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Journal of Photochemistry and Photobiology A: Chemistry 195 (2008) 323–329

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

The observation of photo-Kolbe reaction as a novel pathway to initiate photocatalytic polymerization over oxide semiconductor nanoparticles

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Received 24 May 2007; received in revised form 22 September 2007; accepted 30 October 2007
Available online 4 November 2007

Abstract

Polymerization of vinyl acetate is achieved under the photocatalysis of TiO_2 nanoparticles in aqueous suspensions. It is clarified that the photocatalytic polymerization is due to the acetic acid generated from the hydrolysis of vinyl acetate. ^{13}C NMR analysis further demonstrates by using 2-^{13}C-acetic acid that vinyl acetate is initiated by methyl radical that results from the photo-Kolbe reaction. This result reveals a new function of the photo-Kolbe reaction as a pathway to realizing photocatalytic polymerization. A free radical chain mechanism is established for the polymerization. Kinetics studies show that the rates of initiation increase with the amounts of acetic acid added increasing. If the vinyl acetate aqueous solution is replaced by a vinyl acetate bulk, no polymerization is detected under the identical irradiation condition. This difference is correlated with the acid–base equilibria of the TiO_2 nanoparticles and the anionic CH_3COO^- from the ionization of acetic acid.

Keywords: Photopolymerization; Photo-Kolbe reaction; NMR; Methyl radical; Semiconductor nanoparticles; Vinyl acetate

1. Introduction

UV excitation of semiconductor nanoparticles (NPs) yields electron and hole in pairs that perform surface-mediated redox [1]. The photocatalysis has attracted much attention from a broad community motivated by ambitions of environmental purifications, bacterial disinfection, splitting water, and solar cells. Polymerization initiated by the photo-excited semiconductors NPs, which is called photocatalytic polymerization, extends potentials of the photocatalysis. Semiconductor nanoscale colloids and particles were applied to the polymerizations of several alkenes monomers in organic solvents or in bulk [2–7]. Recently we have reported the photocatalytic polymerization of methyl methacrylate by using TiO_2 NPs in aqueous suspensions [8–10]. Distinguished from usual photopolymerizations, in which the organic photo-sensitizers split after light absorption to the formation of initiating radicals, the semiconductor NPs are retained during photocatalytic polymerization. Hence, such polymerization provides a strategy to fabricate polymer/inorganic nanocomposite, while this method takes advantage of a simplified process since the polymer and the composite are simultaneously achieved. Owing to synergetic effects of polymers and semiconductors, the heterojunction composites generally perform special functions concerning photoelectrical properties [11]. Moreover, the photocatalysis at visible-light has been elucidated for lots of kinds of nanoscale semiconductors including TiO_2 [12], from which follows that the solar-utilizing synthesis of great significance is feasible by using the photocatalytic polymerization. This is valuable for developing solar cured films or coatings. Particularly, a low rate of solidification encountered for water-born coatings such as the building coatings can be improved. Therefore, the photocatalytic polymerization has a very promising future in the fields of functional materials and photo-related chemical technology.

Understanding of the photocatalytic polymerization is great significance not only for practical applications of the young technology but also for advancing scientific knowledge about surface chemistry of semiconductors. In the literature pertaining to photocatalytic polymerizations, these reactions have been correlated with nature of semiconductors, colloids sizes, and the irradiation applied, while several groups addressed on mechanisms in the aspects of charges transfer and thermodynamics

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doi:10.1016/j.jphotochem.2007.10.020

[2–7]. Our group manages to draw information about the mechanisms from the chemistry structures of the resulting polymers [8–10]. The initiation of double species and diffusion-controlled kinetics were obtained for methyl methacrylate initiated by TiO_2 NPs in aqueous suspensions. It should be mentioned that mechanisms about photocatalytic polymerizations have been not well understood so far.

Vinyl acetate is known as one of vinyl monomers, and is often employed for synthesizing various plastics and coatings. Hoffman and coworkers [3] have tried polymerization of vinyl acetate in isopropyl alcohol using quantum-sized CdS colloids, but acquired no polymer, although the polymerizations were achieved with other monomers. Implied by the knowledge that water plays an important role in the photocatalytic polymerization of methyl methacrylate, we explore polymerization of vinyl acetate in water and use TiO_2 NPs also. A fascinating phenomenon is observed in the polymerization tests. More importantly, to be reported in this paper, studies of the phenomenon reveal a new pathway to photocatalytic polymerization, in which the photo-Kolbe reaction is related.

