

Supplementary material

Photocatalytic decarboxylation of diacids for initiating free radical polymerization

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S1. ^{13}C -NMR analysis of PVAc obtained by using ^{13}C labeled acetic acid in bulk

Fig S1 shows the ^{13}C -NMR spectrum of PVAc obtained in bulk by adding 0.152 mol L^{-1} of $2\text{-}^{13}\text{C}$ acetic acid. It is clear to see that the spectrum accords well with that of normal PVAc except for a new chemical shift peak at 9.49 ppm. The chemical shifts of carbon atoms are assigned in Table S1.

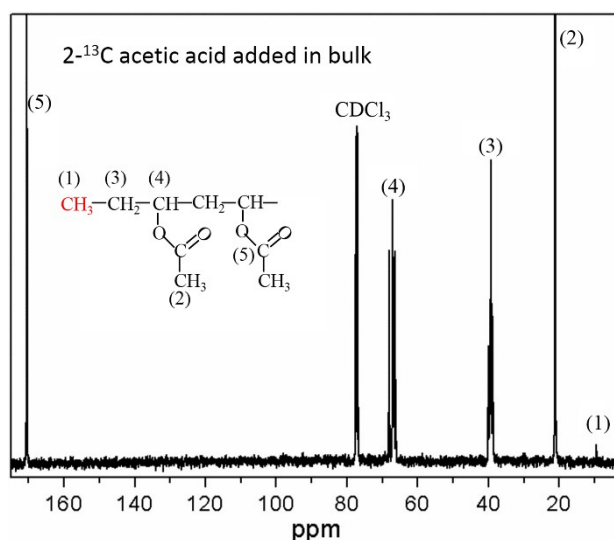


Fig S1. ^{13}C -NMR spectrum of PVAc obtained in bulk by adding 0.152 mol L^{-1} of $2\text{-}^{13}\text{C}$ acetic acid. The amount of TiO_2 nanoparticles is 2 g L^{-1} .

According to the Lindeman–Adams formula¹, the peak at 9.49 ppm is assigned

to the ultimate methyl group, which is derived from photodecarboxylation of the ^{13}C labelled acetic acid.

$$\delta_c(k) = \delta_c(k, \text{RH}) + \sum_i Zk_i(R_i) \quad (1)$$

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

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

where the increments are easily found in the database for various carbon atoms. As for carbon (1) in the chain sequences pictured inside Fig. S1, $A_n = 6.86$, $N_m^\alpha = 1$, $N^\gamma = 1$, $N^\delta = 1$, $\alpha_{nm} = 9.56$, $\gamma_n = -2.99$, $\delta_n = 0.49$, we thus obtain $\delta_c(k, \text{RH}) = 13.86$ ppm, while $Zk_i(R_i) = -4$ ppm due to the substitution of acetate group at β position. Consequently, the chemical shift for carbon (1) is predicted to locate at 9.86 ppm.

Table S1. Assignment of the ^{13}C -NMR peaks of the resultant polyvinyl acetate in CDCl_3 solvent by adding 0.152 mol L^{-1} of $2\text{-}^{13}\text{C}$ acetic acid in bulk.

Peak	Prediction(ppm)	Spectrum(ppm)	Assignment
(1)	9.86	9.49	Ultimate CH_3
(2)	22.50	21.05	Acetate CH_3
(3)	39.86	38.72-39.97	Main-chain CH_2
(4)	66.90	66.09-68.08	Main-chain CH
(5)	170.0	170.47	Main-chain $\text{C}=\text{O}$

S2. Characterization of the PVAc obtained by adding malonic acid in bulk

Fig S2 shows the ^{13}C -NMR spectrum of PVAc obtained by using malonic acid, which is the same to the ^{13}C -NMR spectrum of the normal PVAc. The result indicates that no chemical shift peak of the terminal group can be detected due to the fraction of the terminal carbon in the total-chain carbons is too small.

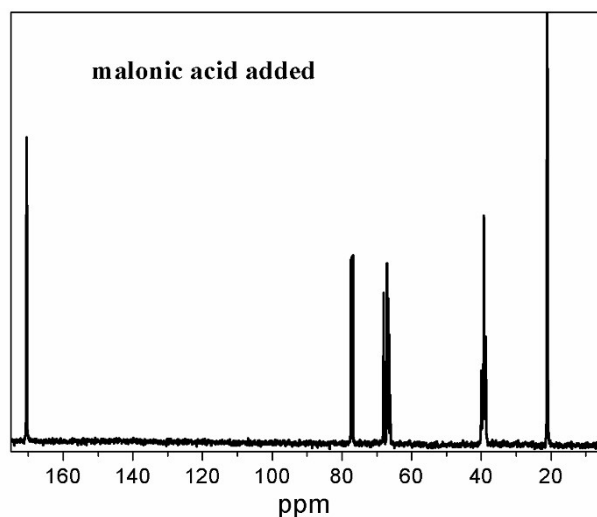


Fig S2. The ^{13}C -NMR spectrum of PVAc obtained in aqueous medium by adding 0.01 mol L^{-1} of malonic acid.

