80) was used to study the kinetics of the radical polymerization of Gd(MAA)₃ in aqueous solution using ammonium persulphate as initiator. With the presumption that the heat flow, dH/dt, was proportional to the rate of reaction dα/dt, it is possible to determine the extent of conversion, α, directly from the experimental curve by partial intergration [10]:

$$\alpha = \frac{1}{\Delta HT} \int_0^t \frac{dH}{dt} dt \quad (2)$$

where Δ HT stands for the total heat of polymerization. The dependence of polymerization rate on initiator and concentration was determined by varying concentration of one species while keeping the other constant and vice versa. The effect of temperature on the conversion was investigated at constant monmer and initiator concentrations.

Element analysis method was used to calculate monomer reactivity ratios of MMA/Gd(MAA)₃. The gadolinium (Gd) contents of the copolymer were obtained by ash determination method.

3. Results and discussion

Fig.1 shows the FT-IR spectra of MAA and Gd(MAA)₃. The bands characteristic of the nonionized carboxyl groups ν(C=O) that lies in the interval 1690-1710 cm⁻¹ in fig.1A disappear and new bands appear in the regions 1520-1580 cm⁻¹ and 1395-1430 cm⁻¹ respectively

which belong to the stretching vibrations $\nu(\text{COO}^-)$ and $\nu(\text{C}=\text{C})$ of carboxylate ion in fig.1B. It means the gadolinium ion and carboxyl groups have coordination reaction with each other. The frequencies of stretching vibrations $\nu(\text{C}=\text{C})$ does not change significantly between MAA and $\text{Gd}(\text{MAA})_3$, that signify $\text{Gd}(\text{MAA})_3$ had the ability of polymerization.

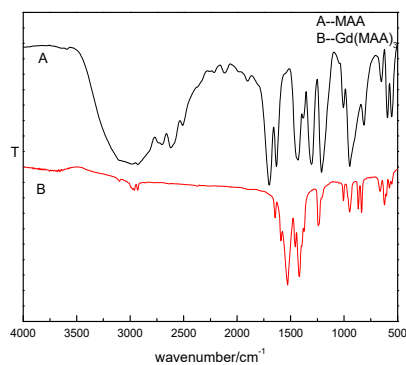


Fig.1 FT-IR spectra of (A) MAA; (B) $\text{Gd}(\text{MAA})_3$

In order to confirm the polymerization ability of $\text{Gd}(\text{MAA})_3$, the thermal analysis is taken as showed in fig.2. Two sharp endothermic peaks at 141 and 192°C in fig.2A can be related to the melting of $\text{Gd}(\text{MAA})_3$ crystals. Generally rare earth ion has a large coordination number, so that there may be two different kinds of crystalline structure in the $\text{Gd}(\text{MAA})_3$ powder [11]. There is a significant exothermic peak at 220-350°C in fig.2A. The TG curve in fig.2C exhibit almost no mass loss from 220-350°C. Therefore, the exothermic peak may be attributed to the self-polymerization of $\text{Gd}(\text{MAA})_3$ rather than the decomposition of $\text{Gd}(\text{MAA})_3$. What's more, endothermic peaks and exothermic peaks are all disappeared in fig.2 B. It also proves that $\text{Gd}(\text{MAA})_3$ has been self-polymerization at 220-350°C during the first heat up process. $\text{Gd}(\text{MAA})_3$ is changed to be the poly($\text{Gd}(\text{MAA})_3$) because of the self-polymerization which breaks the crystal structure of $\text{Gd}(\text{MAA})_3$ leading to the disappearance of endothermic peaks in fig.2B.

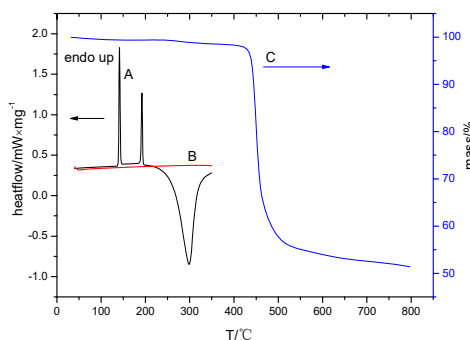


Fig. 2 Thermal analysis curves of $\text{Gd}(\text{MAA})_3$: (A) DSC for the first heat up; (B) DSC for the second heat up; (C) TG

It has confirmed that $\text{Gd}(\text{MAA})_3$ can be induced self-polymerization initiated by thermal at 220-350°C from above analysis. As shown in fig.3, T_p is raised from 282.5 to 315.9°C along with the heating rate from 5 to 20°C/min and the activation energy (E_a) of polymerization is 103.35kJ/mol calculated by Eq (1).

