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Preparation of polystyrene-g-starch copolymer initiated by potassium diperiodatocuprate(III)

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ABSTRACT

In this article, graft copolymerization of styrene (St) onto cassava starch via potassium diperiodacuprate (III)–starch redox system as an initiator was investigated in an alkaline medium. The graft copolymer was characterized with Fourier-transform infrared spectra analysis (FTIR), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). FTIR spectra indicated the presence of PSt-g-starch copolymer. XRD analysis exhibited insignificant changes in crystalline structure and degree of crystallinity. SEM micrographs also showed PSt adhering on the starch. A mechanism was proposed to explain the generation of radicals and the initiation. The effects of reaction variables were investigated, and the grafting conditions were optimized. The value of the overall activation energy of styrene-starch polymerization (49.4kJ/mol) and the equation of the polymerization rate were obtained, $R_p = k \cdot C^{1.09}(St)C^{0.50}(Cu(III))$.

KEYWORDS

Starch;
Styrene;
Potassium diperiodatocuprate(III) [DPC];
Redox initiation;
Graft copolymerization.

INTRODUCTION

In the last three decades, there has been tremendous interest in bioplastic and biodegradable polymers. Starch can be easily degraded by microorganisms, so it is suitable for blending with bioplastics and biodegradable polymers. Various polymer synthesized by starch and thermoplastic polymer have been reported. Unfortunately, the mechanical properties of these blends are very poor due to the incompatibility and hydrophilic nature of starch. For this purpose, graft polymerization of thermoplastic polymers onto starch is an excellent method for preparing composites of starch with synthetic polymers[1].

In 1958, Mino and Kaizerman reported that Cerium(IV) as initiator could not give a styrene-g-starch, but a graft copolymer could be obtained when styrene is mixed with an active monomer[2]. Fanta, Burr, Doane, and Russell, prepared starch graft copolymers with styrene using 60Co irradiation have been reported[3]. They also reported that starch-g-polystyrene could be obtained by persulfate initiation in the slurry state. Cho and Lee prepared PSt-g-starch copolymer by emulsion polymerization[4]. Recently, ozone was used to synthesize starch graft with poly(styrene-co-n-butyl acrylate) latexes[5]. Kaewta Kaewtatip, Varaporn Tanrattanakul prepared PSt-g-starch copolymer via suspension polymerization using PPS as initiator[6]. And Graaf, Janssen synthesized PSt-g-starch copolymer using benzoyl peroxide and PPS as the thermal initiators[7].

To the best of our knowledge, there is no report on graft copolymer of starch and PSt using potassium diperiodacuprate (III)–starch redox system as an initiator. In recent years, we have also obtained some achievements on the homopolymerization and graft copolymerization of vinyl monomers initiated by supernormal valence transition metals[8-10]. And we prepared PSt-g-casein copolymer using potassium diperiodatonickelate(IV) as initiator[11]. In this paper, graft copolymerization of St onto starch has been investigated in detail, using DPC-starch redox pair as initiator and in an alkaline medium. High grafting efficiency indicated that potassium diperiodacuprate(III)–starch redox system was an efficient initiator for this graft copolymerization. At the same time, some structure and properties of graft copolymers were characterized by SEM, IR and TGA. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

EXPERIMENTAL

Materials

Cassava starch was kindly supplied by Biaozhun Ltd., Tianjin. Styrene monomer (from Beijing reagent Ltd) was used after inhibitor was extracted with 5% sodium hydroxide aqueous solution and distilled water sequentially. The inhibitor-free styrene was dried with anhydrous calcium chloride and stored at 4°C. DPC was synthesized and measured according to the reported procedure[12]. The concentration of DPC was obtained by its absorption at λ=414nm using a shimadzu UV-265 spectrophotometer (Japan). The concentration of base DPC was calculated as 3.65×10^{-2} mol/L.

