

# Polymerization of Maleic Acid and Itaconic Acid Studied by FT-Raman Spectroscopy

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**ABSTRACT:** In this research, we used a new redox free radical initiation system consisting of potassium persulfate ( $K_2S_2O_8$ ) and sodium hypophosphite ( $NaH_2PO_2$ ). In the presence of  $NaH_2PO_2$ , the thermal decomposition of  $K_2S_2O_8$  is accelerated, and the temperature required for the formation of free radical is reduced. We polymerized maleic acid (MA) using the  $K_2S_2O_8/NaH_2PO_2$  initiation system in an aqueous solution, and monitored the polymerization process with FT-Raman spectroscopy. The Raman spectroscopy data indicate the formation of a saturated carboxylic acid with the disappearance of the characteristic bands of MA as the thermal decomposition of  $K_2S_2O_8$  progresses, thus indicating the formation of poly(maleic acid) (PMA). We also found that itaconic acid (IA) polymerizes in the presence of the new initiation system. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 223–228, 2001

**Key words:** free radical polymerization; FT-Raman spectroscopy; itaconic acid; maleic acid; poly(maleic acid); poly(itaconic acid); reactive polymers; redox initiation

## INTRODUCTION

Historically, MA and IA were extremely difficult to homopolymerize in comparison to other monosubstituted ethylenical acid monomers such as acrylic acid. In the past, PMA was synthesized by free radical polymerization of maleic anhydride in organic solvents, such as toluene, to form poly(maleic anhydride) (PMAN) followed by hydrolysis of PMAN to form PMA.<sup>1–3</sup> MA was polymerized in the presence of polyvinylpyrrolidone in water at 50–80°C with potassium persulfate ( $K_2S_2O_8$ ) as an initiator to form a polymer complex with polyvinylpyrrolidone, in which the MA-to-vinylpyrrolidone ratio was 1 : 1.<sup>4</sup> Low molecular weight PMA was also produced by polymerizing alkali or ammonium salts of MA in aqueous solutions in the presence of peroxide initiators,<sup>5,6</sup>

hydrogen peroxide and a polyvalent metal ion,<sup>7</sup> or water-soluble transition metal salts (such as iron sulfate heptahydrate) as “promoters” in combination with a water soluble initiator.<sup>8</sup>

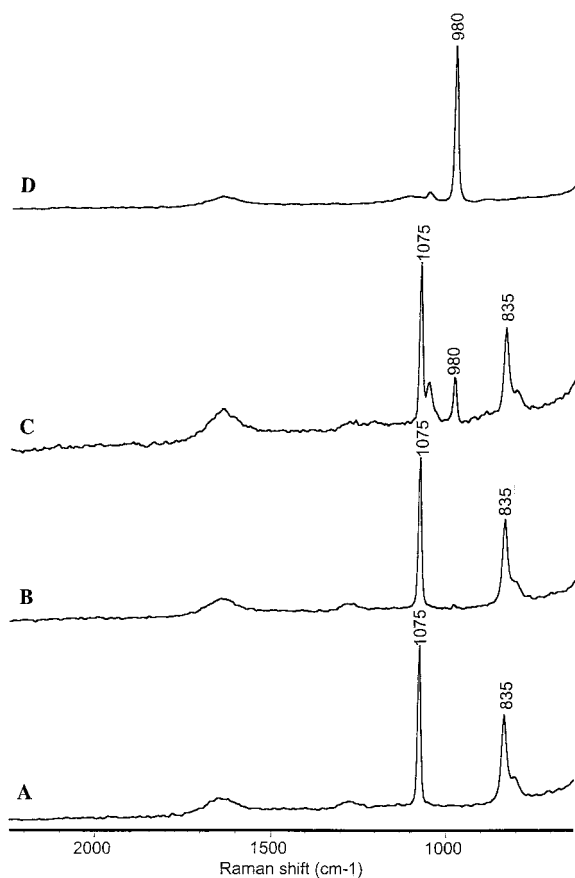
IA is easier to polymerize than MA because of its 1,1-disubstitution structure rather than the 1,2-disubstitution structure of MA. The first homopolymerization of IA was reported in 1959, which was carried in a 0.5M hydrochloric acid solution with  $K_2S_2O_8$  as an initiator, and it took several days to achieve 35% yield.<sup>9</sup> IA was polymerized in methanol at room temperature with AIBN as a free-radical initiator, but it took 30 days for the polymerization process to reach 70% yield.<sup>10</sup> The derivatives of IA can be easily free-radical polymerized to give high molecular weight polymers.<sup>11</sup>

