

Notes

FT-RAMAN SPECTROSCOPY FOR MONITORING THE POLYMERIZATION OF ACRYLIC ACID IN AQUEOUS SOLUTION

Jiang Yu*, Hui-zhou Liu and Jia-yong Chen

*Young Scientist Laboratory of Separation Science & Engineering, Institute of Chemical Metallurgy,
Chinese Academy of Sciences, Beijing 100080, China*

Abstract FT-Raman spectroscopy was used to monitor the polymerization of acrylic acid in aqueous solution. A simple method to avoid the noise in the background during the signal processing via Fourier transformation was used in this work. The effects of the amount of initiator used on the polymerization are studied. When the amount of the initiator in the polymerization was increased, both the rate and extent of polymerization of acrylic acid will be increased.

Keywords Acrylic acid, FT-Raman spectroscopy, Polymerization

INTRODUCTION

Among other techniques, vibrational spectroscopy as a prime analytical tool in the study of polymer systems has been widely applied in the study of polymer structure and polymerization reaction^[1-4]. For vinyl monomers the C=C group exhibits the behavior of changes in intensity during the progress of polymerization that can be used for monitoring the polymerization reaction by Raman technique^[5]. The advantages of monitoring polymerization by FT-Raman spectroscopy are well known. It is a nondestructive method and does not require any pretreatment. In addition, it can avoid the strong fluorescence background with NIR laser source exciting samples^[6], and there is also no interference from water molecules in aqueous solution as FT-IR spectroscopy shows. Recently, some studies on the specifications of a measuring cell capable of operating inside the sample compartment of standard FT-Raman spectrometer and of holding large volumes of reactants were carried out^[5, 7]. In those cell designs, the circulation mechanism provided by a magnetic stirrer for stirring and pumping results in low quality FT-Raman spectra. In the meantime, the very fine bubbles created by the stirrer will generate noise in the background during the signal processing through Fourier transformation^[6]. In our work, the monomer acrylic acid (AC) was selected as a model compound. An aliquot portion of reactants was drawn at a definite time interval, and cooled in an ice-water bath to stop the polymerization. Therefore, problems encountered in cell design as mentioned above are prevented. The effects of the amount of initiator added on the process of polymerization were studied in this work.

EXPERIMENTAL

Materials and Polymerization

Acrylic acid (AC, A.R.), employed in the experiments was obtained from Beijing Industrial Works.

* Corresponding author: Jiang Yu (余江), E-mail: yj0017@home.icm.ac.cn

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A 250 mL reaction vessel equipped with a reflux condenser, a thermometer, a stirrer and nitrogen-feeding system was used to study the polymerization reaction. AC monomers were polymerized in the aqueous solution. The free radical polymerization initiated by $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_3$ ($W/W = 1/1$) was carried out at 70°C . All the chemicals in the solution were bubbled continuously for 30 min before starting the reaction in order to remove all the oxygen inside the reactor. The amounts of chemicals used in the reaction are typically: 20 mL AC, 100 mL deionized water and 10 mg $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_3$. Nitrogen gas was bubbled continuously through the solution to prevent the inhibiting action of oxygen during reaction. For example, an aqueous solution of 10 mL initiator was mixed with an aqueous solution of 100 mL AC. At a specified time interval, 1 mL sample was taken out and put it into a tube that was placed in an ice-water bath in order to stop the reaction rapidly.

FT-Raman Spectroscopic Measurement

FT-Raman spectra were recorded with a FTS100 FT-Raman Spectrometer (Brucker, Germany). An excited wavelength at 1064 nm was provided by a cw Nd:YAG laser with a power of 200 mW. All data were collected at a spectral resolution of 4 cm^{-1} from 3500 to 50 cm^{-1} . 400 scans were accumulated to ensure acceptable signal-to-noise ratio and took about 10 min. It is noted that it generally takes about 5–8 min to record the FT-Raman spectra.