Preparation of PSt-g-starch copolymer

In a typical experiment, the graft copolymerization was carried out as follows: a required amount of pregelatinized starch was dissolved in water in a 50 mL conical flask. The flask was stoppered and deaerated sufficiently by sparging with nitrogen and were equilibrated at required temperature with constant stirring. Then the monomer was injected, followed by DPC aqueous solution, and the total volume of the reaction mixture was made up to 28 mL with distilled water. After a required reaction time, the reactant was cooled and neutralized by aqueous acetic acid solution and then it was poured into excess of methanol to precipitate the crude copolymer. The precipitated product was filtered through weighed sintered glass funnel, washed to neutral with methanol and dried to a constant weight under vacuum at 60°C. Polystyrene homopolymer was removed by Soxhlet extraction with toluene. The extraction was done at 120°C for 24 h. The PS-g-starch copolymer was kept in the desiccator after it was dried in a vacuum oven at 60°C until a constant weight.

Characterization of PSt-g-starch copolymer

The products before and after Soxhlet extraction were weighed and characterized by various techniques. The percentage parameters, such as PG, GE, and PC were defined and calculated as follows:

PC / %= [total weight of PSt/ weight of St charged] ×100

GE / %= [weight of PSt grafted/ total weight of PSt] ×100

PG / %= [weight of PSt grafted/ weight of starch] ×100

The Fourier Transform Infrared Spectrometer BIO-RAD was used to determine the presence of PSt in the graft copolymer. The dried powder samples were mixed with potassium bromide and pressed into discshape. A scanning election microscope (KYKY-1006) was used to observe the presence of PSt on starch. Several drops of pregelatinized starch solution or PSt-g-starch solution were dropped to coverslip and then aired forming film. The films were coated with gold prior to observation. Thermal properties were evaluated by thermogravimetric analysis (PerkinElmer TGA 7). TGA analysis was operated at a heating rate of 10°C /min from 50 to 600°C under nitrogen atmosphere. Semi-crystalline structure of pregelatinized starch was detected by using a Y-4Q X–ray diffraction instrument (Dandong Ray Apparatus Corporation, China). The X-ray diagrams were made with Ni-filtered Cu Ka radiation at 30KV and 20mA.

RESULTS AND DISCUSSION

Graft copolymerization on starch

The Cu(III) is soluble in water and attacks the OH

TABLE 1 : The effects of reaction variables on graft parameters

Number	Time(min)	Ratio of St/starch	[DPC]	pH	Temperature(°C)	TC	PG	GE
1^a	90	5.4	4.38×10^{-3}	12.35	45	32%	49%	50%
2^a	120	5.4	4.38×10^{-3}	12.35	45	39%	73%	55%
3^a	150	5.4	4.38×10^{-3}	12.35	45	53%	180%	56%
4^a	180	5.4	4.38×10^{-3}	12.35	45	75%	255%	56%
5^a	210	5.4	4.38×10^{-3}	12.35	45	75%	255%	55%
1^b	150	5.4	4.38×10^{-3}	12.35	40	33%	62%	35%
2^b	150	5.4	4.38×10^{-3}	12.35	50	70%	250%	62%
3^b	150	5.4	4.38×10^{-3}	12.35	55	89%	285%	65%
4^b	150	5.4	4.38×10^{-3}	12.35	60	80%	210%	52%
1^c	150	5.4	2.50×10^{-3}	12.35	45	30%	42%	30%
2^c	150	5.4	3.63×10^{-3}	12.35	45	32%	115%	52%
3^c	150	5.4	4.05×10^{-3}	12.35	45	46%	168%	63%
4^c	150	5.4	5.12×10^{-3}	12.35	45	40%	120%	55%
1^d	150	2.2	4.38×10^{-3}	12.35	45	50%	10%	12%
2^d	150	3.3	4.38×10^{-3}	12.35	45	56%	73%	40%
3^d	150	4.7	4.38×10^{-3}	12.35	45	57%	180%	75%
4^d	150	6.2	4.38×10^{-3}	12.35	45	40%	80%	35%
1^e	150	5.4	4.38×10^{-3}	10.50	45	42%	110%	40%
2^e	150	5.4	4.38×10^{-3}	11.15	45	45%	130%	44%
3^e	150	5.4	4.38×10^{-3}	11.82	45	47%	160%	49%
4^e	150	5.4	4.38×10^{-3}	12.62	45	40%	145%	54%

group of starch, causing free-radicals on the starch molecules. Then these free-radicals will initiate the double bonds of vinyl monomers to obtain graft copolymer. In the present study, various conditions were investigated, and the grafting conditions were optimized.