In the past, a mixture of IA, MA, sodium hypophosphite ( $NaH_2PO_2$ ) and  $K_2S_2O_8$  was applied to cotton fabric, and the treated cotton fabric exposed to elevated temperatures shows improved wrinkle resistance.<sup>12–14</sup> We identified a saturated

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**Figure 1** Raman spectra of 6%  $K_2S_2O_8$ : (A) before heating; (B) heated at 65°C for 60 min; (C) heated at 100°C for 10 min; and (D) Raman spectrum of 6%  $K_2SO_4$ .

multifunctional carboxylic acid and decreased alkene double bond concentration on the treated fabric after heat exposure.<sup>13,14</sup> The data indicated that IA and MA polymerized *in situ* on cotton under elevated temperatures.<sup>13,14</sup> In this research, we studied the  $K_2S_2O_8/NaH_2PO_2$  initiation system and the polymerization of MA and IA in aqueous solutions with FT-Raman spectroscopy.

## EXPERIMENTAL

### Materials

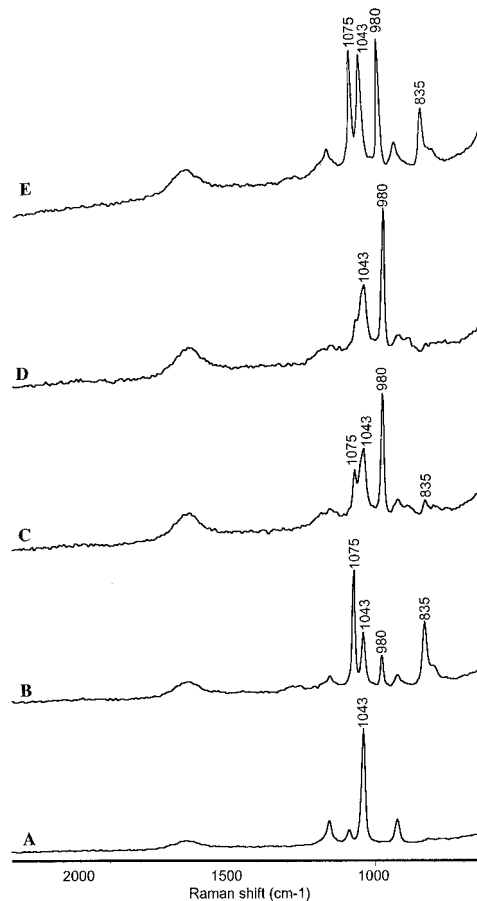
MA, IA,  $NaH_2PO_2$ , and  $K_2S_2O_8$  were reagent-grade chemicals supplied by Aldrich Chemical Company. All the percentage concentrations were based on weight (% w/w).  $N_2$  is used to purge the reaction system during polymerization.