RESULTS AND DISCUSSION

FT-Raman spectra of the monomer AC and polyacrylic acid (PAC) were shown in Fig. 1. It shows that monitoring by FT-Raman spectroscopy is a practical method that gives qualified measurements undisturbed by fluorescence and water molecular vibration. The Raman method is informative and also precise. Figure 2 shows the FT-Raman spectra of acrylic acid between $3600\text{--}2600\text{ cm}^{-1}$ at different reaction time. It is readily observable that the monomer AC has a strong Raman vibration band at 3044 cm^{-1} , which can be assigned to the $\nu_{=\text{CH}_2}$ (Fig. 2a and 2b) [8, 9]. Once the polymerization started, a new vibration band appeared at 2923 cm^{-1} (the $\nu_{=\text{CH}_2}$ of AC monomer disappeared completely (see Fig. 2e)). This phenomenological change is consistent with the well-known polymerization mechanism of AC.

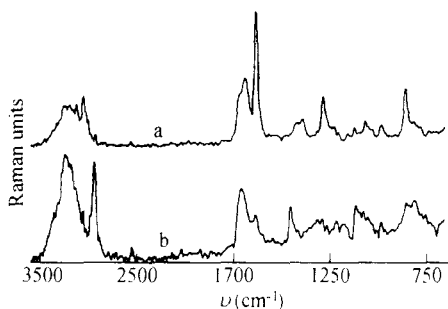


Fig. 1 FT-Raman spectra of AC polymerization in aqueous solution (125 mg initiator)
Recording conditions: resolution = 4 cm^{-1} , power = 200 mW, scans = 400;
a) No Initiator, b) initiator added for 60 min

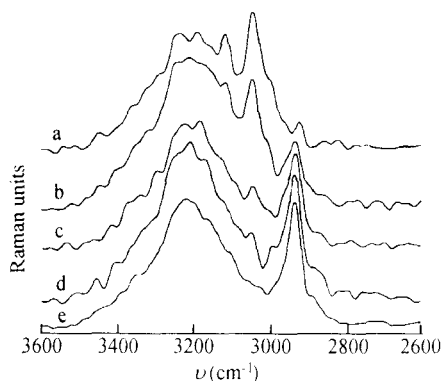


Fig. 2 FT-Raman spectra of acrylic acid in aqueous solution at different polymerization time
Induced by 125 mg initiator, $3600\text{--}2600\text{ cm}^{-1}$:
a) 0 min, b) 4 min, c) 8 min; d) 12 min; e) 60 min

In order to determine the amount of the monomer AC left in the reaction solution, the relationship between the concentration of AC left in aqueous solution and the intensities of $\nu_{\text{C}=\text{C}}$ of

AC was established by FT-Raman spectroscopy. Figure 3 gives the plot of Raman intensities as a function of the content of AC monomer in aqueous solution. The changes in Raman intensities of $\nu_{C=O}$ (1693 cm^{-1}) and ν_{C-O} (1288 cm^{-1}) are not linear with AC concentration, while the changes in the relative intensity of $\nu_{C=C}$ at 1637 cm^{-1} is linear. So the Raman intensity of $\nu_{C=C}$ can be used as a reference band for the calculation of kinetic data.

As $\nu_{C=C}$ (1637 cm^{-1}) can be clearly identified and falls in intensity as the reaction proceeds, the height of $\nu_{C=C}$ which corresponds to the concentration of AC is used to monitor the reaction (as shown in Fig. 3). In this work, we note that the ν_{C-O} appears as a strong overlapped broad band at 1722 and 1694 cm^{-1} , which probably is due to the coupling of $\nu_{C=O}$ and $\nu_{C=C}$ stretching vibration^[3, 10] (as shown in Fig. 4). After the AC monomer was transformed into radicals, the amount of $\nu_{C=C}$ decreased in the system. Finally, the coupling of $\nu_{C=C}$ and $\nu_{C=O}$ no longer exists (Fig. 4e) and they merge into a single band at 1709 cm^{-1} .