S3. The structural characterization of products obtained in aqueous medium by FTIR

Fig S3 exhibits the FTIR spectra of products obtained in aqueous. It reveals that by adding no acid, the FTIR spectrum of products is almost the same as that of pure TiO_2 nanoparticles². In comparison, by using diacids (from malonic acid to adipic acid), the characteristic peaks of PVAc are observed³. It can be concluded that both carboxylic diacid and TiO_2 nanoparticles are essential to initiate the photo polymerization of VAc.

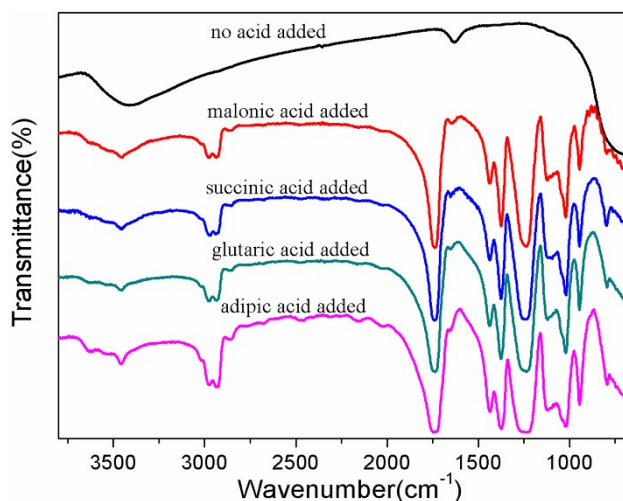


Fig S3. FTIR spectra of TiO_2 and products obtained by adding different acid in VAc aqueous solution.

S4. The TGA analysis of products obtained in aqueous medium

Fig S4 shows the TGA curves of products obtained by adding 5.5 mmol L⁻¹ of diacids in water. After being heated to 700 °C, the products obtained by adding no acid showed little weight loss, which may be attributed to the water adsorbed on TiO₂. On the contrary, the products obtained by adding malonic acid, succinic acid, glutaric acid or adipic acid exhibit significant weight loss. From the DTG curves, the peak around 340 °C refers to the cleavage of acetate group and the weight loss after 400 °C is resulted from the breakdown of the PVAc C-C backbones⁴. Therefore, it is infeasible for TiO₂ nanoparticles to initiate the photopolymerization of VAc in aqueous without diacid. Similarly, in the case of bulk reaction, almost no PVAc was observed by adding no diacid into the reaction mixture containing TiO₂ nanoparticles.

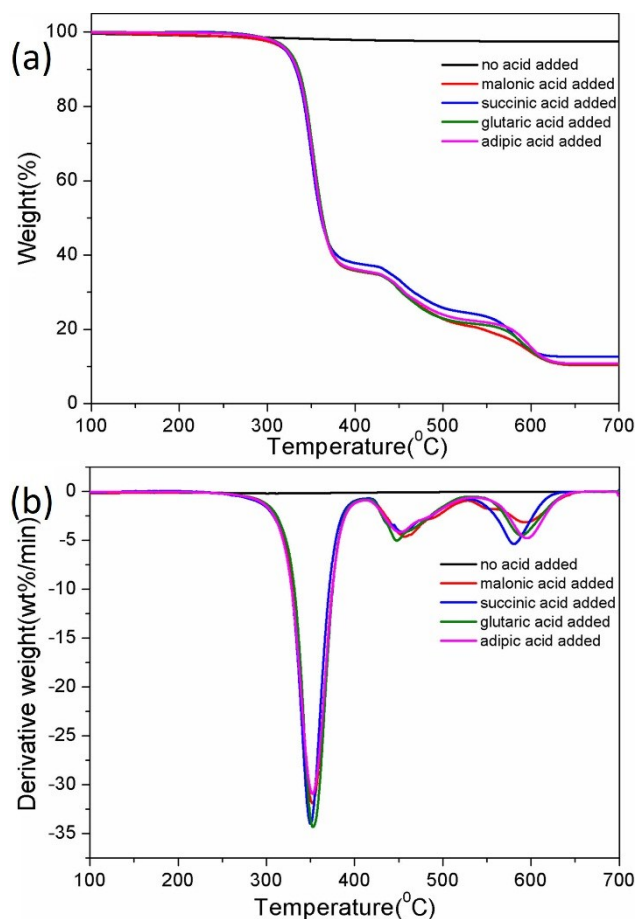


Fig S4. TGA (a) and DTG (b) curves of products obtained by adding different dicarboxylic acids in VAc aqueous solution. The amount of TiO₂ nanoparticles is 1 g L⁻¹.

References:

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