

The Effect of Agitation, Purge Time, and Nonsimultaneous Addition of Acid and Initiator on Xanthated Cellulose–Polystyrene Graft Copolymer

TOMASZ GRACZYK* and VLADIMIR HORNOF, *Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4*

Synopsis

Conversion to polymer and molecular weight of grafted copolymer in the graft copolymerization of styrene initiated by the xanthate method is strongly dependent on reaction conditions even in the range of agitation speed when the effect of diffusion of monomer is neglected. When sulfuric acid and hydrogen peroxide are added simultaneously after 15 min of purging with nitrogen 99.99%, conversion and molecular weight vary little with stirring speed. Both parameters decrease with increasing stirring speed when H_2SO_4 is added 1 min earlier than H_2O_2 and nitrogen is purged 15 min before starting the reaction. Both parameters increase when H_2SO_4 and H_2O_2 are added simultaneously after 60 min of purging with nitrogen. Highest conversion is observed when both reagents are added after 15 min of purging with nitrogen. Molecular weight is the highest at 310 rpm when H_2SO_4 is added 1 min earlier than H_2O_2 , and at 1100 rpm when nitrogen is purged for 60 min.

INTRODUCTION

Graczyk and Hornof have shown in several papers¹⁻⁴ that the reaction of grafting by the xanthate method is strongly affected by agitation. Maximum conversion on the conversion vs. stirring rate curve is observed followed by a drop in conversion to zero in most cases. The shape of the curves is dependent on the concentration of reagents as well as the shape of stirrer and the geometry of the reactor. An increase in conversion in a low range of agitation speed is caused by an increase in the diffusion of monomer from monomer droplets into cellulose fibers. On the other hand, a decrease in conversion at high stirring speed is caused by the termination of the reaction by oxygen in reaction medium or passing gas.

Graczyk has recently reported⁵ that removal of oxygen from swollen pulp is very difficult. At least 1–2 h of purging with oxygen-free nitrogen or argon is required as well as efficient mixing and a low concentration of pulp (not higher than 1%). On the other hand, during the grafting reaction, in which the xanthated cellulose was a part of the redox system, the concentration of

*Present address: Department of Chemistry, McGill University, 801 Sherbrook West, Montreal, Canada H3A 2K6.

oxygen fell to zero and stabilized at this level even if air was purged through the system or a high rate of stirring was applied. This phenomenon was caused by oxidation of primary sulfur radicals, created in the reaction of the xanthated group with H_2O_2 , by particles of oxygen dissolved in the reaction mixture. The role of oxygen in the secondary oxidation increased with decreasing concentration of H_2O_2 .

Grafting onto cellulose is a heterogeneous reaction. Kokta and Valade⁶ found that, in the case of grafting by the xanthate method, a 15 min soaking period before starting the reaction was sufficient to have good penetration of monomer into cellulose fibers. However, as was shown by Graczyk,⁵ removal of oxygen originally in the reaction mixture may not be complete after such a short purging time. Hasan⁷ has suggested that small quantities of oxygen are needed in the reaction mixture to create styrene-oxygen diradicals and to initiate the thermal polymerization, although again large quantities of oxygen acted as an inhibitor.

Xanthate cellulose is only stable in the form of sodium salt at $pH > 7$. Graft copolymerization is started by conversion of stable sodium salt to xanthogenic acid by an addition of acid, and in the second stage an addition of an initiator (e.g., H_2O_2). The initiator creates radicals on unstable xanthate groups in the acid medium. Unfortunately, in the acidic medium, hydrolysis of xanthated groups occurs, leading to hydroxy groups on cellulose which are less reactive to grafting. The extent to which such cleavage (and therefore loss of the more reactive sites on cellulose) occurs is probably affected by how much sooner H_2SO_4 is added before H_2O_2 . Having fewer active sites available on the cellulose substrate could affect the molecular weight of grafted polystyrene.

The purpose of this paper is to determine how the rate of stirring influences the conversion and molecular weight for reactions with the simultaneous and nonsimultaneous addition of H_2SO_4 and H_2O_2 , under different purging times.

EXPERIMENTAL

Never-dry pulp (Tembec Inc.) was used as the grafting substrate. Styrene (Scientific Polymer Products, Inc.) was purified by vacuum distillation and the middle fraction was stored in a refrigerator prior to use. All other chemicals were reagent grade.

Graft Copolymerization

Graft copolymerization was carried out in a 1-L glass reactor equipment with a Teflon paddle stirrer, as described previously.⁴ Stirrer speeds were measured with a photoelectric tachometer.

The emulsion method of xanthation gave $y = 11$ (i.e., approximately 11 xanthate groups per 100 glucose units) as has been described previously.⁸

The reactions were carried out under positive pressure of nitrogen 99.99% which was purged at the rate of 12–15 L/h. Different methods of adding initiator reagents and different purging times were applied.

Method 1: H_2SO_4 was added at 14 min, and H_2O_2 added at 15 min; purging time was 15 min.