### Polymerization

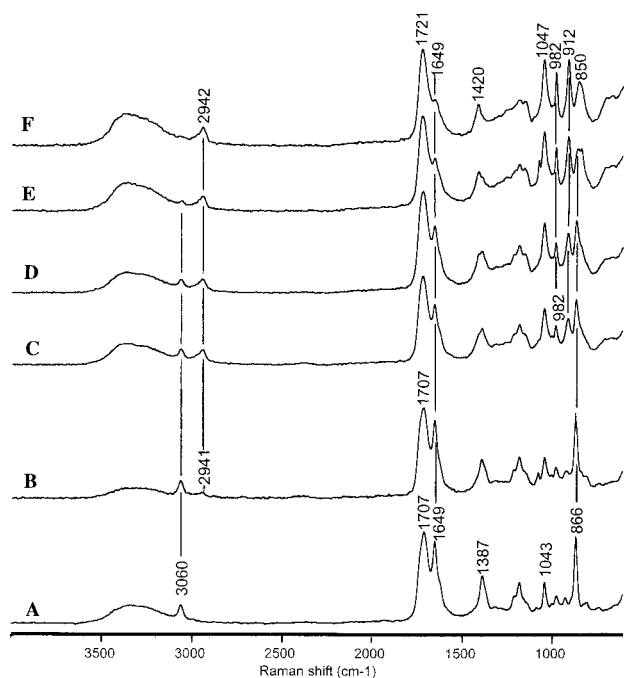
Into a 250-mL three-neck flask equipped with a thermometer, a condenser and a magnetic stirrer were added MA (or IA),  $NaH_2PO_2$  and water. Nitrogen was used to purge the system. The reaction mixture becomes clear upon heating.  $K_2S_2O_8$  (solid powder) was added batchwise when the polymerization temperature was reached. The reaction mixture was taken to put in liquid sample tubes at different times during a polymerization process, and was then analyzed by FT-Raman spectroscopy.

### FT-Raman Spectroscopic Measurements

A Nicolet 950 FT-Raman spectrometer with a liquid sample accessory and an InGaAs detector was



**Figure 2** Raman spectrum of (A) the aqueous solution of 10%  $NaH_2PO_2$ ; (B) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  at 65°C; (C) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  heated at 65°C for 10 min; (D) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  heated at 65°C for 20 min; and (E) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  heated at 50°C for 15 min.



**Figure 3** Raman spectra of the mixture of 25% MA and 10%  $\text{NaH}_2\text{PO}_2$ : (A) before heating; (B) after the first  $\frac{1}{4}$  of 3.1%  $\text{K}_2\text{S}_2\text{O}_8$  was added when the temperature reaches  $90^\circ\text{C}$ ; (C) after the second  $\frac{1}{4}$  of 3.1%  $\text{K}_2\text{S}_2\text{O}_8$  was added when the mixture was kept at  $90^\circ\text{C}$  for 10 min; (D) after the third  $\frac{1}{4}$  of 3.1%  $\text{K}_2\text{S}_2\text{O}_8$  was added when the mixture was kept at  $90^\circ\text{C}$  for 20 min; (E) after the fourth  $\frac{1}{4}$  of 3.1%  $\text{K}_2\text{S}_2\text{O}_8$  was added when the mixture was kept at  $90^\circ\text{C}$  for 30 min; and (F) when the mixture is kept at  $90^\circ\text{C}$  for total 75 min.

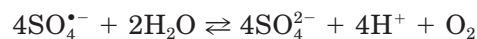
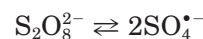
used to collect all the Raman spectra. The resolution was  $8\text{ cm}^{-1}$ , and there were 100 scans for each spectrum. No baseline correction or smooth function was used to process the data.

## RESULTS AND DISCUSSION

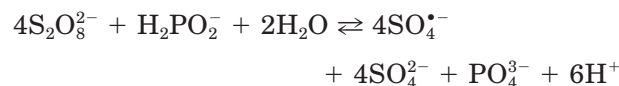
### Decomposition of $\text{K}_2\text{S}_2\text{O}_8$ in the Presence of $\text{NaH}_2\text{PO}_2$

The Raman spectrum of an aqueous solution of 6%  $\text{K}_2\text{S}_2\text{O}_8$  was presented in Figure 1(A), in which the bands at  $1075$  and  $835\text{ cm}^{-1}$  were the symmetric stretching mode of  $\text{S}=\text{O}$  and the stretching mode of  $\text{S}-\text{O}$ , respectively, of  $\text{S}_2\text{O}_8^{2-}$ .<sup>15</sup> These two bands remained unchanged when the  $\text{K}_2\text{S}_2\text{O}_8$  solution was heated at  $65^\circ\text{C}$  for 60 min [Fig. 1(B)]. When the  $\text{K}_2\text{S}_2\text{O}_8$  solution was heated at  $100^\circ\text{C}$  for 10 min, a new band at  $980\text{ cm}^{-1}$  appeared in the spectrum [Fig. 1(C)]. The band at

