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Effects of electric fields in polymerization on enthalpy of PMAA anhydridization

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Abstract

PMAA (polymethacrylic acid) polymerized by γ-irradiation in electric field forms six-membered cyclic anhydride during heating process and the enthalpy of PMAA anhydridization was determined by DSC. Why the endothermic peak of PMAA anhydridization in DSC curve between 200 and 300 °C appears is particularly explained by calculation. The relations between applied electric field and the enthalpy of PMAA anhydridization are studied. The results show that, with the increases of the intensity of electric field in polymerization, the enthalpy of PMAA forming anhydrides nonlinearly increase, which might be related to orientation of carboxylic acid groups of the PMAA in an electric field.

Keywords: Electric field; PMMA; Enthalpy; DSC; Irradiation polymerization

1. Introduction

MAA is a kind of important monomer used for synthesizing functional polymer. PMAA and its copolymers were widely used as paint, adhesive and thickener. It is also used as an enteric-coating polymer in the pharmaceutical industry because of its carboxylic groups that can transform to carboxylate groups in the pH range 5–7 by salt formation with alkali or amines [1,2].

As now well known, the cyclic anhydrides within and/or between PMAA chains might be formed by heating PMAA [3,4]. Lin et al. [5] reported temperature-dependent anhydride formation of a copolymer of MAA and MMA (methyl methacrylate) determined by reflectance FTIR/DSC microspectroscopy. In their paper, a rough explanation on the DSC curve of PMAA forming anhydride with an endothermic peak appearing above 200 °C was given. But the further studies were not reported. The enthalpy of PMAA anhydridization is influenced not only by reaction heating of carboxyl acid forming anhydride but also by chain structure changes. Especially, PMAA contains carboxyl group is of strongly hydrogen bonded, which affects the enthalpy of PMAA anhydridization. So it is very helpful to study the enthalpy of PMAA anhydridization finely.

A lot of papers reported the electric field-induced orientation of polymers and LC materials [6–10]. It is sure that an extra electric field will influence the chain structure of PMAA during polymerization. In this paper, the enthalpy of PMAA forming anhydride determined by DSC was studied in detail. The electric field-induced enthalpy changes of PMAA anhydridization were also studied, which were favorable to realizing the effects of the electric field on the orientation of molecules containing carboxylic groups in the polymerization.

2. Experiment

2.1. Materials

MAA (ShangHai Chemical Reagent Factory of China) was purified by distillation under reduced pressure and stored under N_2 at $-5\,^{\circ}C$ prior to use. Aether and acetone were purified by general purification. The mixed solvent is $47.5\,wt.\%$ aether $+ 47.5\,wt.\%$ acetone $+ 5\,wt.\%$ water.

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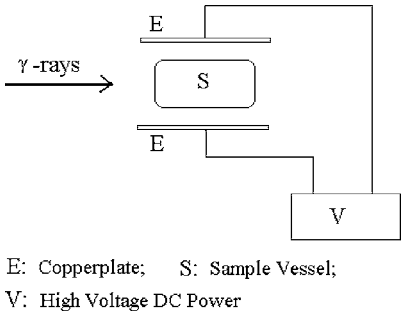


Fig. 1. Experimental scheme.

2.2. Polymerization

The experimental scheme is shown in Fig. 1. The polymerization was carried out in a sealed vessel that is laid between two copperplates linked up with high voltage DC power. The distance between two copperplates is 45 mm. The area of a copperplate is 50 mm × 30 mm. Adjusting the output voltage in high voltage DC power can get the expected electric field intensity. The procedure is as follows: MAA and the mixed solvent were added into a vessel. Then the mixture were degassed by three freeze–thaw cycles and the vessel was sealed under vacuum, and then subjected to ^{60}Co γ-ray irradiation with 70 Gy/min doserate for the prescribed time. The vessel was immediately cooled by liquid nitrogen after irradiation.

To characterize the polymers, there were two ways of purifying the polymer: (1) Vacuum the polymers under 667 Pa at 40 °C for 24 h. The purified polymers were used for investigating polymer's structure. (2) The polymers were diluted with ethanol, and then the solution was poured into a 10-fold excess of acetic ether, after that the precipitation occurs. The deposits were separated by filtration and dried in a vacuum oven at 40 °C for 24 h, such purified polymers were used for investigating molecular weight.