Method 2: H_2SO_4 and H_2O_2 were added simultaneously after a 15 min purging period.

Method 3: H_2SO_4 and H_2O_2 were added simultaneously after a 60 min purging period.

Homopolymer from the grafted product was removed by a Soxhlet extraction of 3–4 g samples of products with acetone for 24 h.

Separation of Grafted Polystyrene from Cellulose

Graft polystyrene was separated from cellulose backbone by a modified method published by Nakamura.⁹ Thus, approximately 1.5 g of graft copolymer was boiled for 2 h in 100 mL of mixture of 50:50 acetic acid/acetic anhydride to which 0.5 mL of 96% H_2SO_4 was added to degrade the cellulose into glucose and other residue. The precipitated polystyrene was filtered and washed twice with about 10 mL of glacial acetic acid to remove degraded cellulose. Acetic acid residue was washed out with water until the characteristic odor of acetic acid could not be detected. For the complete removal of acetic acid the polymer was washed twice with about 10 mL of methanol and later was dried overnight in a vacuum oven at 60°C. Undissolved polystyrene was yellowish white in color, indicating little or no degradation.

Intrinsic viscosities were determined at 30°C in benzene using an Oswald-Fenske viscometer. The average molecular weights were calculated by using May's equation for polydisperse polystyrene¹⁰:

$$\text{MW} = 167,000 [\eta]^{1.37}$$

RESULTS AND DISCUSSION

Conversion of Styrene

It has been found by Graczyk⁵ that the low rate of grafting at lower agitation speeds is caused by agglomeration of monomer molecules to bigger particles and, as a result, decreased diffusion of monomer to active centers. Above 300 rpm, the effect of monomer diffusion diminishes (creation of vortex in reaction mixture) and any further increase in conversion is caused by a higher rate of oxygen diffusion to active centers from the reaction mixture or passing gas.

Thus, the effect of simultaneous and nonsimultaneous addition of reagents and purging time on conversion and molecular weight was studied above 300 rpm, mostly at two stirring speeds: 310 and 1100 rpm. The latter speed was arbitrarily selected as being high enough for purpose of comparison but low enough to prevent significant shearing.

Figure 1 illustrates the effect of the stirring rate on conversion for the three methods of initiation of reaction. When the acid and hydrogen peroxide were simultaneously added after 15 min of purging with nitrogen 99.99%, the conversions were almost equal (86.8% at 310 rpm and 83.3% at 1100 rpm). The stirring rate did not greatly affect the conversion in the studied range and this may be the case over a wide range of stirring speeds, provided that shearing of

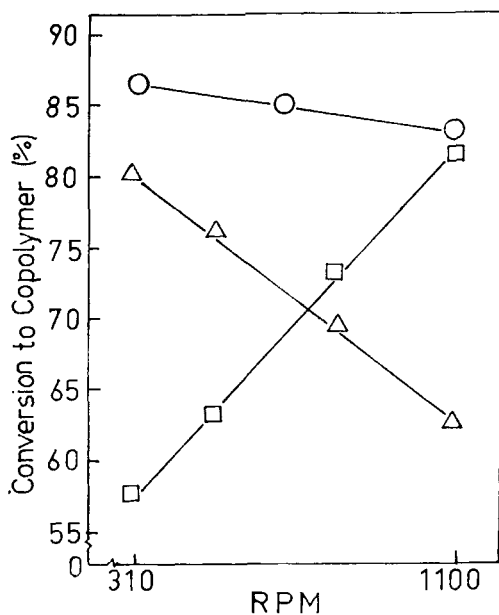


Fig. 1. Conversion to polymer as a function of stirring speed: [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; [H₂O₂] = 0.0245 mol/L; (Δ) method 1; (○) method 2; (□) method 3.

polymer remains negligible and the oxygen content remains within a range that effectively initiates creation of styrene–oxygen diradicals and oxidation of sulfur macroradicals but does not significantly inhibit polymerization.

When adding acid after 14 min and the initiator after 15 min of purging with nitrogen (Method 1), the conversion decreased with increasing stirring rate (80.1% at 310 rpm; 62.8% at 1100 rpm). The conversion was also seen to be slightly less than that found when adding reactions simultaneously after 15 min of purging and stirring rate of 310 rpm. The 1-min lag between the addition of the reactants increased the neutralization of xanthate groups and, therefore, increased the cleavage of carbon disulfide from xanthated cellulose at a higher stirring rate. This, combined with a higher oxygen content (and therefore a higher termination by oxygen), led to a lower amount of polymer being formed.

The above results show that high stirring speed has a tremendous effect on conversion when H₂SO₄ is added earlier than H₂O₂, e.g., 1 min earlier. Although one can presume, on the basis of a vortex creation in the reaction mixture (310 rpm), that efficient mixing of reagents occurs, it is not efficient to instant neutralization and later hydrolysis of the xanthate groups of cellulose. At 1100 rpm nearly full hydrolysis of xanthate groups occurs immediately and the reaction slows considerably.

