

GRAFT COPOLYMERIZATION OF VINYL MONOMERS ONTO STARCH INITIATED BY TRANSITION METAL-THIOUREA REDOX SYSTEMS

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ABSTRACT

In this paper, the capabilities of grafting acrylonitrile (AN) onto starch initiated by Fe(III)-TU, V(V)-TU, Cr(VI)-TU, Mn(VII)-TU redox systems were compared in the presence of sulfuric acid of different concentrations. It was shown that the grafting capability of Mn(VII)-TU is the highest in these initiating systems. Using Mn (VII)-TU as initiator, the effects of various acids (HClO_4 , H_2SO_4 , HNO_3 , HCl) on the graft copolymerization of acrylonitrile onto starch were discussed, and the capabilities of graft copolymerization of methyl methacrylate (MMA), acrylamide (AM), acrylic acid (AA) onto starch were investigated. The experimental results show that the order of the influences of different acids is $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$, and the order of grafting capabilities of different monomers grafted onto starch is $\text{MMA} > \text{AN} > \text{AM} > \text{AA}$. The structure and morphology of graft copolymers were studied with infrared spectroscopy and scanning electron microscopy. The size, shape and roughness of surface of the grafted starch granules are changed after grafting.

INTRODUCTION

Using transition metals or their chelates as initiators in the graft copolymerization of vinyl monomers onto natural macromolecules has received considerable attention in recent years^[1,2]. Hebeish^[3] et al. had reported the grafting of acrylonitrile onto starch by using KMnO_4 as a initiator, and other metals such as Mn(VII)^[4,5], Cr(VI)^[6], V(V)^[7], Ce(IV)^[8], and Co(III)^[9] were also reported for use as initiators in the graft of starch. They initiated and yielded free radicals directly at backbone, the monomer then was grafted at those active sites.

Another type of initiator, the commonly used fenton reagent^[10,11] ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), behaves in a contrary fashion. It first reacts with itself to give free radicals, which

react further with starch leading to the formation of free radical centers on the backbone. Similarly, hydrazine redox^[12], redox comprising persulfate^[13], as well as metal acetyl acetonate^[14] have also been reported as chain-transfer initiators used in the graft copolymerization of natural macromolecules.

Recently, Nayak and his co-workers used thiourea redox, such as V(V)-TU^[15,16,17], Fe(III)-TU^[18] and Cr(V)-TU^[19] etc. as initiator systems to graft vinyl monomers onto fiber or cellulose. But the use of transition metal-thiourea systems in the grafting of monomers onto starch has not been reported. The present paper selects the higher capability thiourea redox systems to study the effects of acids on the grafting of acrylonitrile onto starch.

EXPERIMENTAL

Materials

Acrylic acid (Beijing Chemical Factory), acrylamide (Linhai Chemical Factory), acrylonitrile and methyl methacrylate (Tianjin Second Chemical Reagent Factory) were purified before use.

Starch was obtained from Tianjin Red-Flag Starch Factory, and other chemicals such as FeCl₃, CrO₃, KMnO₄, NH₄VO₃, and thiourea were all provided by Tianjin Chemical Co.

Preparation of graft copolymer

A weighed amount of starch was placed in a three-necked flask, and then distilled water was added. Under a N₂ atmosphere, the slurry was heated and preheated at 75° for about half an hour. After it was cooled to 40°C, monomers, redox initiating systems, and acids were added.

The reaction mixture was allowed to react under slow stirring for 3h. All the operations were carried out under a N₂ atmosphere. The products were precipitated out with alcohol, filtered, dried and weighed.

Table 1 Extractants for homopolymers

Homopolymers	PAN [4]	PAA [18]	PMMA [19]	PAM [2]
Extractants	DMF	Methanol	Acetone	Glycol/glacial acetic acid
Temperature (°C)	50	40	52	50
Time (h)	48	72	72	48

The above dried products were extracted with different extractants for several hours to remove the homopolymers. The extractants pertinent to the homopolymers and extracting conditions are listed in Table 1.

