Journal of Rare Earths 36 (2018) 298–303

Contents lists available at ScienceDirect

Journal of Rare Earths

journal homepage: http://www.journals.elsevier.com/journal-of-rare-earths

Self-polymerization and co-polymerization kinetics of gadolinium methacrylate☆

Chunhong Wang [a], Shuai Wang [a], Yujuan Zhang [a,*], Zhifeng Wang [b], Junliang Liu [a], Ming Zhang [a]

[a] School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China
[b] Testing Center, Yangzhou University, Yangzhou 225002, China

ARTICLE INFO

Article history:
Received 27 April 2017
Received in revised form
26 August 2017
Accepted 25 September 2017
Available online 2 December 2017

Keywords:
Gadolinium methacrylate
Thermal analysis
Polymerization kinetic
Thermal neutron shielding
Rare earths

ABSTRACT

Gadolinium methacrylate ($Gd(MAA)_3$) was synthesized by using gadolinium oxide and methacrylic acid as the starting materials and its self-polymerization kinetic was studied based on non-isothermal and isothermal analysis. Moreover, the monomer reactivity ratios of methyl methacrylate (MMA) and $Gd(MAA)_3$ were evaluated by using Kelen-Tüdõs method. The thermal neutron shielding properties of PMMA and poly(MMA-co-$Gd(MAA)_3$) were calculated by MCNP program. The results show that the self-polymerization of $Gd(MAA)_3$ can be initiated by thermal and free radical and its activation energy is 103.35 kJ/mol or 58.55 kJ/mol correspondingly in the solid state or aqueous solution. The polymerization rate, R_p, under low conversion at 65 °C is expressed as $R_p = K[M]^{1.05}[I]^{0.60}$. The reactivity ratios of r_1 (MMA) and r_2 ($Gd(MAA)_3$) are 0.225 and 1.340, respectively. The ability of thermal neutron shielding of poly(MMA-co-$Gd(MAA)_3$) is increased by gadolinium contents and is far better than PMMA.

1. Introduction

Recently rare earth-containing polymer as a kind of functional material has received more and more attention, because it combines 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,[1,2] so that it has wide applications in the fields of fluorescence, magnetism, hydrogen storage, and radiation protection.[3–9]

Generally rare earth can be induced into the polymer matrix by physical blending or chemical bonding.[10] Physical blending is a simple way to produce rare earth-containing polymer, but most rare earth compounds have bad compatibility with polymer which will cause uneven dispersion and poor mechanical properties. The chemical bonding method consists of two parts: (1) the interaction of rare earth ion with linear functionalized (such as carboxyl-containing) polymers; (2) the polymerization and copolymerization of rare earth monomers. Okamoto et al have produced a lot of rare earth containing polymers through method (1) for the first time in 1980.[11] They found that the fluorescence intensities of the rare earth containing polymers were increased linearly with the rare earth ion content. However the disadvantage of method (1) is the low rare earth content and being hard to quantify. The advantage of method (2) is that high rare earth content can be gotten and easy to quantify. Although there have been some rare earth-containing polymers synthesized by method (2),[12,13] the parameters about the polymerization kinetics of rare earth monomers are nearly empty.

Gadolinium has the highest thermal neutron capture cross section of the periodic table. As a result, gadolinium was taken as the research object in this paper and gadolinium methacrylate ($Gd(MAA)_3$) was synthesized and its polymerization kinetics was studied through the thermal analysis. The reactivity ratios of $Gd(MAA)_3$ and methyl methacrylate were investigated and calculated by *K-T* method. The thermal neutron shielding properties of PMMA and poly(MMA-co-$Gd(MAA)_3$) were calculated by MCNP program.

☆ **Foundation item:** Project supported by Graduate Student Research Innovation Project (KYLX_1337).
* Corresponding author.
E-mail address: lxyzhangm@yzu.edu.cn (Y.J. Zhang).

https://doi.org/10.1016/j.jre.2017.09.015
1002-0721/

2. Experimentation

2.1. Materials

Gadolinium oxide (Gd_2O_3, 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 recrystallized before used.

