

Graft Copolymerization of Methacrylic Acid onto Guar Gum, Using Potassium Persulfate as an Initiator

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Received 21 April 2005; accepted 26 September 2005

DOI 10.1002/app.23325

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Graft copolymerization of methacrylic acid (MAA) onto guar gum (GG) was carried out by free radical initiation mechanism by using potassium persulfate (PPS) as an initiator. It was found that % grafting, grafting efficiency, and % conversion were all dependent on the concentration of PPS, MAA, reaction temperature, and reaction time. Using PPS, the maximum % grafting was ascertained to be 241 at the optimum conditions of 60°C reaction temperature, 3 h of reaction time, 1.1 mmol of PPS, and 0.058 mol of MAA.

Plausible mechanism for grafting reaction was suggested. The graft copolymer formed was characterized by Fourier transform infrared and differential scanning calorimetry. The graft copolymer formed could find applications in drug delivery. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 618–623, 2006

Key words: guar gum; graft copolymers; methacrylic acid; polysaccharides; free radical polymerization; initiators

INTRODUCTION

Graft copolymerization of monomers has been the most widely used method of chemical modification of natural¹ and synthetic polymers.² Among the many naturally occurring polymers, guar gum (GG) is a branched polygalactomannan isolated from the seeds of leguminous herbs.³ It is a linear β (1→4) mannose to which α (1→6) galactopyranoside single subunits are attached as side chains.⁴ There are nearly 1.5–2 mannose residues for every galactose residue. The ratio of galactose to mannose and degree of branching is found to vary from species to species. GG is a nonionic polydisperse rod-shaped polymer consisting of about 10,000 residues. GG is used in pharmaceutical, food processing, textile, and paper industries because of its solubility in water and high viscosity of the aqueous solutions.⁵ However, its viscosity is difficult to control because of its quick biodegradation,⁶ making it unsuitable for use in its natural form. Enzymatic hydrolysis of the galactose side chains take place through legume α -galactosidase, which is widely found in colon.⁷

Grafting has been used to modify physicochemical properties of the polymers for applications in agriculture, biomedical, drug delivery, etc. Grafting can be

carried out by various techniques, using chemical initiator, γ -radiation, microwave irradiation, etc. Number of studies^{8–10} have been done on graft copolymerization of vinyl monomers as methyl methacrylate on curdlan, *N*-vinyl pyrrolidone on gelatin, methyl acrylate (MA) on potato starch, MA on sago starch, vinyl pyrrolidone on chitosan, etc. The use of persulfate radicals for the grafting of vinyl monomers on natural polymers has been studied^{11,12} to get the desired grafting ratio, wherein it was shown that reaction could occur between KSO_4 radical and polysaccharide to form radicals on the polymer backbone directly. Lokhande et al.¹³ reported the graft copolymerization of acrylonitrile on GG through (γ -radiation. Recently, grafting of polyacrylonitrile¹⁴ on GG was successfully done by using microwave irradiation in the absence of initiator.

Modification of GG by grafting onto water-soluble vinyl monomers was reported¹⁵ to offer the desirable properties. MAA has been used to synthesize pH-sensitive polymers¹⁶ for drug delivery applications. Singh et al.¹⁷ reported that grafting of polyacrylamide on polysaccharides improved its flocculating characteristics. The studies¹⁰ on physical properties of acrylamide graft copolymer onto cellulose or GG revealed an improvement in properties such as flocculation, solubility, thermal stability, binding strength, and water retention. Soppimath et al.¹⁸ synthesized the graft copolymer of polyacrylamide with GG to improve the physicochemical properties of GG and developed microspheres for controlled release applications. In this article, we report the grafting reaction of MAA onto GG and investigate the effect of reaction temperature, time, initiator concentration, monomer concentration

This paper is CEPS Communication No. 77.

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Contract grant sponsor: University Grants Commission (UGC), New Delhi, India; contract grant number: F1-41/2001/CPP-II.

as well as different initiators on grafting parameters. To the best of our knowledge, it is the first of its kind of study reported in the literature by using PPS as an initiator over ceric ammonium nitrate (CAN) to achieve grafting of MAA onto GG.