2. Experimental

The TiO_2 semiconductors NPs used was Degussa P25 TiO_2 (80% anatase and 20% rutile) with an average diameter of 21 nm and a BET surface area of 50 m^2/g. It was supplied by Degussa Company. 2-^{13}C-acetic acid ($^{13}CH_3COOH$) was supplied by Aldrich Company. All the chemicals used were of analytical reagent grade. Vinyl acetate was distilled before use. Deionized water was employed in experiments.

Vinyl acetate was added into water to prepare aqueous solution with the vinyl acetate concentration at 15 g/l. Then, the TiO_2 NPs powders were dispersed into the vinyl acetate aqueous solution using the ultrasonic dispersion technique. The content of TiO_2 in the suspension was 1 g/l. The suspension of 120 ml was moved into a quartz reactor which was equipped with a magnetic stirrer and a water jacket connected to a circulator of $CuSO_4$ solution. UV irradiation towards the reactor was carried out using a mercury vapor lamp, characterized by two chief peaks at 254 and 365 nm in its emission spectrum. The mixture can avoid being irradiated by the rays exclusive of 365 nm, due to the cutting off of $CuSO_4$ solution. The light intensity was measured by radiometry (UV-A, BJNU photoelectrical Co.) to be 13 mW/cm^2 at 365 nm and only 0.085 mW/cm^2 at 254 nm. The irradiation lasted for 3 h. The precipitations were obtained by centrifugation of the reacted mixture, washed by water, and then dried under vacuum for 24 h at room temperature.

Fourier-transform infrared (FTIR) spectra were carried out on a Magna-IRTM550 spectrometer. Thermogravimetry analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 TGA instrument in air atmosphere. ^{13}C NMR spectra were recorded on a Bruke DMX500 spectrometer at 300 K using $CDCl_3$ as solvent. UV–vis absorptions were recorded using a Lambda 35 Perkin-Elmer UV–vis spectrophotometer in the spectral range of 190–1100 nm.

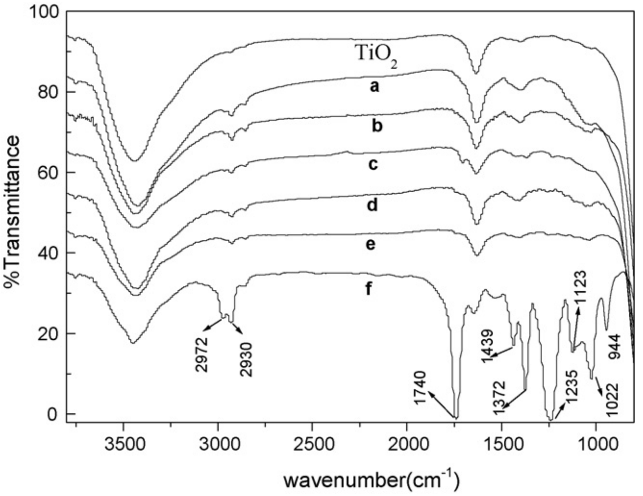


Fig. 1. FTIR spectra of the reacted mixture after irradiation obtained by using monomer aqueous solution conserved at 25 °C for (a) 0 h, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h and (f) 120 h in comparison with the spectrum of neat TiO_2. The concentration of vinyl acetate is 15 g/l.

3. Results and discussion

3.1. Photocatalytic polymerization of vinyl acetate

We observed by accident the phenomenon as follows during exploring photocatalytic polymerization with vinyl acetate and TiO_2 NPs semiconductor in aqueous suspensions. The irradiation did not yield any polymer if the vinyl acetate aqueous solutions were freshly prepared, but the polymerization come true when the pure solution of vinyl acetate was stored for some time before the polymerization test. Experiments were designed systematically to probe into the reasons accountable for the behavior of interest. Fig. 1 demonstrates that the photocatalytic polymerization takes place when the vinyl acetate aqueous solution was stored at 25 °C for 120 h. As seen in the FTIR spectrum obtained for the composite product, the absorption band at 1740 cm^{-1} is indicative of the C=O stretching of poly(vinyl acetate). The other new bands are also assigned to PVAc [13]: 2972 cm^{-1} (–CH_3 stretching); 2930 cm^{-1} (–CH_2 stretching); 1439 cm^{-1} (–CH_3 bending); 1372 cm^{-1} (CH_3C=O stretching); 1235 cm^{-1} (O=C–O vibration); 1123 cm^{-1} (OCH_3 or OCH_2 vibration); 1022 cm^{-1} (O–C vibration). The bands at 3470 cm^{-1} and 1640 cm^{-1} are indicative of stretching and bending vibrations of surface OH groups of anatase TiO_2 NPs, respectively [14]. Moreover, the thermal scission behaviors of the resulting polymer, characterized by the two degradation stages as shown in the DTG curve in Fig. 2, confirms the production of PVAc because the two peak temperatures are inhere to this polymer [15]. As indicated, the first stage with the peak at 340 °C is referred to the removal of side acetic acid group from PVAc, and the weight loss occurred after 400 °C is due to the cleavage of the backbone.