$980\text{ cm}^{-1}$  is due to the  $\text{S}=\text{O}$  stretching mode of  $\text{SO}_4^{2-}$ , as seen in the spectrum of 6%  $\text{K}_2\text{SO}_4$  [Fig. 1(D)]. Because  $\text{SO}_4^{2-}$  is the decomposition product of  $\text{S}_2\text{O}_8^{2-}$ , the intensity of the band at  $980\text{ cm}^{-1}$  relative to that at  $1075\text{ cm}^{-1}$  can be used to monitor the thermal decomposition of  $\text{S}_2\text{O}_8^{2-}$ . The data indicate that the thermal decomposition of  $\text{K}_2\text{S}_2\text{O}_8$  takes place when the temperature is increased to  $100^\circ\text{C}$ .



Shown in Figure 2(A) was the Raman spectrum of the aqueous solution of 10%  $\text{NaH}_2\text{PO}_2$ . The strong band at  $1043\text{ cm}^{-1}$  in Figure 2(A) was due to the  $\text{P}-\text{O}$  stretching mode of  $\text{H}_2\text{PO}_2^-$ .<sup>16</sup> An aqueous solution of 4.7%  $\text{NaH}_2\text{PO}_2$  and 6%  $\text{K}_2\text{S}_2\text{O}_8$  was prepared, and its temperature was increased to  $65^\circ\text{C}$  [Fig. 2(B)]. The two bands at  $1075$  and  $835\text{ cm}^{-1}$  were due to  $\text{S}_2\text{O}_8^{2-}$ , whereas the band at  $1043\text{ cm}^{-1}$  was due to  $\text{H}_2\text{PO}_2^-$  in Figure 2(B). A band at  $980\text{ cm}^{-1}$  due to  $\text{SO}_4^{2-}$  also appeared in the Raman spectrum, thus indicating the decomposition of  $\text{S}_2\text{O}_8^{2-}$  at  $65^\circ\text{C}$  [Fig. 2(B)]. The bands at  $980\text{ cm}^{-1}$  becomes much stronger, and the two bands at  $1075$  and  $835\text{ cm}^{-1}$  become much weaker when the solution was heated at  $65^\circ\text{C}$  for 10 min [Fig. 2(C)]. The data indicate that a reduction-oxidation reaction between  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{NaH}_2\text{PO}_2$  shown below took place, and the free radicals were formed as a result of the reduction-oxidation reaction.



The two bands at  $1075$  and at  $835\text{ cm}^{-1}$  disappeared completely when the solution of 6.0%  $\text{K}_2\text{S}_2\text{O}_8$  and 4.7%  $\text{NaH}_2\text{PO}_2$  was heated at  $65^\circ\text{C}$  for 20 min [Fig. 2(D)]. Comparison of the spectra of  $\text{K}_2\text{S}_2\text{O}_8$  (Fig. 1) and those of the mixture of  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{NaH}_2\text{PO}_2$  (Fig. 2) clearly demonstrates that the thermal decomposition of  $\text{S}_2\text{O}_8^{2-}$  and the formation of free radicals were accelerated in the presence of  $\text{NaH}_2\text{PO}_2$ . Presented in Figure 2(E) is the mixture of 6.0%  $\text{K}_2\text{S}_2\text{O}_8$  and 4.7%  $\text{NaH}_2\text{PO}_2$  heated at  $50^\circ\text{C}$  for 30 min. The intensities of the two bands at  $1075$  and  $835\text{ cm}^{-1}$  due to  $\text{S}_2\text{O}_8^{2-}$  was significantly reduced compared with those in Figure 2(B), and the intensity of the