EXPERIMENTAL

Materials and methods

Guar gum (GG), potassium persulfate (PPS), ceric ammonium nitrate (CAN), acetone, and methanol were all purchased from s.d. Fine Chemicals, Mumbai, India. MAA monomer was obtained from Himedia Laboratories, Mumbai, India. Throughout the experiment, double distilled water was used.

Graft copolymerization

The graft copolymer derived from MAA and GG was prepared by the free radical polymerization. Briefly, 0.5 g of GG was dispersed in 30 mL of water and dissolved overnight under constant stirring condition in a 250 mL round-bottom flask. Then, 0.029, 0.058, or 0.08 mol of MAA were mixed with 10 mL of water, added to GG solution, and stirred for 1 h. A quantity of initiator equivalent to 0.73, 1.14, or 1.8 mmol was dissolved in 10 mL of water and was added to the above solution. Polymerization was carried out at 40, 50, or 60°C under continuous purging of nitrogen gas for 60, 120, or 180 min in a thermostatic water bath under constant stirring. After complete polymerization, the product was cooled by running under tap water and poured into excess acetone to induce precipitation. The graft polymer (solid) was washed several times with methanol/water (80 : 20, v/v) mixture¹⁹ to remove the homopolymer formed in the grafting reaction and was vacuum dried at 40°C to a constant weight. The % grafting (% G), grafting efficiency (% GE), and % conversion (% C) were calculated^{19–21} by using the following equation:

$$\% \text{ Grafting (\% G)} = \left(\frac{W_1 - W_0}{W_0} \right) 100 \quad (1)$$

% Grafting efficiency (% GE) =

$$\left(\frac{W_1 - W_0}{W_2} \right) 100 \quad (2)$$

$$\% \text{ Conversion (\% C)} = \left(\frac{W_1}{W_2} \right) 100 \quad (3)$$

where, W_0 , W_1 , and W_2 denote the weight of GG, graft copolymer, and monomer, respectively.

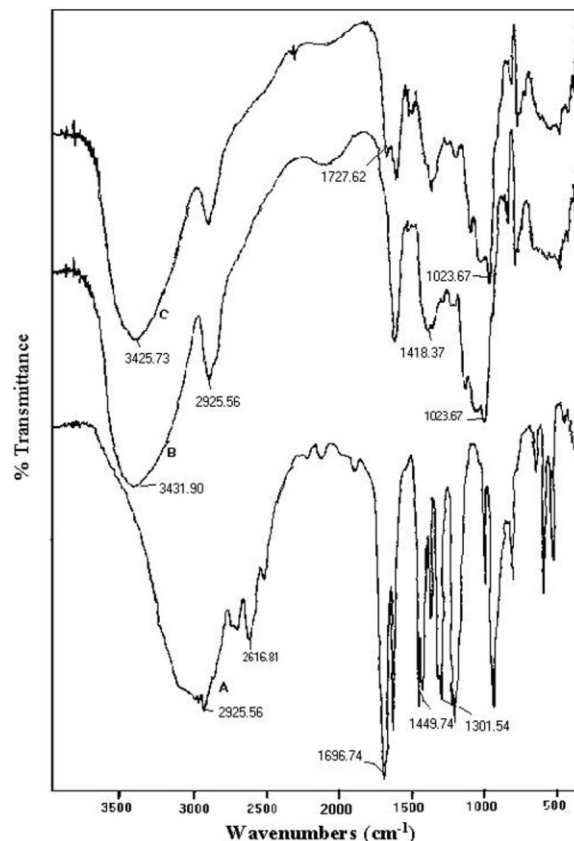


Figure 1 FTIR spectra of (A) MAA, (B) GG, and (C) MAA-g-GG.

FTIR analysis

GG, MAA-g-GG, and MAA were analyzed by FTIR to confirm the grafting reaction by using KBr pellet technique. In case of MAA, NaCl cell was used. Spectra were scanned on a Model Impact 410, (Nicolet, WI) in the range of 400 and 4000 cm^{-1} .