IR spectra and photomicrograph of SEM

The infrared spectra of the samples were determined with a 170 SXFT-IR spectrometer. The photographs of the scanning electron microscope of the samples were tested with a Hitachi X-650 scanning electron microscope after spraying with gold.

Determination of the percentage of grafting, grafting efficiency and percent conversion of monomer

The percentage of grafting (P), grafting efficiency (E), and percent conversion of monomer (C) were calculated by weighing the original starch and grafting products

$$P(\%) = \frac{\text{weight of grafted polymer branch}}{\text{weight of starch}} \times 100$$

$$E(\%) = \frac{\text{weight of grafted polymer branch}}{\text{weight of monomer reacted}} \times 100$$

$$C(\%) = \frac{\text{weight of monomer reacted}}{\text{weight of monomer added}} \times 100$$

RESULTS AND DISCUSSION

The capability of transition metal-TU redoxes in the graft reaction of acrylonitrile onto starch.

The graft copolymerization of acrylonitrile (AN) onto starch initiated by Mn(VII)-TU, Cr(VI)-TU, V(V)-TU and Fe(III)-TU, redox systems at two different sulfuric acid concentrations was studied. Figure 1 to Figure 4 show the results with $[\text{H}_2\text{SO}_4] = 2 \times 10^{-2} \text{ mol/L}$, and Table 2 with $[\text{H}_2\text{SO}_4] = 5 \times 10^{-2} \text{ mol/L}$.

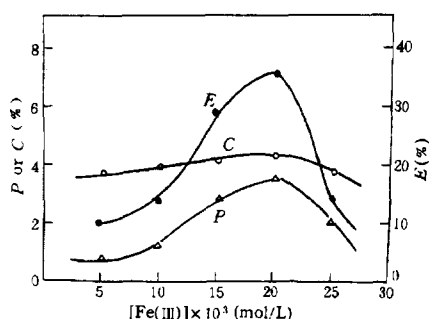


Fig. 1 Effect of $[\text{Fe(III)}]$ on grafting

$[\text{AGU}] = 0.11 \text{ mol/L}$, $[\text{AN}] = 0.76 \text{ mol/L}$,
 $[\text{H}_2\text{SO}_4] = 2.0 \times 10^{-2} \text{ mol/L}$, $[\text{TU}] =$
 $1/2[\text{Fe(III)}]$, Temp. = 40°C , Time = 3h

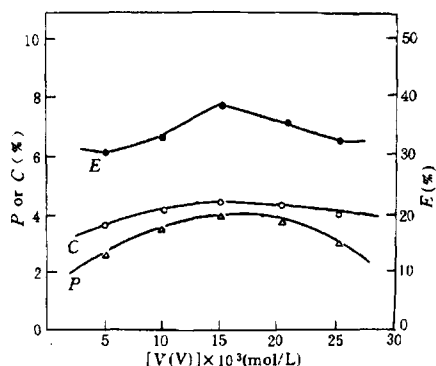


Fig. 2 Effect of $[\text{V(V)}]$ on grafting

$[\text{TU}] = 1/2[\text{V(V)}]$, other conditions as in
 Fig. 1

By comparing the data in the figures, the following facts can be drawn: (1) The percentage of grafting, grafting efficiency and percent conversion of monomer all have a maximum value with the increasing of initiator concentration at two different acid concentrations for each of the four thiourea redox systems.