**Table I** The Frequencies of the Characteristic Bands and Their Assignment in the FT-Raman Spectra

Compound	Band Frequency (cm <sup>-1</sup> )	Assignment
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1075	symmetric stretching mode of S=O
	835	stretching mode of S—O
K <sub>2</sub> SO <sub>4</sub>	980	stretching mode of S=O
NaH <sub>2</sub> PO <sub>2</sub>	1043	stretching mode of P—O
MA	3060	stretching mode of =C—H
	1707	stretching mode of C=O (unsaturated carboxylic acid)
	1649	stretching mode of C=C
	1387	combination of C—O stretching and —O—H deformation (dimmer, unsaturated carboxylic acid)
PMA	866	out-of-plane deformation of =C—H
	2942	stretching mode of saturated C—H
	1721	stretching mode of C=O (unsaturated carboxylic acid)
	1420	combination of C—O stretching and —O—H deformation (dimmer, saturated carboxylic acid)
IA	912	OH . . . O out of plane deformation
	3117	asymmetric stretching modes of =CH <sub>2</sub>
	3007	symmetric stretching modes of =CH <sub>2</sub>
	2936	asymmetric stretching mode of —CH <sub>2</sub> —
	1703	stretching mode of C=O (unsaturated carboxylic acid)
	1642	stretching mode of C=C
PIA	1400	combination of C—O stretching and —O—H deformation (dimmer, unsaturated carboxylic acid)
	819	out-of-plan deformation of =CH <sub>2</sub>
	2942	asymmetric stretching mode of saturated CH <sub>2</sub>
	1718	stretching mode of C=O (saturated carboxylic acid)
	1415	combination of C—O stretching and —O—H deformation (dimmer, saturated carboxylic acid)

band at 980 cm<sup>-1</sup> due to SO<sub>4</sub><sup>2-</sup> was strong in Figure 2(E). All the data indicate that the temperature required for the thermal decomposition of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was reduced in the presence of NaH<sub>2</sub>PO<sub>2</sub>.

### Polymerization of MA

An aqueous solution of 25% MA and 10% NaH<sub>2</sub>PO<sub>2</sub> was prepared. The stretching modes of the unsaturated =C—H and the alkene (C=C) of MA appear at 3060 and 1649 cm<sup>-1</sup>, respectively, in the Raman spectrum of the solution [Fig. 3(A)].<sup>16,17</sup> The strong band at 866 cm<sup>-1</sup> in Figure 3(A) is due to out-of-plane deformation of the unsaturated =C—H of MA.<sup>17</sup> In a MA molecule, the carboxylic acid carbonyl is conjugated with C=C, thus reducing the frequency of the carboxylic carbonyl stretching mode to 1707 cm<sup>-1</sup> [Fig. 3(A)].

The P—O stretching mode of H<sub>2</sub>PO<sub>2</sub><sup>-</sup> appeared at 1043 cm<sup>-1</sup> in Figure 3(A).

A total 3.1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, based on the weight of the reaction solution, was added to the MA/NaH<sub>2</sub>PO<sub>2</sub> mixture batchwise after the temperature was increased to 90°C. One-fourth of 3.1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added instantly when the temperature reached to 90°C [Fig. 3(B)], and one-fourth of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added after each additional 10 min. When the reaction mixture was kept at 90°C for 10 min and the second  $\frac{1}{4}$  of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added, one observes that the band at 2942 cm<sup>-1</sup> due to the stretching mode of saturated C—H as well as a band at 982 cm<sup>-1</sup> due to SO<sub>4</sub><sup>2-</sup> emerged, whereas the bands at 3060, 1649, and 866 cm<sup>-1</sup> due to MA reduced their intensity in the spectrum [Fig. 3(C)]. The data indicate that polymerization of MA took place under such a condition. The last  $\frac{1}{4}$  of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added when the reaction mixture was kept at