Differential scanning calorimetric analysis

Differential scanning calorimetry (DSC) experiments were performed on GG and MAA-g-GG by using DSC SP, (Rheometric Scientific, Surrey, UK) thermal analyzer. Samples were heated at the rate of 10°C/min from ambient temperature to 500°C under an inert nitrogen atmosphere at the flow rate of 10 mL/min.

RESULTS AND DISCUSSION

FTIR analysis

Grafting of MAA on GG was confirmed by FTIR studies. FTIR spectra of (A) MAA, (B) GG, and (C) MAA-g-GG are displayed in Figure 1. FTIR spectrum of GG exhibits characteristic absorption bands at 3431 and 2925 cm^{-1} because of O—H stretching vibrations of the polymer associated with C—H stretching vibrations. Additional characteristic absorption bands of

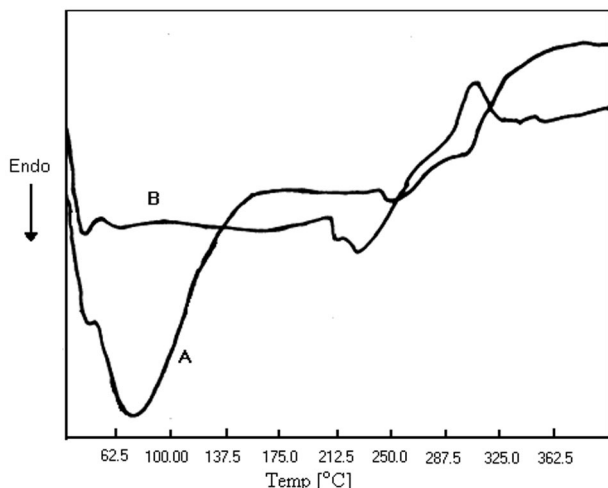


Figure 2 DSC thermograms of (A) GG and (B) MAA-g-GG.

GG appear at 1418 and 1023 cm^{-1} because of C—H bending and O—H bending vibrations, respectively. In the FTIR spectrum of MAA, we have observed characteristic absorption bands at 2616 and 1696 cm^{-1} , which are assigned to carboxylic acid groups and carbonyl stretching vibrations, respectively. Additional characteristic absorption bands of MAA appear at 1449 and 1301 cm^{-1} because of C—C multiple bond stretching and C—H bending vibrations, respectively. The appearance of a new characteristic absorption band at 1727 cm^{-1} in the FTIR spectrum of the MAA-g-GG because of carbonyl stretching vibrations of carboxylic acid groups along with other bands with weak intensity indicate the formation of graft copolymer. Similar findings were observed by Kang et al.²²

There is no characteristic absorbance band in this region (1770–1735 cm^{-1}) because of ester moiety and no possibility of ester formation in the grafting reaction, which could be an effective evidence for the absence of formation of esters, and hence, formation of any esters is excluded. Further, the formation of MAA-g-GG is supported by a weak intensity band at 3425 cm^{-1} because of O—H stretching vibrations as compared to FTIR spectrum of the neat GG (3431 cm^{-1} (s)). The weakening of the band is due to utilization of some -OH groups of GG during the formation of the graft copolymer.

Differential scanning calorimetric analysis

DSC is a useful technique to explain the formation of graft copolymers. DSC curves of GG (A) and graft copolymer (B) are reproduced in Figure 2. GG showed an endothermic transition at about 248°C, whereas the graft copolymer exhibited two endothermic transitions, one at 230°C and another at ~320°C. The new endothermic transition at 320°C in the thermogram of DSC of the graft copolymer may be due to enhanced interaction between carbonyl groups of the grafted

copolymer and hydroxyl groups of GG. These results could confirm the grafting of MAA onto GG.