2.2. Synthesis of gadolinium methacrylate ($Gd(MAA)_3$)

$Gd(MAA)_3$ was prepared by adding Gd_2O_3, MAA and H_2O with the molar ratio of 1:10:20 into a 500-mL three-necked flask. The reaction was carried out at 90 °C for 1 h until all the powders were dissolved and the solution became transparent. The solution was filtered while still hot, and the filtrate was concentrated by distilling water for about 2 h. White precipitates were obtained by adding ethyl alcohol in excess to the filtrate. The solid was filtered off, washed with ethyl alcohol and dried under vacuum. The yield ratio of the final product was about 80% yield.

2.3. Polymerization

Self-polymerization of $Gd(MAA)_3$ was carried out in a 5 mL vessel using water as a reaction medium and APS as an 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).

Copolymerization of MMA and $Gd(MAA)_3$ was carried out in a three-necked flask at 70 °C under nitrogen atmosphere using DMF as a reaction medium and AIBN as an 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). Mild agitation was used in the polymerization process to throw off the reaction heat instantaneously. The copolymerization was terminated by adding excess methanol below the conversion of 10%. Then the precipitate mixture was filtered, washed successively with water and ethyl alcohol, and dried under vacuum at 60 °C. The conversions were measured by weighing method.

2.4. Characterizations

XRD pattern was obtained on a Bruker-AXS X-ray equipped with a graphite monochromator and Cu Kα radiation ($\lambda = 0.15406$ nm). The scanning speed was 4°/min and the scanning angle was from 5° to 60°.The Fourier transform infrared (FT-IR) spectra of samples were recorded with a resolution of 1 cm^{-1} on a Varian Cary 5000 spectrometer. The thermal characteristics of $Gd(MAA)_3$ were 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 a 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 knows as the Kissinger method.[14] Kissinger method is based on a linear relationship between the logarithm of β/T_p^2 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), T_p the endothermic peak temperature (°C), R 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 an initiator. With the presumption that the heat flow, dH/dt, was proportional to the rate of reaction $d\alpha/dt$, it is possible to determine the extent of conversion, α, directly from the experimental curve by partial integration[15]:

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

where ΔH_T 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 monomer and initiator concentrations.

Element analysis method was used to calculate monomer reactivity ratios of MMA/$Gd(MAA)_3$. The gadolinium content in the copolymer was obtained by ash determination method.

The thermal neutron shielding properties of PMMA and poly(MMA-co-$Gd(MAA)_3$) were calculated by MCNP program. The input file was listed in supporting information. The calculation model is shown in Fig. 1. The neutron energy was 0.025 eV and the sample was cylinder with different thickness. A was the test face used to calculate the number of unshielded neutron. The original number of neutron was 10^6, the parameter of the sample is listed in Table 1.

3. Results and discussion

From the XRD spectra as shown in Fig. 2, characteristic diffraction peaks in Gd_2O_3 disappear in $Gd(MAA)_3$ which means the synthetic reaction of $Gd(MAA)_3$ is sufficient and the product is pure. The intensity diffraction peak at 8.9° in $Gd(MAA)_3$ reveals the product is highly crystallized.

Fig. 3 shows the FT-IR spectra of MAA and $Gd(MAA)_3$. The characteristic bands of the nonionized carboxyl groups ν(C=O) that lies in the interval 1690–1710 cm^{-1} in Fig. 3(1) disappear and new bands appear in the regions 1520–1580 cm^{-1} and 1395–1430 cm^{-1} respectively which belong to the stretching vibrations, ν_{as}(COO−) and ν_s(COO−) of carboxylate ion in Fig. 3(2). It means the gadolinium ion and carboxyl groups have coordination reaction with each other. Frequencies of stretching vibrations ν(C=C) do not change significantly between MAA and $Gd(MAA)_3$, that signify $Gd(MAA)_3$ has the ability of polymerization.

In order to confirm the polymerization ability of $Gd(MAA)_3$, the thermal analysis is shown in Fig. 4. Two sharp endothermic peaks at 141 and 192 °C in Fig. 4 can be related to the melting of $Gd(MAA)_3$ crystals. Generally rare earth ion has a large coordination number, so that there may be two different kinds of crystalline structure in the $Gd(MAA)_3$ powders.[16] There is a significant exothermic peak at

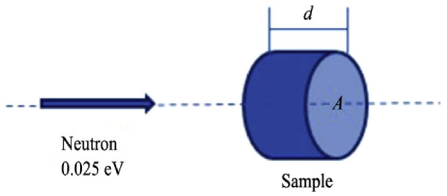

Fig. 1. The schematic of thermal neutron shielding calculation model.