2.3. Characterization of the polymers

Molecular weight was determined by gel permeation chromatograph (GPC) with Waters Styragel HR 5E columns. Tetrahydrofuran (1.0 ml/min) was used as eluent and the calibration was carried out based on polystyrene standard. Shimadzu DSC-50 was used for differential scanning calorimetry curve under N_2 with the temperature range from 30 to 300 °C and heating rate of 10 K/min. TGA (thermogravimetric analysis) curves were obtained at WRT-3 thermogravimetric analyzer (ShangHai Balance Instrument Factory of China) with heating rate of 10 K/min and a closed pan system in steam of N_2 gas. Infrared spectra were recorded on Magana-IR 750 spectrometer (USA).

3. Results and discussion

The properties of PMAA polymerized by γ-ray initiated polymerization in various electric field intensities were shown in Table 1. To explore the relations between the enthalpy of PMAA during heating processes and applied electric field, one should know what reaction will be taken place in PMAA heating processes. IR spectra of PMAA after heating at 300 °C were shown in Fig. 2. The peaks near in 1800 and 1760 $\mathrm{cm^{-1}}$ were ascribed to CO stretching vibration of acid anhydrides and near in 1020 $\mathrm{cm^{-1}}$ was COC antisymmetric stretching [11]. In fact, the carbonyl stretching vibration of six-membered ring cyclic anhydride is near 1800 $\mathrm{cm^{-1}}$ (weak) and 1760 $\mathrm{cm^{-1}}$ (strong), rather than near 1850 $\mathrm{cm^{-1}}$ (weak) and 1775 $\mathrm{cm^{-1}}$ (strong) for five-membered ring cyclic anhydride [12] and 1803 $\mathrm{cm^{-1}}$ (strong) and 1743 $\mathrm{cm^{-1}}$(weak) for isobutyric acid anhydride [13]. So it can be seen that the prepared PMAA is head–tail chain structure and six-membered ring cyclic anhydrides is formed during the heating process. This process is shown in Scheme 1. As shown in Fig. 3, there is an endothermic peak for DSC curve between 200 and 300 °C at which the anhydridization reaction takes place in the PMAA system. Why did it appear an endothermic peak for PMAA anhydridization between 200 and 300 °C? The reasons can be explained by rough calculation. The enthalpy of PMAA during heating process between 200 and 300 °C mainly consists of chemical reaction heat produced by forming anhydrides and water and the enthalpy of breaking hydrogen bond of PMAA and

Table 1
Molecular weight, DSC and TGA data of PMAA polymerized by γ-irradiation initiated polymerization in various electric fields

	Sample[a]					
	A	B	C	D	E	F
Electric field (V/cm)	0	133	267	400	533	667
$M_{\mathrm{n,GPC}}$[b]	65462	44897	56323	55688	67216	49974
Temperature[c] (°C)	238	240	240	241	237	240
Enthalpy (DSC)[d] (J/g)	198.74	235.56	273.17	297.38	320.02	417.84
Weight loss[e] (%)	9.1	9.0	9.3	9.0	9.2	9.4

[a] The mixture consists of 1.5 g MAA, 1.5 g mixed solvent. Dose rate is 70 Gy/min and reaction time is 70 min.
[b] Molecular weight (M_n) are determined by GPC.
[c] It is the temperature of peak maximum in DSC curve between 200 and 300 °C.
[d] It is the endothermic value determined by DSC between 200 and 300 °C.
[e] Weight loss is determined by TGA.