It is critical that what occurs during the storage of the vinyl acetate solution. Hydrolysis of vinyl acetate comes to our attention finally. The hydrolysis of vinyl acetate produces acetaldehyde and acetic acid [16].

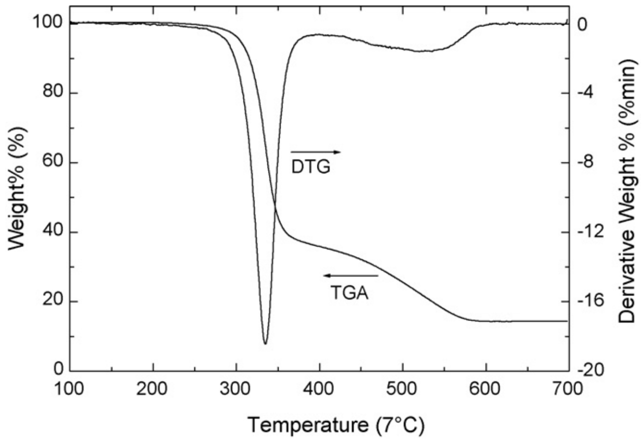
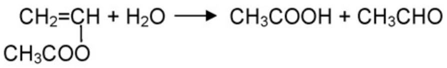


Fig. 2. The thermal properties of the product obtained using the vinyl acetate aqueous solution conserved at 25 °C for 120 h.



$$CH_2{=}\underset{\displaystyle CH_3COO}{CH} + H_2O \longrightarrow CH_3COOH + CH_3CHO$$

It is measured that acetaldehyde has the UV absorption at $\lambda_{max} = 275$ nm (Fig. 3A), while acetic acid shows the absorption at λ_{max} of ca. 200 nm (Fig. 3B). During the storage of the vinyl acetate solution, the newly appearing band at 275 nm is obviously assigned to the formation of acetaldehyde (Fig. 3C), indicating the occurrence of hydrolysis. Although the adsorption of acetic acid overlaps that of vinyl acetate, the observed increase in the intensity of acetaldehyde with time clearly indicates that acetic acid is also continuously produced. To check if the hydrolyzed products have the effect of determining the polymerization, experiments are carried out by adding acetaldehyde and acetic acid into the fresh vinyl acetate aqueous solution, respectively. It is seen that adding acetaldehyde does not lead to any polymerization, but the polymerization occurs once acetic acid is added, as evidenced by the FTIR spectra in Fig. 4. Hence, it is clarified that the acetic acid from the hydrolysis dominates the polymerization observed. Since acetic acid itself never initiates polymerization of vinyl acetate based on the principles of polymer chemistry, the mechanisms about the role of acetic acid arise. Note that in absence of TiO_2, the irradiation did not yield any polymer when acetic acid was added into the vinyl acetate aqueous solution. Therefore, the polymerization must be dominated by photocatalytic reaction of acetic acid over TiO_2 NPs.

3.2. The photo-Kolbe reaction pathway

Kraeutler and Bard [17] found the photocatalytic decarboxylation (or called β scission) of acetic acid on N-type TiO_2 and named the reaction the “photo-Kolbe reaction”:

$$CH_3COOH + h^+ \rightarrow CH_4 + CO_2 \qquad (2)$$

They suggested methyl radical ($^{\bullet}CH_3$) as an intermediate. This hints at the possibility of a correlation between the current polymerization and methyl radical. To study the mechanism in mind, ^{13}C NMR spectroscopy is used to analyze the polymer structures. In Fig. 5A showing the ^{13}C spectrum of the polymer obtained by adding acetic acid to the reactor, the chemical shifts detected are totally characterized by PVAc [18]: 20.9 ppm (acetate CH_3); 38.6–39.8 ppm (main-chain CH_2), 66.0–67.8 ppm (main-chain CH); 170.2 ppm (main-chain C=O). The weak peak at chemical shift of 29.6 ppm is assigned to the side-chain branch β CH_2 that was identified to generate from the chain transfer to polymer [18]. In order to make clear termi-