TABLE 1 numbera illustrates the influence of reaction time on grafting parameters. It can be seen that GE keeps unchanged during the course of the reaction, whereas PG and TC increase steadily with prolonging the reaction time up to 180 min, and then maintain a plateau, which is in consistent with the general rule of conventional radical polymerization. So the optimized reaction time is 180 min. The grafting reactions were carried out at different temperatures between 40°C and 65°C, keeping the other variables constant. As shown in TABLE 1 numberb, TC, GE and PG increase in the beginning up to 55°C and decrease to some extent with further increase of temperature to 65°C. The improvement in TC, GE and PG may be due to the higher rate of decomposition of initiator with increasing reaction temperature, as well as the quickened diffusion and mobility of the monomer molecule. The decline of TC, GE and PG with further increasing temperature can be explained as the enhanced radical termination reaction through oxidation by DPC and the increased chance of chain transfer reaction. Similar result was reported, the maximum grafting efficiency in graft copolymerization of starch and PMMA with PSt was at 50°C[13]. Singh and Sharma also showed the optimum temperature in preparation of PSt-g-starch copolymer[14].

When the other factors are kept invariable, the effect of DPC concentration on graft parameters is shown in TABLE 1 numberc. With increasing DPC concentration, PC, GE and PG increase. However, beyond the optimum DPC concentration of 4.38×10-3mol/L, they are found to decrease. The initial increasing trend may be due to the fact that in this concentration range, DPC attacks the characteristic group OH of starch backbone directly, and creates a great deal of grafting sites, which will initiate the grafting in the presence of St. As a result, PC and PG grow sharply. However, an excess of DPC will accelerate the oxidation of radicals by DPC, which will result to chain termination, hence PC, PG and GE decline.