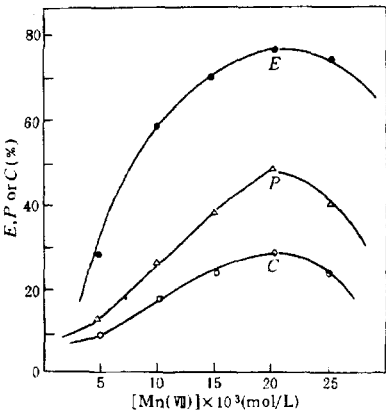
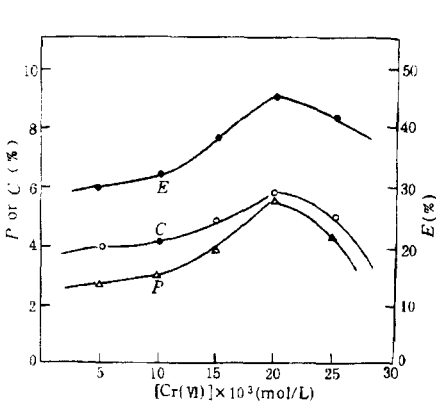


Fig. 3 Effect of [Cr(VI)] on grafting
[TU]= 1/2[Cr(VI)], other conditions as
in Fig. 1

Fig. 4 Effect of [Mn(VII)] on grafting
[TU]= 1/2[Mn(VII)], other conditions as
in Fig. 1

Table 2 Initiating ability of different metals used in the redox system

[Metal]×10 ³ mol/L	5	10	15	20	25	other conditions
Fe(III)	<i>E</i> (%)	11	13	27	41	16
	<i>P</i> (%)	0.8	1.3	2.9	4.1	1.7
	<i>C</i> (%)	3.7	3.9	4.2	4.3	4.0
V(V)	<i>E</i> (%)	32	36	41	38	33
	<i>P</i> (%)	3.1	3.6	4.5	4.0	3.5
	<i>C</i> (%)	4.2	4.6	5.0	4.7	4.4
Cr(VI)	<i>E</i> (%)	33	37	46	50	44
	<i>P</i> (%)	3.1	3.9	5.9	6.5	5.1
	<i>C</i> (%)	4.2	4.8	5.3	6.0	5.4
Mn(VIII)	<i>E</i> (%)	30	63	78	81	77
	<i>P</i> (%)	4	29	56	86	67
	<i>C</i> (%)	6	17	32	44	37

(2) The initiator concentration, which corresponds to the maximum value, depends on the initiator. Evidently, V(V) is at a concentration of 1.5×10^{-2} mol/L, and the other three metals are at 2×10^{-2} mol/L. Besides, this initiator concentration

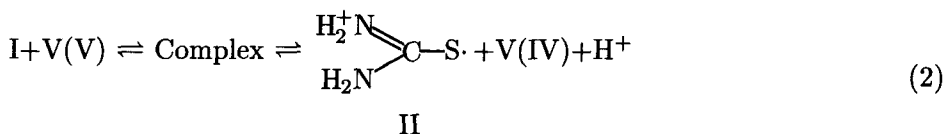
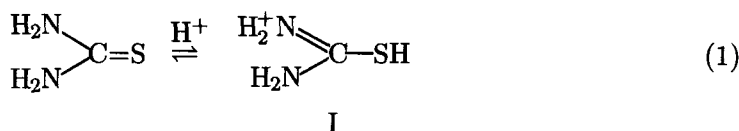
is not affected by acid concentration.

(3) The percentage of grafting, grafting efficiency and percent conversion of monomer of the Fe(III)-TU, Cr(VI)-TU, and V(V)-TU systems are slightly affected by the increasing of acid concentration with the exception of Mn(VII)-TU redox system, especially the percentage of grafting, since its maximum value increases from 48.7% to 86.0% with increasing $[H_2SO_4]$ from 2×10^{-2} to 5×10^{-2} mol/L.

(4) The initiating capacities of Fe(III)-TU, V(V)-TU, and Cr(VI)-TU are similar, but are much lower than that of Mn(VII)-TU.

The above four points show that the initiating capabilities of the redox systems are different, and Mn(VII)-TU is the best one among the four redox systems. This can be attributed to the redox potential of the transition metal.