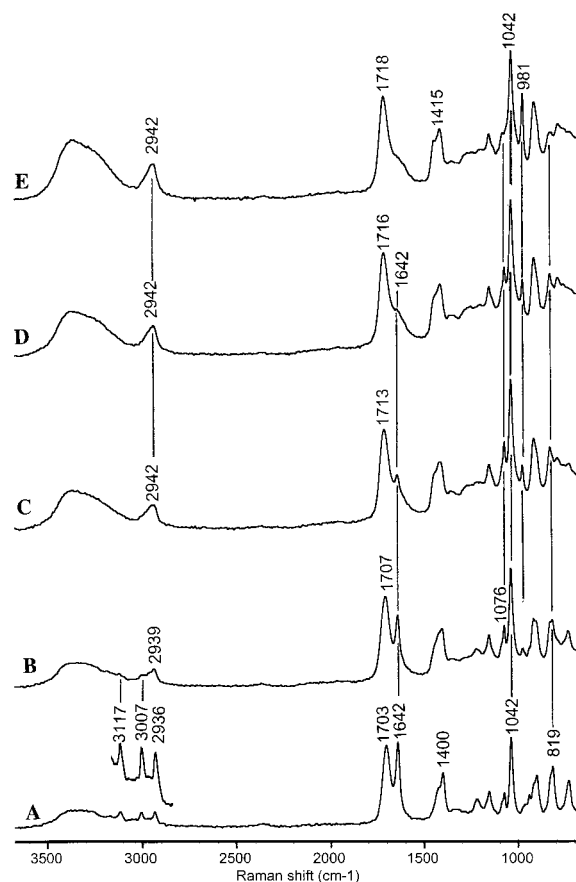
90°C for 30 min [Fig. 3(E)]. The band at 3060  $\text{cm}^{-1}$  due to unsaturated  $\text{=C—H}$  and the band at 1649  $\text{cm}^{-1}$  due to  $\text{C=C}$  appeared to be very weak and the band at 982  $\text{cm}^{-1}$  due to  $\text{SO}_4^{2-}$  further increased its intensity [Fig. 3(E)].

When the reaction mixture was kept at 90°C for a total time of 75 min, the characteristic bands of MA at 3060, 1649, and 866  $\text{cm}^{-1}$  almost disappeared [Fig. 3(F)]. The only  $\text{C—H}$  stretching band appearing in Figure 3(F) was the one due to the saturated  $\text{C—H}$  at 2942  $\text{cm}^{-1}$ . One also observes that the frequency of the carbonyl band shifted from 1707  $\text{cm}^{-1}$  in Figure 3(A) to 1721  $\text{cm}^{-1}$  in Figure 3(F). In an MA molecule, it is the conjugation between  $\text{C=C}$  and the carboxyl  $\text{C=O}$  shifts the carbonyl stretching mode to a lower frequency. As MA polymerized, the unsaturated  $\text{C=C}$  of MA was converted to saturated  $\text{C—C}$  of PMA, and the carboxylic carbonyl was no longer conjugated with  $\text{C=C}$ , thus shifting the carboxylic carbonyl band to a higher frequency at 1721  $\text{cm}^{-1}$  [Fig. 3(F)]. The band at 1387  $\text{cm}^{-1}$  in Figure 3(A) is due to the combination of  $\text{C—O}$  stretching and  $\text{—O—H}$  deformation of the dimer of MA.<sup>15,16</sup> As MA polymerized, this band shifted to a higher frequency at 1420  $\text{cm}^{-1}$ , which was at the same frequency of the same band of succinic acid. The band at 912  $\text{cm}^{-1}$  in Figure 3(F), which gradually increased its intensity as the polymerization progressed [Fig. 3(C)–(F)], was associated with  $\text{OH} \dots \text{O}$  out of plane deformation of PMA.<sup>15</sup> The assignment of the characteristic bands in the Raman spectra presented in this article are summarized in Table I. One also observes that the band at 982  $\text{cm}^{-1}$  due to  $\text{SO}_4^{2-}$  increased its intensity during the gradual decomposition of  $\text{K}_2\text{S}_2\text{O}_8$  [Fig. 3(C)–(F)]. The Raman spectroscopy data provide definitive evidence for polymerization of MA.

The PMA polymerized using this method was studied with matrix-assisted laser desorption and ionization (MALDI) time-of-flight (TOF) mass spectroscopy. The details of the mass spectroscopy study will be reported in a subsequent article.