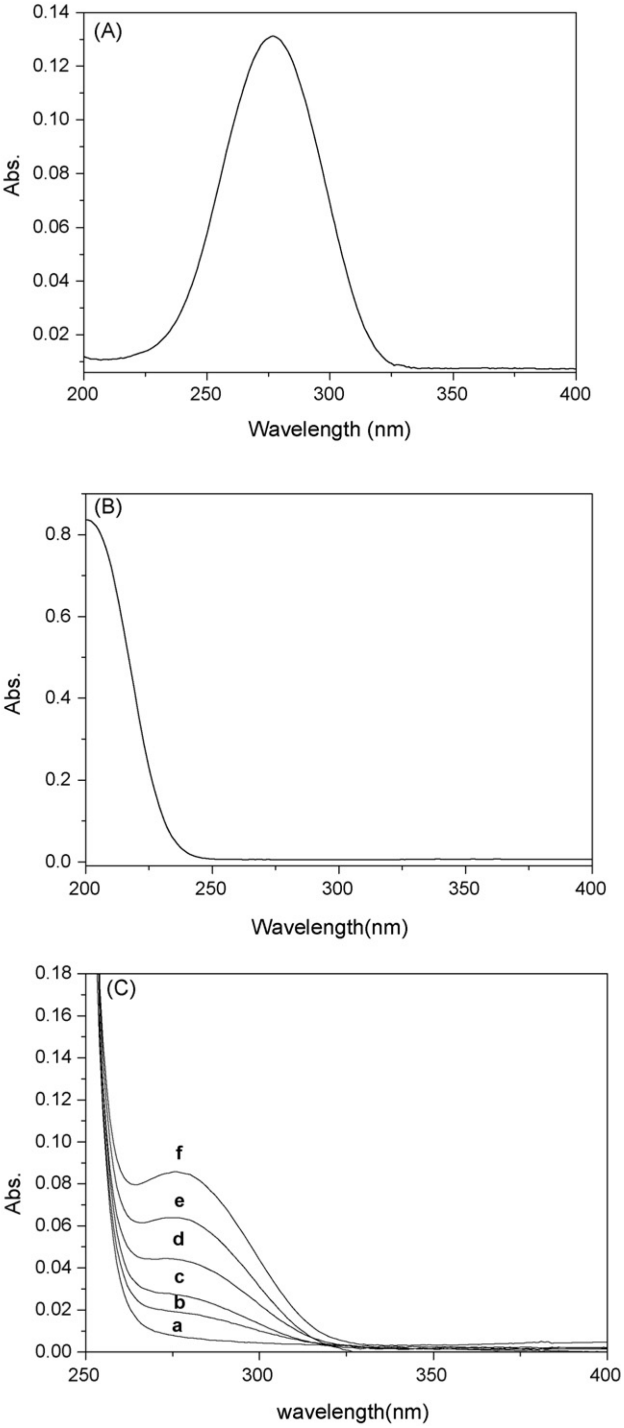


Fig. 3. UV–vis absorption spectra of acetaldehyde (A), acetic acid (B) and vinyl acetate aqueous solution (C) conserved under 25 °C for (a) 0 h, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h and (f) 120 h.

nal structures, which are directly related to initiation reactions of monomers, ^{13}C labeled acetic acids are employed to magnify the signal intensity of terminal groups. Fig. 5B shows the typical ^{13}C NMR spectrum of the polymer obtained by adding 2-^{13}C-acetic acid ($^{13}CH_3COOH$). A new peak is found to appear at the chemical shift of 9.3 ppm. With the exception of this difference, the spectra of the two polymers obtained by using regular acetic acid and $^{13}CH_3COOH$, respectively, well accord with each other in the respects of chemical shifts and relative intensities of peaks.

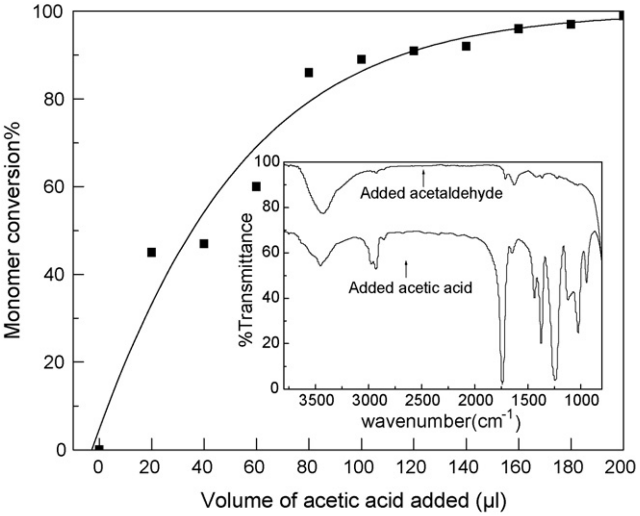


Fig. 4. Conversion of vinyl acetate vs. the volume of acetic acid added. The inserted FTIR spectra indicate that adding acetic acid does lead to polymerization but not as for acetaldehyde (the amount of acetic acid added is 100 μl in both cases).