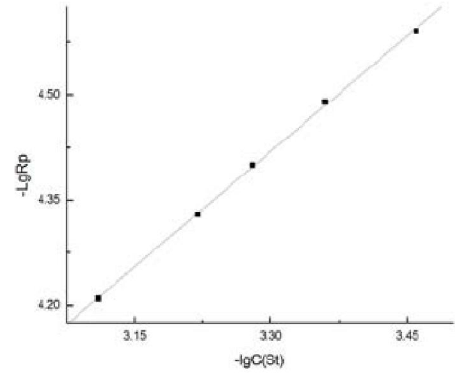


Figure 1 : Kinetics of polymerization: LgC(St) vs LgRp

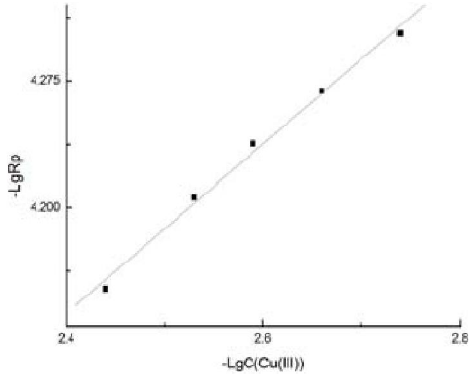


Figure 2 : Kinetics of Polymerization: LgC(Cu(III)) vs LgRp

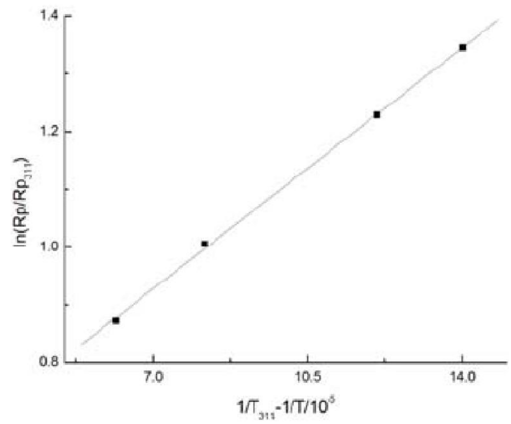


Figure 3 : Overall activation energy: 1/T vs LnRp

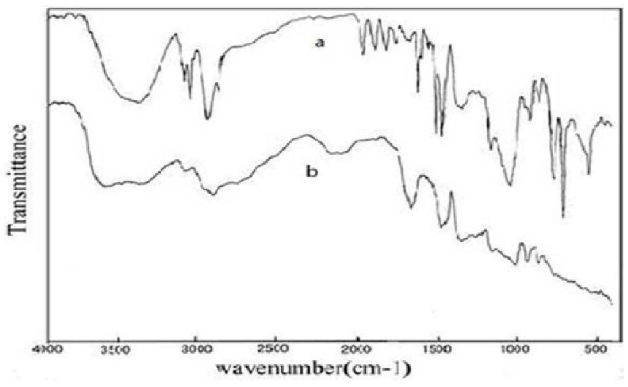


Figure 4 : The IR spectra of grafted copolymer PSt-g-starch and pure starch

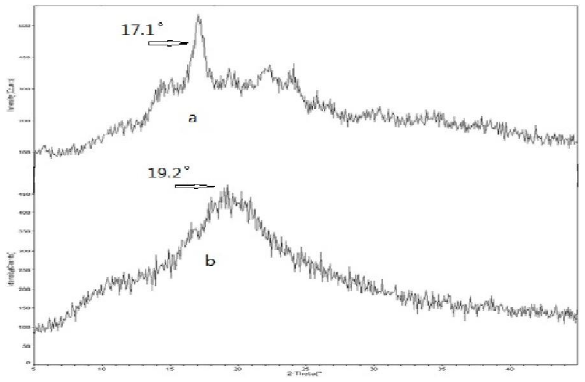


Figure 5 : The X-ray diffraction spectra of starch and PSt -g- starch

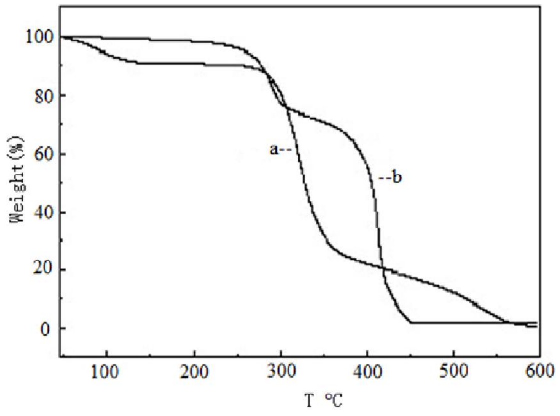
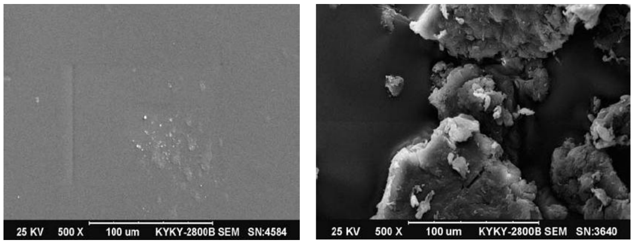


Figure 6 : TGA thermograms of starch and PSt -g- starch

The effect of St-to- starch Ratio on graft copolymerization is depicted in TABLE 1 number^d. It is observed from these data that GE and PG increase initially with the increasing St-to-starch Ratio, but beyond St/starch=4.7, GE, PG decreases. The initial increasing trend of GE and PG may be explained as follows: the increase of St's amount assists in the proximity of monomer to the growing chains and active sites on the starch. With an increase in St-to-starch Ratio, GE and PG increase. Because the total volume was fixed, the water volume will decrease relatively with the increasing amount of St. So the DPC concentration in aqueous phase increased. DPC react not only with reactant to produce radicals initiating polymerization, but also with radicals terminating polymerization. When DPC concentration is too large, the result is the reduction of



(a) (b)

Figure 7 : SEM micrographs of the starch and starch-g-PSt

GE and PG. The optimal St-to-starch ratio is 4.7.

Potassium hydroxide and hydrogen chloride are employed to maintain required alkalinity in the reaction solution. TABLE 1 numbere shows the effect of pH on graft parameters. In the studied pH range, graft parameters changed with pH increasing. They increased slightly firstly and then decrease to some extent. These can be explained as follows: two forms of DPC, H3IO62- and H3IO63-, have different activation. In alkali aqueous solution, the ratio of the two forms change with pH, which directly influences the amount of radicals produced in the reaction system. It is found that the optimum pH is 12.35.