### Polymerization of IA

A solution of 25% IA and 9%  $\text{NaH}_2\text{PO}_2$  were prepared, and the temperature of the reaction mixture was increased to 95°C. The Raman spectrum of the IA/ $\text{NaH}_2\text{PO}_2$  mixture was presented in Figure 4(A). The asymmetric and symmetric stretching modes of unsaturated  $\text{=CH}_2$  of IA were shown



**Figure 4** The Raman spectra of the mixture 25% IA and 9%  $\text{NaH}_2\text{PO}_2$ : (A) when the temperature is increased to 95°C; (B) when the first  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  is added, then the mixture is kept at 95°C for 10 min; (C) when the second  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  is added and the mixture is kept at 95°C for another 10 min; (D) when the third  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  is added and the mixture is kept at 95°C for another 10 min; and (E) when the mixture is kept at 95°C for total of 60 min.

at 3117 and 3007  $\text{cm}^{-1}$ , respectively, and the stretching mode of  $\text{C=C}$  is at 1642  $\text{cm}^{-1}$ , whereas the asymmetric stretching mode of the saturated  $\text{—CH}_2\text{—}$  appeared at 2936  $\text{cm}^{-1}$  in Figure 4(A). The band at 819  $\text{cm}^{-1}$  in Figure 4(A) was due to out-of-plan deformation of  $\text{=CH}_2$ .

One-third of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  was added to the IA/ $\text{NaH}_2\text{PO}_2$  mixture as soon as the temperature reached 95°C. The intensities of the bands at 3117, 3007, 1642, and 819  $\text{cm}^{-1}$  due to the unsaturated moiety of IA were significantly reduced, whereas the intensity of the band at 2939  $\text{cm}^{-1}$  due to saturated  $\text{CH}_2$  asymmetric stretching mode increased 10 min after the addition of  $\text{K}_2\text{S}_2\text{O}_8$  [Fig. 4(B)]. The second portion of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  was added and the mixture was kept at



95°C for another 10 min [Fig. 4(C)]. The last portion of  $K_2S_2O_8$  was added, and the polymerization continued at 95°C for another 10 min [Fig. 4(D)]. One observes that the band at  $1642\text{ cm}^{-1}$  due to  $C=C$  diminished, and the two bands at  $3117$  and  $3007\text{ cm}^{-1}$  due to stretching modes of unsaturated  $=CH_2$  were no longer visible in the spectrum [Fig. 4(D)]. The intensity of the band at  $819\text{ cm}^{-1}$  due to out-of-plane deformation of  $=CH_2$  decreased and the intensity of the band at  $981\text{ cm}^{-1}$  due to  $SO_4^{2-}$  increased as the polymerization took place [Fig. 4(B)–(D)]. The band at  $1642\text{ cm}^{-1}$  disappeared completely when the total reaction at 95°C reached 60 min, thus indicating that the conversion from IA to poly(itaconic acid) (PIA) was complete [Fig. 4(E)]. One also observes that the carboxyl carbonyl band shifted from  $1703\text{ cm}^{-1}$  in Figure 4(A) to  $1718\text{ cm}^{-1}$  in Figure 4(E). This was another indications of the disappearance of  $C=C$ , which is conjugated with  $C=O$  in a IA molecule and shifts the carboxylic carbonyl stretching mode to a lower frequency [Fig. 4(A)]. As the polymerization was complete, the band at  $1400\text{ cm}^{-1}$  in Figure 4(A) due to the combination of  $C-O$  stretching and  $-O-H$  deformation of the dimmer of MA shifted to a higher frequency at  $1415\text{ cm}^{-1}$  in Figure 4(E).

## CONCLUSIONS

The presence of  $NaH_2PO_2$  accelerates the thermal decomposition of  $K_2S_2O_8$  and formation of free radicals. Maleic acid and itaconic acid polymerize in aqueous solutions in the presence of the  $K_2S_2O_8/NaH_2PO_2$  initiation system. We also found that the required concentration of the initiation system is much higher than those commonly used in free radical polymerization. This

phenomenon needs to be further investigated and explained.

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