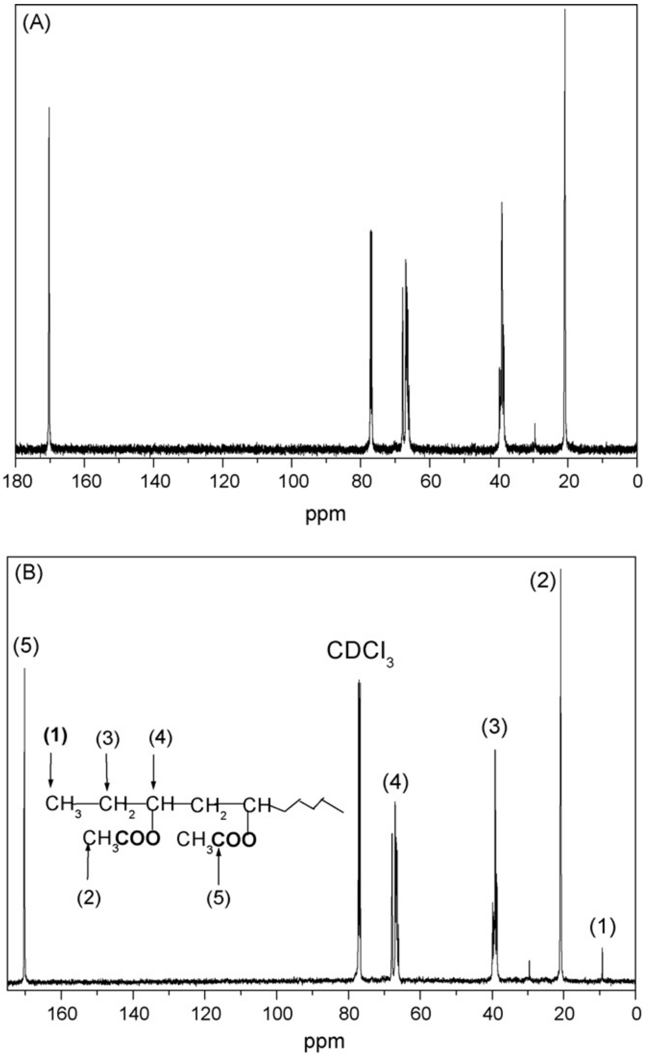


Fig. 5. ^{13}C NMR spectra of poly(vinyl acetate) obtained by adding (A) 100 μl regular acetic acid and (B) 100 μl $^{13}CH_3COOH$. The concentration of vinyl acetate is 15 g/l.

Since the two carbons at acetic acid have the chemical shifts at 22 ppm and 170 ppm [19], respectively, possible acetic acid trace that may remain after the purification is ruled out from the reasons for the new peak at 9.3 ppm. Calculations are carried out according to the increment rule of Lindeman and Adams [20], which is the traditional model for predictions of chemical shifts [21]. The results demonstrate that the peak of interest is referred to the terminal CH_3 group onto the saturated vinyl acetate. The sequences of chain are given in the inset of Fig. 5B. In details, according to this rule, the chemical shift of carbon k, $\delta_c(k)$ is expressed as

$$\delta_c(k) = \delta_c(k, \mathrm{RH}) + \sum_i Z_{ki}(R_i) \tag{3}$$

where $\delta_c(k, \mathrm{RH})$ is the increment for the unsubstituted carbon atom at k position ($k = \alpha, \beta, \gamma, \delta$). $Z_{ki}(R_i)$ is the increment due to the substitution of R_i. $\delta_c(k, \mathrm{RH})$ is described by

$$\delta_c(k) = A_n + \sum_{m=0}^{2} N_m^{\alpha} \alpha_{\mathrm{nm}} + N^{\gamma} \gamma^n + N^{\delta} \delta_n \tag{4}$$