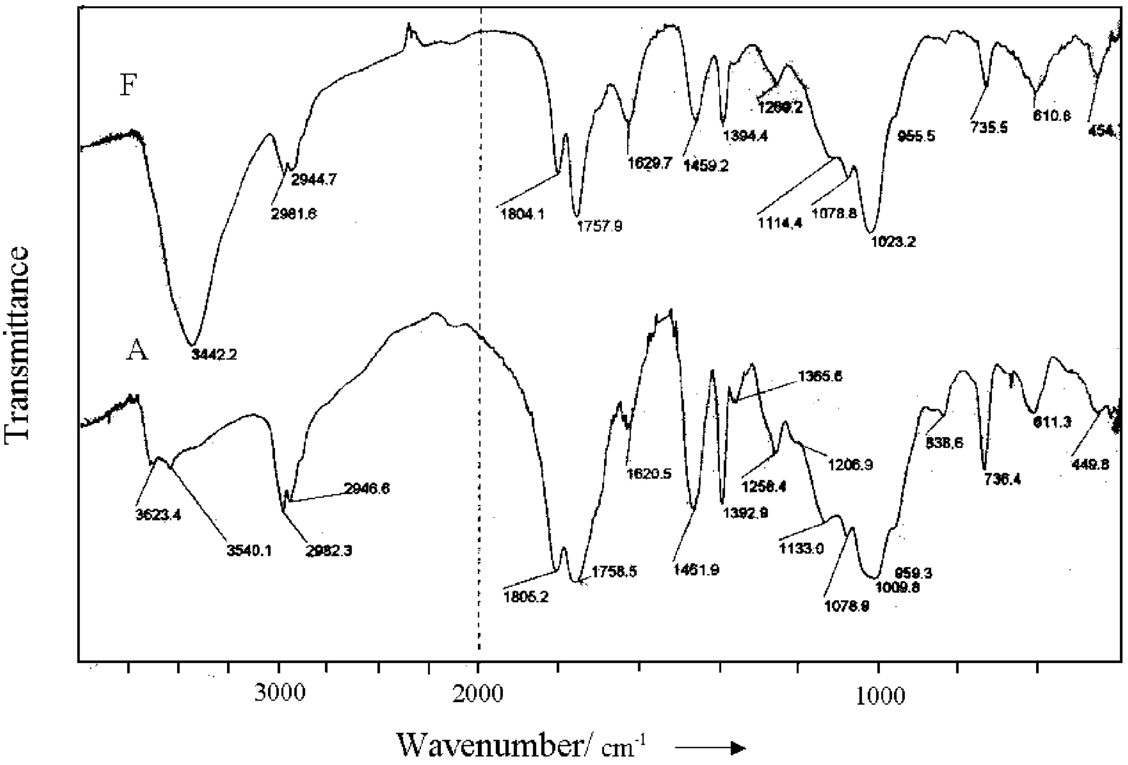
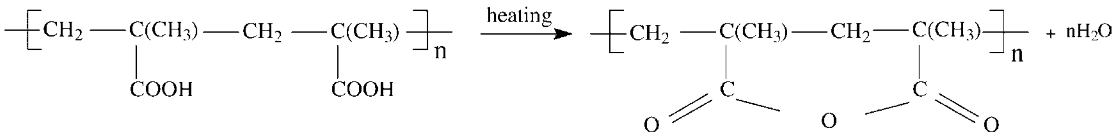


Fig. 2. IR spectra of sample A polymerized without electric field and sample F polymerized in electric field after heating at 300 °C.



Scheme 1.