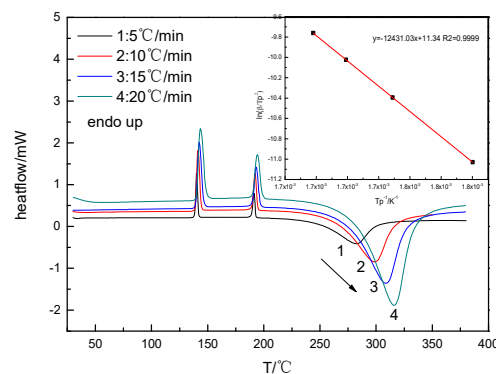


Fig. 3 DSC curves of $\text{Gd}(\text{MAA})_3$ at different heating rates:(1) 5;(2) 10;(3) 15; (4) 20°C/min.Inset: Kissinger method plot for activation energy determination of $\text{Gd}(\text{MAA})_3$

Most of previous workers used the dilatometer and gravimetry technique to study the radical chain polymerization [12-13]. Here isothermal analysis by micro-DSC is used to study the kinetics of the radical polymerization of $\text{Gd}(\text{MAA})_3$ in aqueous solution. The conversion-time curves are generally S-shaped as shown in fig.4. At the very beginning of the polymerization, conversion and time are appeared approximate linear relationship. As the reaction going, the poly($\text{Gd}(\text{MAA})_3$) is precipitated from the solution that cause the gel effect and increase the polymerization rate rapidly. Generally the dependence of polymerization rate on monomer and initiator concentrations is a important part of the kinetic study. The polymerization rate, R_p , is obtained from the slope of the conversion versus time curve. The relationship of R_p with monomer and initiator concentration is obtained by plotting the $\ln[R_p]$ versus $\ln[M]$ and $\ln[I]$, and the form $R_p \propto [M]^{1.05} \times [I]^{0.60}$ is obtained from the line of the slope as shown in fig.5. The polymerization kinetics equation of $\text{Gd}(\text{MAA})_3$ is quite consistent with the classical kinetic theory. The effect of temperature on polymerization rate is shown in fig.6. As the temperature increased, the rate of production of primary free radicals increased, thus increasing the polymerization rate [14]. The activation energy is 58.55kJ/mol determined by plotting $\ln[R_p]$ versus $1/T(K)$. This value corresponds well with the typical activation energies of propagation in free radical polymerization [15] and it reveal that $\text{Gd}(\text{MAA})_3$ was easier

to polymerization in solution state than in solid state.

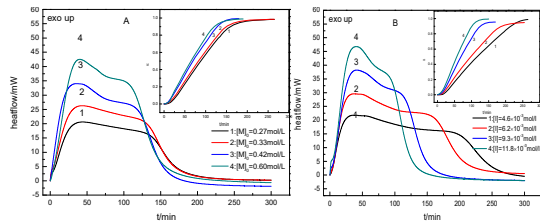


Fig.4 micro-DSC curves recorded for the polymerization of Gd(MAA)₃. Inset: polymerization conversion of Gd(MAA)₃ as a function of time. A: [M]₀=0.27-0.60mol/l, [I]=7.7×10⁻³mol/l and T=65 °C B: [I]=4.6×10⁻³-11.8×10⁻³mol/l, [M]₀=0.42mol/l and T=65 °C