where the increments are easily found in the database [22] for various carbon atoms. As for carbon (1) in the chain sequences pictured inside Fig. 5B, $A_n = 6.86$, $N_m^{\alpha} = 1$, $N^{\gamma} = 1$, $N^{\delta} = 1$, $\alpha_{nm} = 9.56$, $\gamma_n = -2.99$, $\delta_n = 0.49$, we thus obtain $\delta_c(k, \mathrm{RH}) = 13.86$ ppm, while $Z_{ki}(R_i) = -4$ ppm due to the substitution of CH_3COO^- at β position. Consequently, the chemical shift for carbon (1) is predicted to locate at 9.86 ppm. This is very close to the spectroscopic data detected. Moreover, the predicted values for the other carbon atoms, based on this rule, well agree with the spectroscopic data (see Table 1), illustrating the reliability of the calculations. Until now, it is clear that that vinyl acetate is initiated by the methyl radical from acetic acid. Therefore, we describe the polymerization as in the following sequences:

$$^{13}CH_3COOH + h^+ \rightarrow \bullet^{13}CH_3 + CO_2 + H^+ \tag{5}$$

$$\bullet^{13}CH_3 + M \rightarrow {}^{13}CH_3M^{\bullet} \tag{6}$$

Table 1
Assignments of the ^{13}C NMR peaks of the resultant poly(vinyl acetate) in $CDCl_3$ solvent

Peaks	Prediction (ppm)	Spectrum (ppm)	Assignments
(1)	9.86	9.3	Terminal CH_3
(2)	22.50	20.9	Acetate CH_3
(3)	39.86	38.6–39.8	Main-chain CH_2
(4)	66.90	66.0–67.8	Main-chain CH
(5)	170.0	170.2	Main-chain C=O

$$\bullet^{13}\mathrm{CH_3M}^{\bullet} + (n-1)\mathrm{M} \rightarrow {}^{13}\mathrm{CH_3(M)}_n \tag{7}$$

The β scission of acetic acid (Eq. (5)) is the only photochemical step involved in this polymerization. Once the monomer is initiated by the addition reaction of the methyl radical (Eq. (6)), the adducted radical reacts with another monomer to give a chain propagated radical and eventually the polymer.

Kinetics studies are carried out by changing the concentrations of vinyl acetate and the usages of acetic acid. In a free radical polymerization, the kinetic chain length (v) is defined as [23]

$$v = \frac{k_\mathrm{P}[\mathrm{M}]}{2k_\mathrm{t}^{1/2}R_\mathrm{i}^{1/2}} \tag{8}$$

where k_P is the rate constant of polymerization, k_t is the rate constant of termination. R_i is the initiating rate. The number-average molecular weight of polymer is known to be the kinetic chain length timing 1 or 2 depending on the type of chain termination [23]. Fig. 6A shows that the NMR peak of the terminal methyl is intensified with the monomer concentration decreasing, compared with that of Fig. 5B by taking any main-chain carbon as reference. This indicates that the molecular weight of polymer increases with the increase in the monomer concentration, being consistent with the prediction on Eq. (8). The result thus confirms the free radical mechanism proposed. By comparing the results shown in Fig. 6A and B, the peak intensity of the terminal methyl is found to increase with increasing the amount of $^{13}\mathrm{CH_3COOH}$ added. The result reveals that the rate of initiation increase with the concentration of acetic acid based on Eq. (8).