As we all know, the metal-TU redox is a chain transfer redox initiator, and free radicals are produced by the reaction between metal and thiourea. The mechanism of the graft copolymerization, taking V(V)-TU as an example, is described below:^[15]



Obviously, the higher the redox potential of the metal, the more abundant the free radicals will be produced by the reaction of metal with thiourea [see expression (2)]. This makes the graft copolymerization proceed easily.

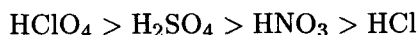
The normal redox potential of the four metals are listed in Table 3. It can be seen that the redox potential of Mn(VII)/Mn(II) is the highest, this may be the reason why its initiating capability is higher.

Table 3 Normal redox potential of the metals

Redox	$\text{Mn}^{7+}/\text{Mn}^{2+}$	$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$	$\text{VO}_2^+/\text{VO}^{2+}$	$\text{Fe}^{3+}/\text{Fe}^{2+}$
N.R.P.	1.51	1.33	1.00	0.77

The effect of various acids on the grafting of acrylonitrile onto starch.

The effects of acids, including HClO_4 , HCl , H_2SO_4 and HNO_3 , on the graft copolymerization of AN onto starch were investigated, and the results are listed in Table 4. It can be seen that the catalytic ability of the acids is:



This catalytic ability increases remarkably with increasing acid concentration.

Table 4 Effects of acids

Acid	HClO_4		H_2SO_4		HNO_3		HCl	
$[\text{H}^+] \times 10^2 (\text{mol/L})$	4	10	4	10	4	10	4	10
<i>C</i> (%)	31.9	50.6	28.6	46.1	24.4	41.9	19.3	34.3
<i>P</i> (%)	56.6	96.7	48.7	85.4	40.4	75.3	30.5	52.2
<i>E</i> (%)	78.0	84.2	75.8	81.5	73.1	79.1	69.4	70.6

$[\text{AGU}] = 0.11 \text{ mol/L}$, $[\text{AN}] = 0.76 \text{ mol/L}$, $[\text{Mn(VII)}] = 2 \times 10^{-3} \text{ mol/L}$

$[\text{TU}] = 1.0 \times 10^{-3} \text{ mol/L}$, Temp. = 40°C , Reaction time = 3h

The mechanism indicates that the catalytic abilities of the acids are related to their capability of providing protons. It is found, by comparison, that the catalytic ability of the four acids are in the same order as their ability to offer protons.

Table 5 Effects of monomers

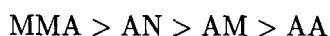
Monomer	AN		MMA		AM		AA	
$[\text{H}^+] \times 10^2 (\text{mol/L})$	4	10	4	10	4	10	4	10
<i>C</i> (%)	28.3	46.1	57.0	48.8	39.9	33.6	24.0	10.7
<i>P</i> (%)	48.7	85.7	204.4	178.2	86.6	71.6	21.4	8.2
<i>E</i> (%)	75.8	81.5	83.1	84.6	70.7	69.6	28.6	24.5

$[\text{AGU}] = 0.11 \text{ mol/L}$, $[\text{Mn(VII)}] = 2 \times 10^{-3} \text{ mol/L}$, $[\text{TU}] = 1 \times 10^{-3} \text{ mol/L}$

$[\text{M}] = 0.76 \text{ mol/L}$, Temp. = 40°C , Reaction time = 3h., Acid: H_2SO_4

Graft copolymerization of various monomers with starch by Mn(VII)-TU redox system.

The grafting of different monomers onto starch under the same reaction conditions using Mn(VII)-TU redox system as initiators were examined. The data in Table 5 indicate that the structure of monomers has a great effect on graft copolymerization, and that the order of grafting ability of different monomers onto starch is:



The reason is not very clear, it may be connected with the formation of complex between monomer and starch^[20,21].