Kinetics of polymerization

For studying the kinetics of the polymerization, the corresponding data were dealt with in some scope of our experiment. The relationship between C and Rp were in agreement with the rule of the polymerization initiated by redox systems of DPC/starch, which were shown in figure 1 and figure 2 respectively. The slopes indicated that Rp was proportional to the 1.09 and 0.5 power of [St] and [DPC]. The equation of the polymerization rate can be written as follows: $Rp= k\cdot C^{1.09}$ (St)$C^{0.50}$ (Cu(II)).

The effect of temperature on the Rp was investigated. From the Arrhenius plot (Figure 3), the overall activation energy was calculated as 49.4kJ/mol.

Characterization of graft copolymer

The IR spectra of grafted copolymer PSt-g-starch along with pure starch is shown in figure 4. Compared with pure starch (b), the final product (a) showed a combination of both PSt's and cassava starch's characteristics. The peaks of CH stretching (2933 and 2881 cm^{-1}), CO stretching (1190–950 cm^{-1}) and the peak of OH stretching at 3444 cm^{-1} of starch were observed. Another, the peaks of PSt: CH stretching of aromatic ring (1601, 1490, 760 and 700 cm^{-1}) and C=C in aromatic ring (2000–1700 cm^{-1}) were detected too. The result indicates that PSt-g-starch copolymer was derived in the present system.

In order to identify changes in crystallinity, the X-ray diffraction spectra of starch and PSt-g-starch were measured, which are shown in figure 5. In the figure 5a, pregelatinized starch had an aculeate X-ray diffraction peak in 17.1o, even though the starch's crystallization degree was only 23%. The gelatinization reaction destroyed intermolecular hydrogen bonding of cassava starch, resulting in a decline in crystallization degree. However, the sharp peak revealed to us that there was still relative perfect crystalline part. In the figure 5b, the sharp X-ray diffraction peak disappeared. In other words, the relative perfect crystalline part was destroyed after grafting reaction. These indicated the incorporation of St has changed the crystal structure of starch.

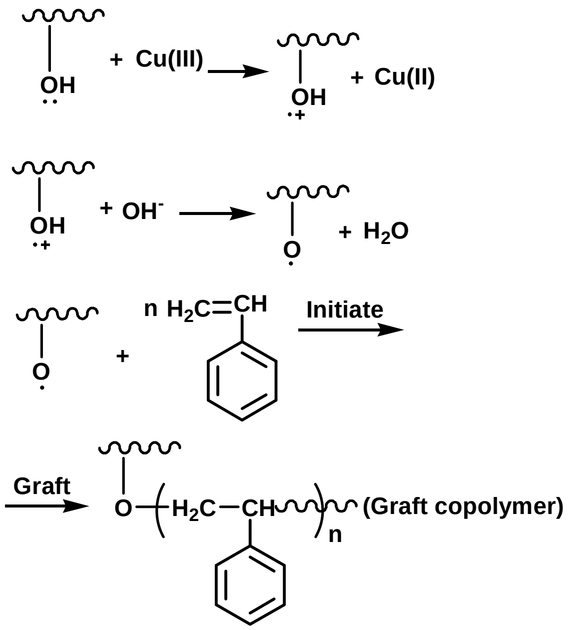
TGA thermograms of polymers are shown in figure 6. The weight loss from 50 to 110°C of starch could be the result of water evaporation and has been reported by others[15,16]. The graft copolymers showed two-step degradation process including the characteristics of both PSt and starch (Figure 6b). The first step was the degradation temperature of starch. The second step was in the degradation temperature of PSt[6]. The TGA results confirmed the achievement of graft copolymerization in the present study and also indicated the increase in thermal stability of starch with PSt-g-starch copolymer. In addition, the high percentage of weight loss (PSt 78%) confirmed the high percentage grafted and this is consisted with above experiment data.

SEM micrographs of the starch and starch-g-PSt are shown in figure 7a and b. It can be seen that the surface of starch is smooth. This can be ascribed to the destroyable starch's crystal structure, caused by gelatinization reaction. When pregelatinized starch solution was aired, the molecule chain curled with the water vaporizing from the starch and formed smooth film. The similar smooth surface can be found in the figure 7b. However, we also find some unshaped parts in the figure 7b. These unshaped parts are PSt. As we all know that the compatibility of PSt/starch blends is very poor. But we do not find any slit between the starch and PSt. On the contrary, the interface of PSt and starch is compatible.