vaporizing water. If the effects of hydrogen bond were not considered, the reaction heat of PMAA anhydridization can be roughly calculated as follows. The standard formation heat of the PMAA and the poly(methacrylic acid anhydride) ($\Delta H_{\mathrm{f(g)},\,298\,\mathrm{K}}$) were calculated by Allen's calculation ($\Delta H_{\mathrm{f(g)},298\,\mathrm{K}} = \sum \nu_i B_i + \sum \Gamma_{XYZ} + \sum \Delta_{XYZ} + [s] + [\mathrm{CRSE}]$) [14], and the results are $-364.26\,\mathrm{kJ\,mol^{-1}}$ (carboxylic acid) and $-506.81\,\mathrm{kJ\,mol^{-1}}$ (acid anhydride), respectively. The heat of vaporization of the PMAA and the poly(methacrylic acid anhydride) ($\Delta H_{\mathrm{v},\,298\,\mathrm{K}}$) was calculated by Fedors's calculation ($\Delta H_{\mathrm{v},298\,\mathrm{K}} = \sum n_i \varepsilon_i + 0.592$) [15], and the results are $28.85\,\mathrm{kJ\,mol^{-1}}$ (carboxylic acid) and $33.01\,\mathrm{kJ\,mol^{-1}}$ (acid anhydride), respectively. The heat capacity of the PMAA and the poly(methacrylic acid anhydride) ($C_{p\mathrm{(s)}}$) were calculated by Kopp rule ($C_{p,298\,\mathrm{K}} = \sum n_i c_i$) [16], and the results are $50.61\,\mathrm{J\,mol^{-1}\,K^{-1}}$ (carboxylic acid) and $65.25\,\mathrm{J\,mol^{-1}\,K^{-1}}$ (acid anhydride), respectively. The standard formation heat of water $\Delta H_{\mathrm{f(g)},\,298\,\mathrm{K}}$ is $241.82\,\mathrm{kJ\,mol^{-1}}$ [17] and the heat capacity of water $C_{p\mathrm{(g)}}$ is as follows: $C_{p\mathrm{(g)}}(\mathrm{H_2O}) = 30.36 + 9.61 \times 10^{-3} T + 11.8 \times 10^{-7} T^2$ [18]. The formation heat of carboxylic acid and acid anhydride in PMAA at 200 °C are calculated as follows:

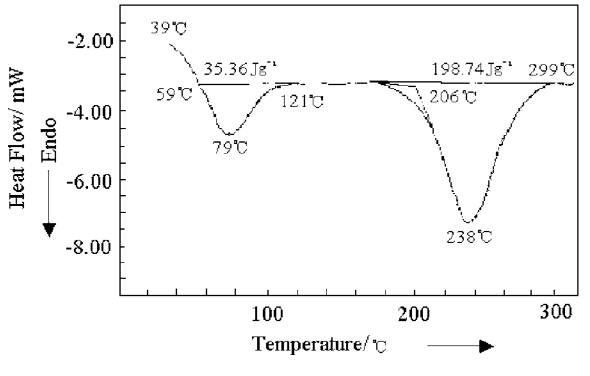


Fig. 3. DSC curve of sample A.

$$\Delta H_{\mathrm{f(s)},473\,\mathrm{K}} = \Delta H_{\mathrm{f(g)},298\,\mathrm{K}} - \Delta H_{\mathrm{v},298\,\mathrm{K}} + \int_{298}^{473} C_p\,\mathrm{d}T$$

So the reaction heat of Scheme 1 (not including the effects of hydrogen bond of PMAA) can be calculated as follows:

$$\Delta H_{\mathrm{r},473\,\mathrm{K}} = \Delta H_{\mathrm{f(s)},473\,\mathrm{K,acid\,anhydride}} + \Delta H_{\mathrm{f(g)},473\,\mathrm{K,water}} - \Delta H_{\mathrm{f(s)},473\,\mathrm{K,carboxylic\,acid}}$$

The result is about 26.01 kJ mol^{-1}. If the effects of hydrogen bond of PMAA were considered, the enthalpy of PMAA anhydridization during heating processes would be larger than that of not including hydrogen bond in PMAA (the experimental enthalpy determined by DSC in our experiment is about 38.88 kJ/mol). So an endothermic peak between 200 and 300 °C appeared on the DSC curve of PMAA.

As shown in Table 1, it can be seen that the enthalpy of PMAA anhydridization increased with the increase of the electric field intensity applied to polymerization. But the TGA data appeared that there were little changes in the weight loss of the PMAA polymerized in various electric field intensities between 200 and 300 °C, which suggests that the increased enthalpy with the increase of the electric field intensity were not caused by forming more anhydride, but by breaking stronger hydrogen bond in average energy. As shown in Fig. 4, it was confirmed by the peaks of C=O stretching vibration of carboxylic acid in PMAA shifting to low wave numbers with the increase of the electric field intensity, that means the hydrogen bonded carboxyl groups in PMAA become strong with the increase of the applied electric field intensity [19–21]. Keeping the same determination conditions, as shown in Fig. 5, the peak of DSC spectra becomes stronger with the increase of electric field intensity. The effect of electric field intensity on enthalpy of PMAA anhydridization determined by DSC instrument is shown in Fig. 6. From this figure, one can find that an electric field imposed on polymerization increased in the enthalpy of PMAA anhydridization as a whole, but the increased rates of the enthalpy are different in three ranges of the electric field