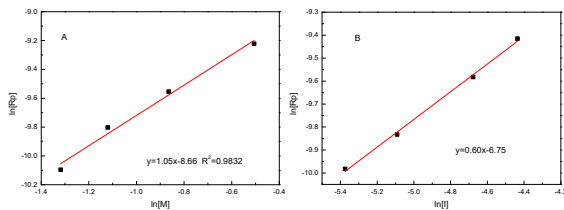


Fig.5 the dependence of Rp [M] (A) and [I] (B) under low conversion

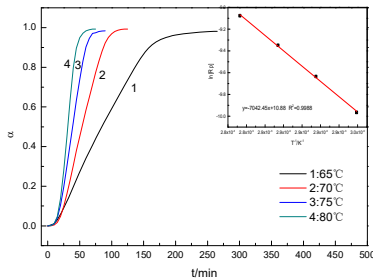


Fig.6 Polymerization conversion of Gd(MAA)₃ as a function of time. T=65-80 °C, [M]₀=0.42mol/l, [I]=7.7×10⁻³mol/l. Inset: the dependence of Rp on T under low conversion

On the basis of the element analysis results of gadolinium (Gd), the reactivity ratios of MMA/Gd(MAA)₃ can be calculated by K-T method [16]. Parameters for copolymerization are detailed in Table 1. Fig.7 is the plot of τ vs. ϵ used to calculate the monomer reactivity ratios by K-T method. The values of r_1 (MMA) and r_2 (Gd(MAA)₃) are 0.225 and 1.340, which imply that both the growing radical $\sim\sim\text{MMA}\cdot$ and $\sim\sim\text{Gd(MAA)}_3\cdot$ prefer to combine with the Gd(MAA)₃ unit. That may be because that the gadolinium ion has a large coordination number and the carboxylic group of $\sim\sim\text{MMA}\cdot$ can supply lone pair electrons to attract the Gd(MAA)₃ monomer, so that the growing radicals are more likely to combine with the Gd(MAA)₃ unit. As a result, in order to obtain the copolymer with uniform distributed gadolinium ion, adding the Gd(MAA)₃ monomer into the solution drop by drop

should be better.

Table 1 Parameters for copolymerization of MMA/Gd(MAA)₃

MMA/Gd(MAA) ₃ (w/w)	90/10	85/15	80/20	75/25	70/30
X (mol/mol)	36.73	23.40	16.23	12.30	9.57
Conversion (%)	3.29	8.50	9.21	7.72	3.89
Gd content (wt%)	11.98	15.76	18.47	21.00	22.78
Y (mol/mol)	8.98	5.85	4.38	3.36	2.77
$G = \frac{X(Y-1)}{Y}$	32.64	19.39	12.52	8.64	6.12
$H = \frac{X^2}{Y}$	150.19	93.66	60.12	45.05	33.00
$\tau = \frac{G}{\alpha + F}$	0.148	0.118	0.096	0.075	0.059
$\epsilon = \frac{H}{\alpha + H}$	0.681	0.571	0.461	0.390	0.319

$$\text{Ps: } \alpha = \sqrt{H_{\min} \times H_{\max}}$$

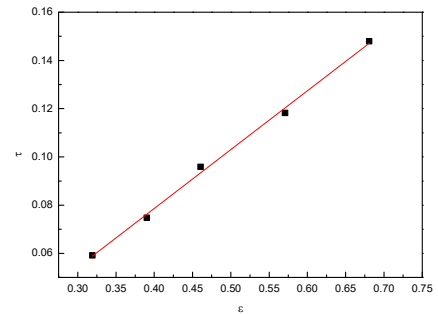


Fig.7 The plot of τ vs. ϵ related to the monomer reactivity ratios of MMA/Gd(MAA)₃ calculated by K-T method

4. Conclusions

In summary, Gadolinium methacrylate as a kind of new monomer can be synthesized through the reaction of gadolinium oxide and methacrylic acid with a quite high yield. As the existence of C=C bond, Gd(MAA)₃ can be self-polymerization initiated by thermal and free radical. The characteristic of polymerization in aqueous solution under low conversion is quite consistent with the classical kinetic theory. Gd(MAA)₃ monomer also shows a quite high reactivity copolymerization with MMA by the inferred from the values of monomer reactivity ratios. The purpose of this paper is to add the basic polymerization parameters of the rare earth monomer and provide a little help to produce a kind of functional rare earth-containing polymer material in the coming future.

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