The aforementioned features indicated the presence of PSt-g-starch copolymer. And the graft copolymer is efficient in improving the compatibility of starch and PSt.

The initiation mechanism of grafting reaction

The FTIR spectrum reveals that PSt has been grafted onto starch. It may be assumed that DPC react with the characteristic groups OH on the starch backbone to originate macro-radicals firstly and then initiate St grafting polymerization. The initiation mechanism may be shown as following:



CONCLUSION

The synthesis of polystyrene grafted cassava starch was carried out from styrene monomer and cassava starch using potassium diperiodacuprate (III)–starch redox system as an initiator. The optimum condition was St/starch Ratio of 4.7, reaction time of 3 h, [Cu(III)] of 4.38×10-3, reaction temperature of 55°C and pH of 12.35. The maximum percentage of grafting could reach 285%. The value of the overall activation energy of styrene-starch polymerization (49.4kJ/mol) and the equation of the polymerization rate were obtained, Rp= k·C1.09 (St) C0.50 (Cu(III)). The formation of the polystyrene grafted on cassava starch was investigated by FTIR technique. The results obtained from SEM, TGA and XRD confirmed the presence of polystyrene grafted on cassava starch. A mechanism was proposed to explain the generation of radicals and the initiation.

REFERENCE

[1] K.H.Lee, C.G..Cho; Polymer, **22**, 570-578 **(1998)**.

[2] G.Mino, S.J.Kaizerman; Polym.Sci., **31**, 242-243 **(1958)**.

[3] G..F.Fanta, R.C.Burr, W.M.Doane, C.Russell; R.Journal of Applied Polymer Science; **15(8)**, 2651-2660 **(1971)**.

[4] C.G..Cho, K.Lee; Carbohydrate Polymers, **48**, 125-130 **(2002)**.

[5] H.De Bruyn, E.Sprong, M.Gaborieau, G..David, J.A.Roper, R.G..Gilbert; Journal Polymer Science Part A: Polymer Chemistry, **44**, 5832-5845 **(2006)**.

[6] K.Kaewta, T.Varaporn; Carbohydrate Polymers, **73**, 647-655 **(2008)**.

[7] R.A.D.Graaf, L.P.B.M.Janssen; Polymer Engineering and Science, **40(9)**, 2086-2094 **(2000)**.

[8] Y. H.Liu, W.Q.Zhou, L.B.Bai, N.Zhao, Y.W.Liu; Journal of Applied Polymer Science, **100(5)**, 4247-4251 **(2006)**.

[9] Y.H.Liu, L.B.Bai, W.Q.Zhou, Y.W.Liu, Y.X.Li; Journal of Applied Polymer Science, **100(2)**, 1312-1317 **(2006)**.

[10] Y.H.Liu, L.B.Bai, R.Y.Zhang, Y.X.Li, Y.W.Liu; Journal of Applied Polymer Science, **96(15)**, 2139-2145 **(2005)**.

[11] L.B.Bai, Y.H.Liu; Journal of Applied Polymer Science, **103(4)**, 2376-2381 **(2007)**.

[12] P.K.Jaiswal, K.L.Yadava; Indian Journal of Chemistry, **11**, 837-839 **(1973)**.

[13] I.Y.M.Qudsieh, A.F.Razi, S.A.Muyibi, M.B.Ahmad, M.Z.A.Rahman, W.M.Z.W.Yunus; Journal of Applied Polymer Science, **94**, 1891-1897 **(2004)**.

[14] B.Singh, N.Sharma; Polymer Degradation and Stability, **92**, 876-885 **(2007)**.

[15] P.Janarthanan, W.M.Z.W.Yunus, M.B.Ahmad; Journal of Applied Polymer Science, **90**, 2053-2058 **(2003)**.

[16] S.Kiatkamjornwong, M.Sonsuk, S.Wittayapichet, P.Prasassarakich, P.Vejjanukroh; Polymer Degradation and Stability, **66**, 323-335 **(1999)**.