When adding acid and an initiator simultaneously after 60 min of purging, the conversion becomes higher with increasing stirring rate (57.4% at 310 rpm; 82.2% at 1100 rpm). At the lower stirring rate of 310 rpm, the oxygen concentration was lower to the extent that determined the rate of creation of styrene–oxygen diradicals and secondary oxidation of sulfur macroradicals. The diffusion of oxygen into the cellulose fibers increased with an increase in

stirring speed, and, consequently, conversion was higher. It is notable that, at the higher stirring speed of 1100 rpm, the conversion was almost the same as when acid and the initiator were simultaneously added after 15 min of purging with nitrogen.

Molecular Weight of Grafted Polystyrene

No maximum of conversion was observed in the studied range of stirring speed for three different reaction conditions. Thus, the data from two points are sufficient to explain the effect of stirring on molecular weight as is shown in Figure 2. The results seem analogous with the conversion results in that increases or decreases in molecular weight due to stirring were similarly dependent on the purging time and time of adding reactants.

Simultaneous addition of reactants after 15 min of purging with nitrogen (Method 2) showed little dependence of the molecular weight of polystyrene copolymer on the stirring speeds (38,000 at 310 rpm; 34,500 at 1100 rpm). This suggests that the rate of neutralization and, therefore, the amount of cleavage of carbon disulfide was not very dependent on the stirring speed as acid and initiator penetrated to the cellulose fibers at about the same rate. Molecular weight changed little as the number of active sites on cellulose changed little. There was also little change in oxygen termination effect.

When adding acid after 14 min, and initiator after 15 min of purging with nitrogen, the molecular weight of grafted polystyrene decreased appreciably with higher stirring speed (48,000 at 310 rpm; 29,200 at 1100 rpm). At the lower speed, during the 1-min lag period, there was greater neutralization of xanthate groups by H_2SO_4 and higher cleavage of carbon disulfide. Since

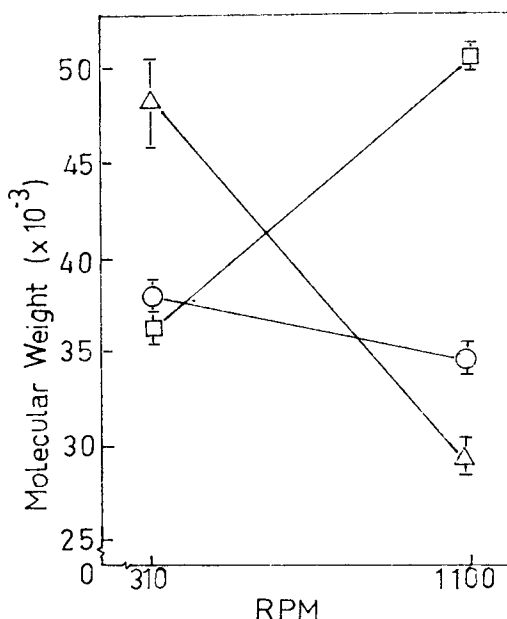


Fig. 2. Molecular weight of graft polystyrene as a function of stirring speed: [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; [H_2O_2] = 0.0245 mol/L; (Δ) method 1; (\circ) method 2; (\square) method 3.

there were less active sites available on the cellulose for the same amount of monomer (and only a small decrease in conversion as compared to simultaneous addition at 15 min), the molecular weights were higher. The lower molecular weight at the higher stirring speed can be explained by increased termination of polymerization by an increased oxygen content.

When adding acid and an initiator simultaneously after 60 min of purging with nitrogen, the molecular weight increased with increasing stirring speed (34,500 at 310 rpm; 50,350 at 1100 rpm). Also, at 310 rpm, the molecular weight after 60 min of purging (34,500) was found to be slightly less than that found for simultaneous addition of reactants at 15 min (38,000). Furthermore, the molecular weight found at 1100 rpm and 60 min of purging with nitrogen (50,350) was only slightly greater than that found after the addition of H_2SO_4 at 14 min, H_2O_2 at 15 min and 310 rpm (48,100).

Grafting by the xanthate method is a complex reaction in which primary sulfur radicals are further oxidized by H_2O_2 or by oxygen dissolved in the reaction mixture. Complex equilibrium between initiation species and the relative rate of initiations could have influence on the apparent rate of initiation and, consequently, on molecular weight. Furthermore, the concentration of oxygen is still very low in comparison with the two other methods and the rate of termination by oxygen is low. Consequently, molecular weight is the highest.

CONCLUSIONS

The conversion of styrene to polymer and molecular weight of polystyrene grafted onto xanthated cellulose is dependent on the method of addition of reagents and purging time.

Presented results clearly show that it is not necessary to completely remove oxygen from the reaction mixture in the reaction of grafting onto xanthated cellulose. High conversion and relatively high molecular weight are obtained when the amount of oxygen is controlled in the reaction mixture. Furthermore, reproducibility of results is very good if the amount of oxygen is kept constant. However, one has to take into account that experimental data will be strongly dependent on reaction conditions in every case. Comparative results will be doubtful unless all parameters of the reaction are known.

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