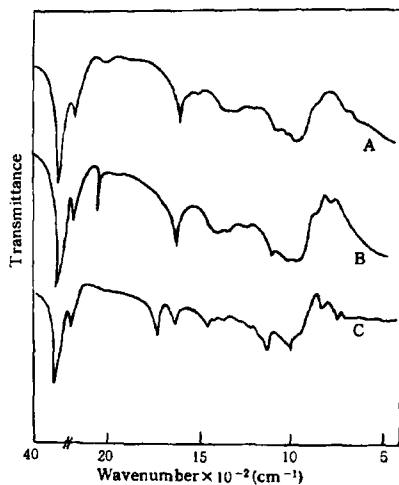


Fig. 5 IR spectra of pure starch (A), starch-g-PAN (B), and starch-g-PMMA (C)

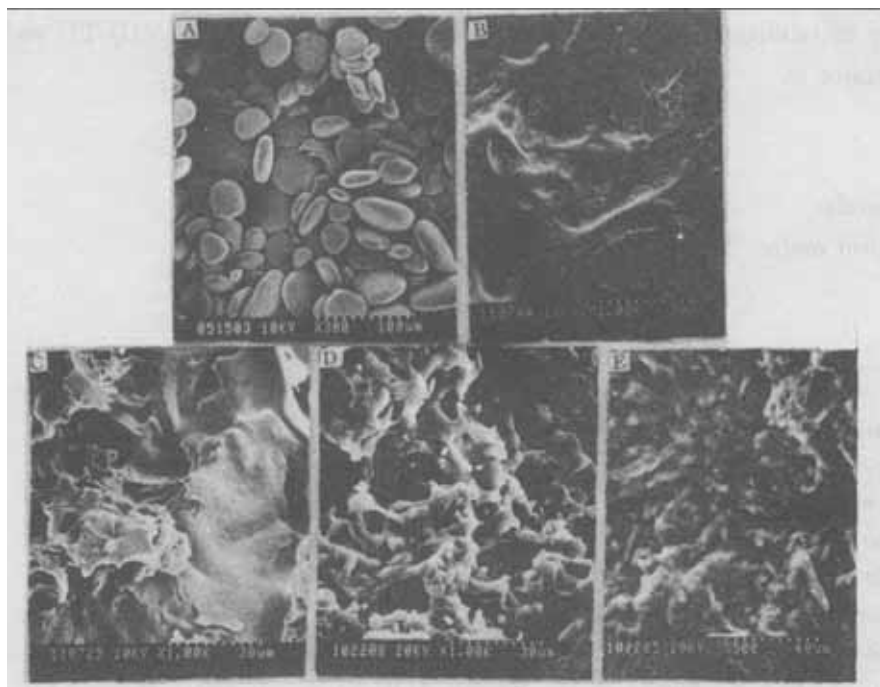


Fig. 6 SEM photos. (A) pure starch, (B) starch-g-PAN, (C) starch-g-PMMA, (D) starch-g-PAM, (E) starch-g-PAA

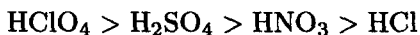
The IR spectra of pure starch (A) and its grafting copolymers, starch-g-PAN(B), starch-g-PMMA(C), are illustrated in Figure 5. It can be seen that the graft copolymers show not only the characteristic absorption bands of starch, but also the characteristic bands of the corresponding branch polymers. This provides proof of grafting.

Analysis of scanning electron microscope

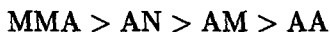
Fig. 6 is the SEM photographs of graft copolymers. The size, shape and roughness of the surface of the grafted starch granules are changed in comparison with the original starch.

CONCLUSION

1. The initiating capability of Mn(VII)-TU redox system is much higher than that of the other three metal-TU redox systems. This is attributed to the higher redox potential of Mn(VII)/Mn(II).
2. The properties of acid have great effects on the grafting of AN onto starch, and the order of catalytic ability of the acids is:



3. The capability of monomer grafted onto starch using Mn(VII)-TU redox as initiator is:



Keywords:

Transition metal; Thiourea; Graft copolymerization; Starch

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