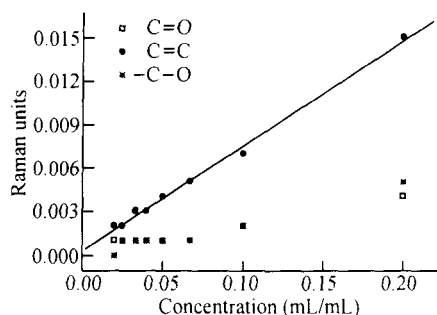


Fig. 3 Raman intensities versus concentration of AC monomer in some bands frequencies

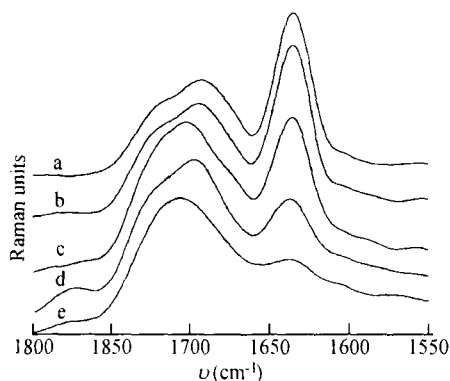


Fig. 4 FT-Raman spectra of $\nu_{C=O}$ and $\nu_{C=C}$ at different time of polymerization Induced by 125 mg initiator; a) 0 min; b) 4 min; c) 8 min; d) 12 min; e) 60 min

Percentage conversions could be calculated in terms of $\nu_{C=C}$ (1637 cm^{-1}) by the following equation:

$$\text{Conversion\%} = \frac{M_0 - M_t}{M_0} \times 100$$

where M_0 is the initial concentration of the monomer and M_t is the concentration of the monomer at time t .

The plot of the conversion percentage of the monomer AC versus polymerization time can be seen in Fig. 5, where the Raman intensities of $\nu_{C=C}$ at 1637 cm^{-1} were employed. The differences in conversion among the polymerizations with 10, 50 and 125 mg of initiator are listed in Table 1. The dependence of the rate of the polymerization is found to be inversely proportional to the amount of initiator, especially, at the initial stage of the polymerization. The plot of the conversion percentage of the monomer AC with respect to time was shown to be linear between 0%~55% conversion in the Raman measurements when 10 mg initiator was added. Also, the polymerization reaction takes place in three successive phases as described by Ozpozan^[5]. The initial phase is known to occur due to the formation of radical species that propagate the reaction. In the present work, different amounts of initiator were used, the polymerization requires less time at the initial phase, namely, the rate of radical species depends on the amount of initiator added at the beginning of polymerization. The second phase can be distinguished from the percentage conversion curve by

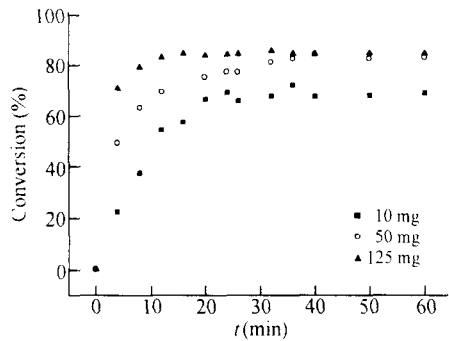


Fig. 5 Percent conversion of AC by using the Raman peak intensities of ν_{C-C} at 1637 cm^{-1} (by 10, 50 or 125 mg initiator) versus time

Table 1. Three successive phases in polymerization with different amounts of initiator added

Amount of initiator	Initial phase (Conversion %)	Second phase (Conversion %)	Third phase (Conversion %)
10 mg	0~12 min (0%~55%)	12~40 min (54%~71.76%)	40~60 min (71.76%)
25 mg	8 min (0%~63.04%)	8~32 min (63.04%~80.98%)	32~60 min (80.98%~84.13%)
125 mg	0~4 min (0%~70.52%)	4~12 min (70.52%~82.89%)	12~60 min (82.89%~86.70%)

abnormal acceleration where the polymer formation increases with retain time. Only 8 min is needed at the second phase for the polymerization with 125 mg initiator, 24 min and 28 min for 25 mg and 10 mg initiator, respectively. The final phase occurs slowly with little changes in the conversion of the monomer AC. Additionally, the results show that the percentage conversion of AC monomer at the end of reaction is increased with the amount of initiator used in polymerization.

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