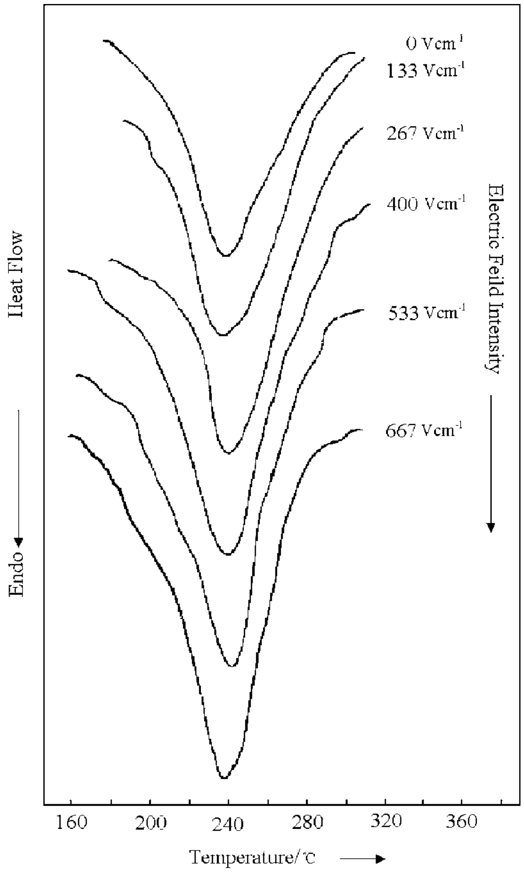


Fig. 5. DSC spectra of PMAA polymerized in various electric field.

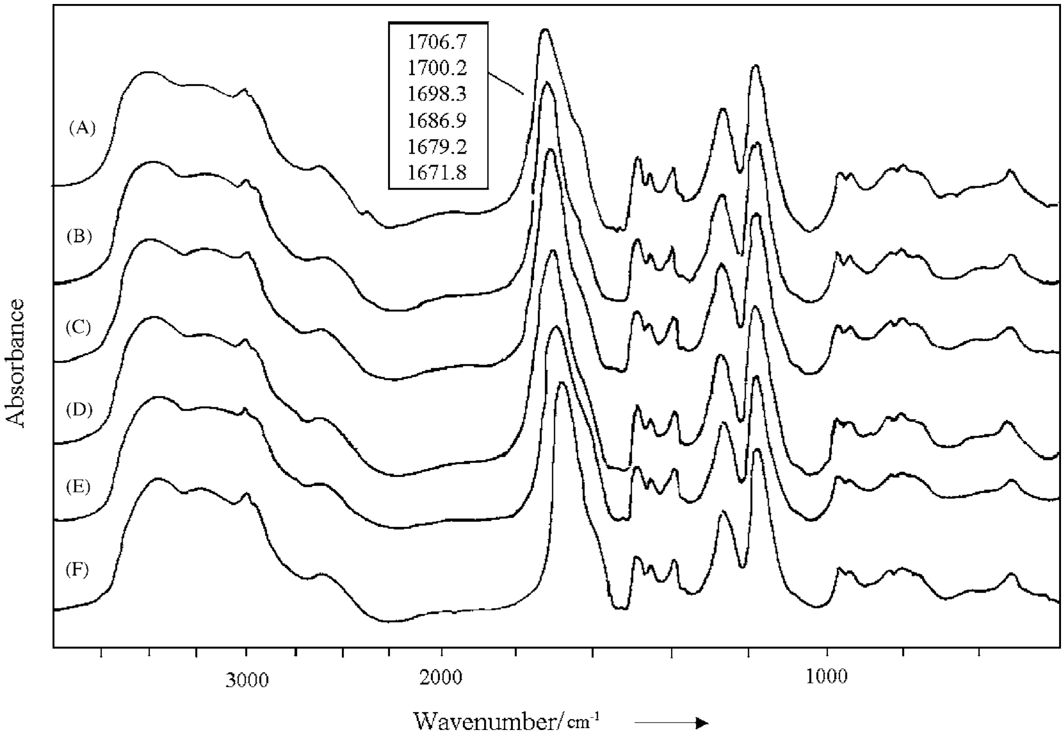


Fig. 4. The IR spectra of samples A–F.