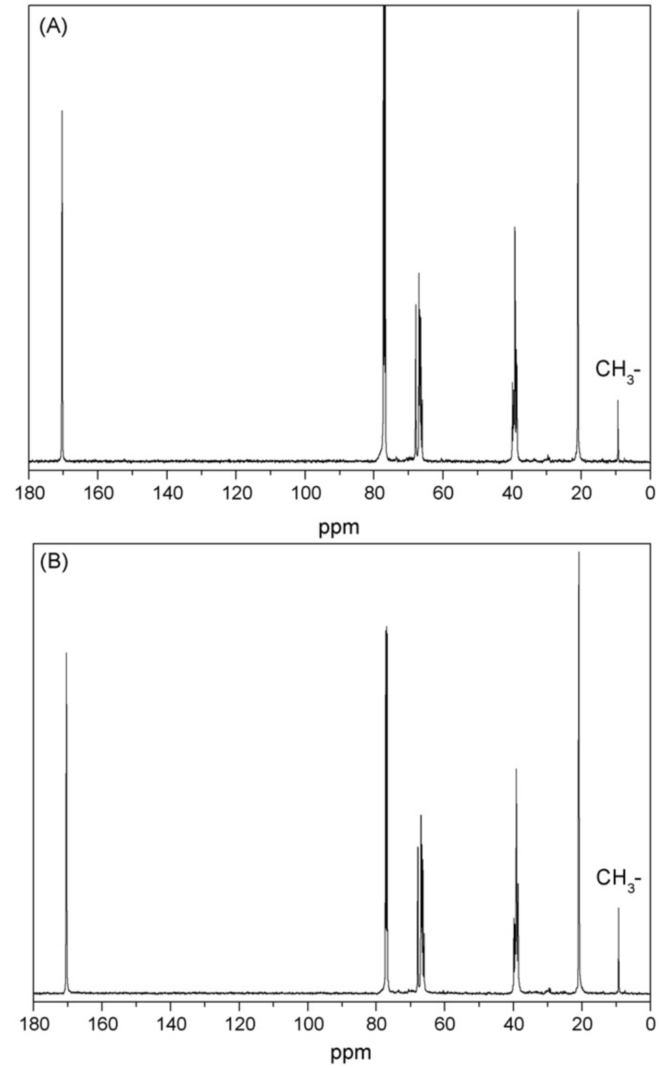


Fig. 6. ^{13}C NMR spectra of poly(vinyl acetate) obtained at vinyl acetate concentration of 10 g/l and adding (A) 100 μl and (B) 250 μl $^{13}\mathrm{CH_3COOH}$.

3.3. Implications to photocatalytic polymerization

The photo-Kolbe reaction has been extensively studied as photochemical cell [17,24], and as a model reaction to put insight into the oxidation of various $\mathrm{TiO_2}$ NPs [25]. The results here reveal another function of the photo-Kolbe reaction as yielding reactive methyl radicals to initiate polymerization. This offers a new pathway to realizing photocatalytic polymerizations. One can find in Fig. 4 the high efficiency of this polymerization in presence of acetic acid and thus the potential applications of this technology. As shown, the usage of acetic acid as low as 20 μl makes the polymerization achievable, and the monomer conversion increases to reach 98% when the usage of acetic acid is 200 μl.

Our result, in turn, evidences the methyl radical as the reaction intermediate mentioned earlier, from a view of point of polymerization. It appears that in the photocatalytic polymerization, vinyl acetate competes for the methyl radical with the side reactions towards methane and ethane, which have been proved to be the products of the photo-Kolbe reaction [17,24]. The occurring of polymerization elucidates that the addition reaction of the methyl radical with vinyl acetate has exerted a powerful competition. It is realized in this section that methyl radical ($^{\bullet}\mathrm{CH_3}$) is one of carbon-centered alkyl radicals. Analysis on the properties of this kind of radicals and vinyl acetate can assign the polymerization to the features that the carbon-centered alkyl radicals prefer to nucleophilic addition with electron-deficient alkenes [26], while vinyl acetate is one of electron-deficient monomers [23]. It is ratiocinated that by means of adding acetic acid as "sensitizer", polymerizations can proceed with lots of suitable monomers. Among those, photocatalytic polymerizations of high efficiency are expected with methyl acrylate, methyl methacrylate and acrylonitrile, because calculations indicated that the carbon-centered radical have higher rate constants for addition reaction with above monomers than vinyl acetate [27]. Followed the concepts, more photocatalytic polymerizations are being achieved by means of using acetic acid. For example, it has been found that the monomer conversation is 78% for methyl acrylate, 53% for methyl methacrylate, and 65% for acrylonitrile after the polymerization of 2 h when 200 μl acetic acid is used.

3.4. The role of $\mathrm{CH_3COO^-}$ absorption in aqueous suspension

It is noted that a contrary result was found if the vinyl acetate aqueous solution was replaced by a vinyl acetate bulk. No polymerization was detected under the identical UV irradiation but an amount of acetic acid, up to 200 μl, was added into the binary mixture containing vinyl acetate and TiO_2 NPs, which is a typical bulk system. This phenomenon is noteworthy since free radical polymerizations consistently take place no matter the monomer is in solution or in bulk, if the radical applied is capable of initiation. There have been records on the photo-Kolbe reaction dealing with pure acetic acid [17], showing that the β scission is feasible under this condition. Taking this into account, the methyl radical may be produced in the bulk system too, but the production is weakened compared to that of the aqueous system, resulting in that the amount of the radicals is not enough to make an effective initiation. It is realized in this discussion that acetic acid in the aqueous medium has two chemical states, i.e. CH_3COO^- and CH_3COOH, where the anion is generated from the ionization. Differently, acetic acid keeps the molecular state in the bulk system. This difference implies that the reasons responsible for the contrary results occurred in the two different systems are related to interactions with the TiO_2 surface.

Metal oxide particles suspended in water are known amphoteric. In titration experiments, metal oxide suspensions behave as if they were simple diprotic. In the case of TiO_2, the principal amphoteric surface functionality is the "titanol" moiety, >TiOH. Hydroxyl groups on the TiO_2 surface undergo the acid–base equilibria [1]:

$$> \mathrm{TiOH_2^+} \overset{\mathrm{p}K^{\mathrm{S}}_{\mathrm{a1}}}{\longleftrightarrow} > \mathrm{TiOH} + \mathrm{H^+} \qquad (9)$$

$$> \mathrm{TiOH} \overset{\mathrm{p}K^{\mathrm{S}}_{\mathrm{a2}}}{\longleftrightarrow} \mathrm{TiO^-} + \mathrm{H^+} \qquad (10)$$

The pH of zero point of charge is defined as $\mathrm{pH_{zpc}} = (\mathrm{p}K^{\mathrm{s}}_{\mathrm{a1}} + \mathrm{p}K^{\mathrm{s}}_{\mathrm{a2}})/2$. In the case of Degussa P25 TiO_2, $\mathrm{pH_{zpc}}$ 6.25 [1]. As for the aqueous system consisting of 1 g/l TiO_2, 200 μl acetic acid, 15 g/l vinyl acetate and water, the pH value was measured to be 3.68. In the case of $\mathrm{pH} < \mathrm{pH_{zpc}}$, the surface of TiO_2 NPs is positively charged [1], and absorbs the anionic CH_3COO^- via the electrostatic attraction. As result of the stronger attraction, the absorption of CH_3COO^- overwhelms that of water, vinyl acetate and CH_3COOH, suggesting that the methyl radical is produced mainly through the reaction with the favored CH_3COO^-:

$$\mathrm{CH_3COO^-} + \mathrm{h^+} \rightarrow {}^{\bullet}\mathrm{CH_3} + \mathrm{CO_2} \qquad (11)$$

Moreover, as the ionization of acetic acid gives CH_3COO^- and H^+ in pairs, it is sure for us to consider the reaction in Eq. (11) equivalent to that of Eq. (5) for the aqueous system.

In the case of bulk system, however, the TiO_2 display no electrostatic selectivity to acetic acid and vinyl acetate molecules. There is hydrogen bonding due to the polar groups in both compounds. Assumed that their affinities to the TiO_2 NPs, which determine their absorption coefficients, do not differ largely, the fraction of acetic acid in the absorbents nears, to certain extent, to that in the bulk, where acetic acid is absolutely the minor component (its concentration in volume is at 0.17% in the reactor, if 200 μl acetic acid is added). It is valid that the photocatalytic reaction of acetic acid is suppressed by the competition of vinyl acetate as the major component, being consistent with the Langmuir–Hinshellwood model, which is often applied to describe photocatalytic reactions of multi-components system [28]. In contrast to the bulk case with less absorption of acetic acid, the absorption of CH_3COO^- is favored in the aqueous case, and this property accounts for the distinct results that the same usages of acetic acid (i.e. the concentration of acetic acid in the reactor is the same) have induced the polymerization in the aqueous suspensions.

4. Conclusions

The present study has shown the polymerization of vinyl acetate photocatalyzed by TiO_2 nanoparticles. It is found that the monomer is initiated by the methyl radical that is produced by the photocatalytic β scission of acetic acid on TiO_2 nanoparticles. It is found that the usage of acetic acid as low as 20 μl makes the polymerization achievable, and the monomer conversion increases to reach 98% when the usage of acetic acid is 200 μl. The polymerization follows a free radical chain mechanism. The rate of initiation reaction is enhanced with an increase in the amounts of acetic acid added. From the phenomenon that no polymerization occurs when the aqueous vinyl acetate is replaced by the vinyl acetate bulk, it is drawn that in the aqueous suspensions, the absorption of CH_3COO^- on the TiO_2 is favored by the electrostatic attraction, and thus dominates the production of methyl radicals. This study shows the first observation of the photo-Kolbe reaction as a pathway to initiate polymerization. The novel pathway found has direct implications to applications of the photocatalytic polymerization.

Acknowledgements

We thank National Nature Science Foundation of China (NSFC) for financial support of this research (20574011). Shanghai Nanotechnology Promotion Center (SNPC) is gratefully acknowledged (05nm05013, 055207080).

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