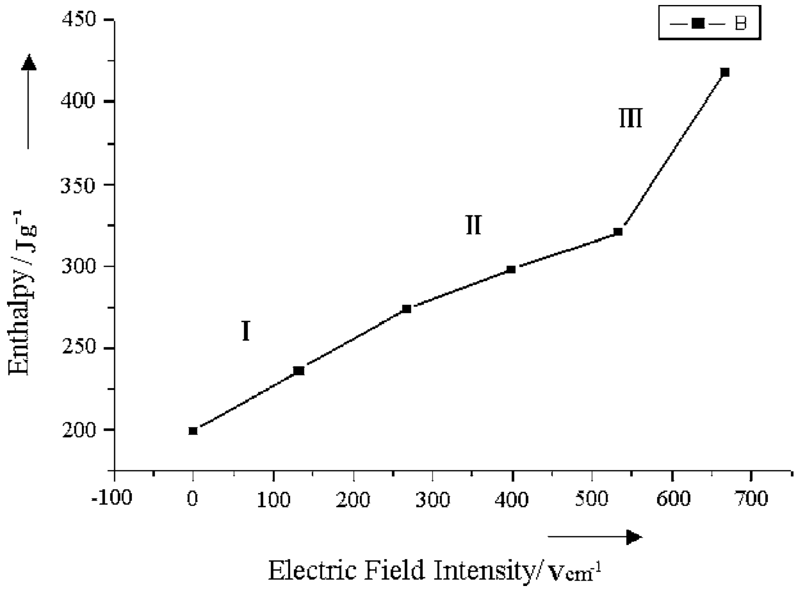


Fig. 6. The enthalpy of PMAA forming anhydrides versus the electric field intensity applied to polymerization.

intensity. The reasons might be that, MAA as a kind of polar monomer in the electric field tend to orient themselves in the direction of the externally applied field [6]. The oriented arrangement of MAA results in forming more hydrogen bonded carboxylic acid groups in PMAA after polymerization, which induces the increases of the enthalpy of PMAA anhydridization. In range I shown in Fig. 6, with the increases of the electric field intensity applied to polymerization, the distance between carboxylic acid groups of the PMAA easily becomes shorter and the hydrogen bond of the PMAA becomes stronger, which induced the faster the increase of the endothermic value produced by the PMAA forming anhydrides. As the electric field intensity further increase, in range II shown in Fig. 6, the distance between the carboxylic acid groups becomes shorter again and the repulsion between the carboxylic acid groups becomes quite large, as a result, the increase in rate of the endothermic values in range II is smaller than that in range I. In range III, the increase in rate of the endothermic values becomes larger again, which might be ascribed to enough electric field intensity to increase in ionization degree of the carboxylic acid of the MAA and the easy-oriented carboxylic acid ions apparently increase with the increase of the electric field intensity. As a result, the average hydrogen bond intensity goes up faster and the increase of the endothermic values of PMAA forming anhydrides becomes sharper in range III. Taken altogether, the more electric field intensity applied to polymerization, the more orientation of the carboxylic acid groups of the PMAA, the shorter the distance between carboxylic acid group, the stronger the hydrogen bond, the more the endothermic value of PMAA forming anhydrides during heating process.

4. Conclusion

The results reported here show that the reaction of PMAA forming six-membered ring cycle anhydrides during heating process is an endothermal reaction, in which breaking hydrogen bond of the PMAA to form anhydrides is a very important factor inducing the endotherm. The reasons why the enthalpy of PMAA forming anhydrides nonlinearly increased with the increases of the electric field intensity imposed on polymerization might be related to the increases of orientation degree of the carboxylic acid groups in PMAA. The measurement of DSC may be a way of studying the hydrogen bond of PMAA and the orientation of the carboxylic acid groups in PMAA.

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