Graft copolymerization mechanism

Graft copolymerization was carried out by free radical initiated process. Several reports have been published in the literature^{23,24} on graft copolymerization mechanism. The probable reaction mechanism of the present study is given in Figure 3. When PPS is used as an oxidizing initiator, grafting reaction is facilitated due to the generation of free radical site by abstracting hydrogen atom from the -OH group of the polymer (GG). Free radicals formed could then react with the double bond of the vinyl monomer, resulting in a covalent bond between the monomer and GG to propagate the chain. However, termination takes place by a combination of two radicals. When CAN is used as an initiator, ceric ion reacts with GG to form GG–ceric complex. The Ce^{4+} ion in the complex can then be reduced to Ce^{3+} ion with the release of a proton and a subsequent formation of a free radical on the backbone of GG. These free radicals could then react with the monomer to initiate graft copolymerization. Termination of the graft copolymer takes place through the combination of radicals. Similar reaction mechanism was also reported earlier by Yoshida et al.²⁴

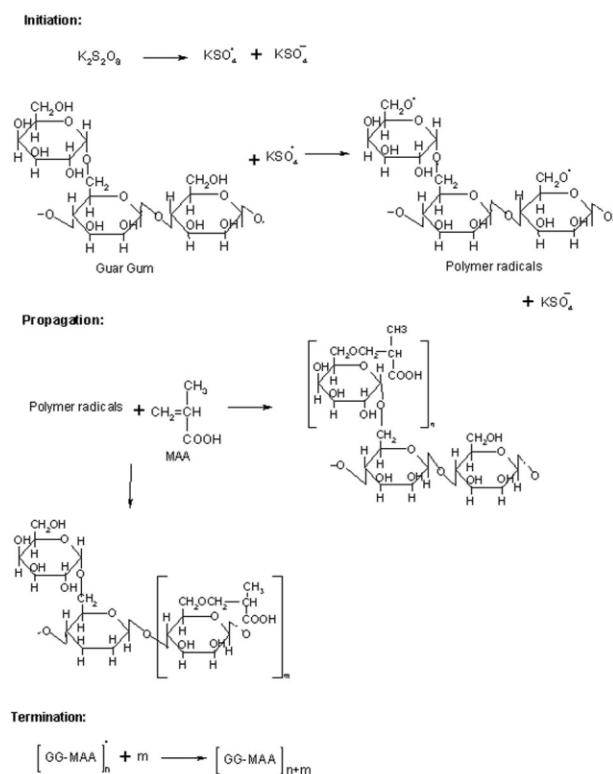


Figure 3 Reaction mechanism for the grafting of MAA onto GG by using PPS.

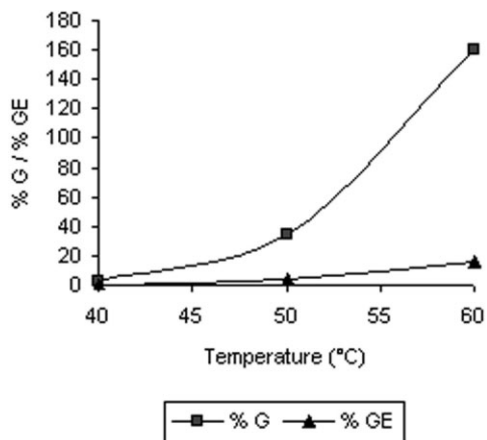


Figure 4 Effect of reaction temperature on the grafting of MAA onto GG, prepared by using PPS as initiator. Other reaction conditions: 0.5 g GG, 0.058 mol MAA, 1.14 mmol PPS, and 2 h reaction time.

Effect of temperature

Temperature is vital in determining the extent of grafting. In general, grafting yield increases with increase in temperature until a limiting value is reached. However, increase of temperature may lead to several effects on grafting such as (a) swelling of GG to a larger extent, (b) increase in solubility of the monomer, (c) increase in monomer diffusion to the grafting sites, (d) easy decomposition of the initiating redox system, (e) enhancement of the rate of initiation and propagation, and (f) increase in the rate of termination. Note that factors (a) to (e) could increase grafting, while factor (f) may have the reverse effect on grafting.

In the present study, effect of temperature on grafting was investigated at 40, 50, and 60°C, keeping other conditions constant (see Fig. 4). It is seen that increase in temperature from 40 to 60°C causes a significant effect on grafting as shown in Table I. At low temperature, %G was low, which increased with increase in temperature. This could be due to a slow reaction between PPS and the substrate. With increasing temperature, because of higher collisions between GG and PPS, an increase in GG macroradicals is possible, thereby enhancing the graft polymerization.

Effect of reaction time

The results of the effect of reaction time on grafting are shown in Table II. The maximum %G was found to be

TABLE I
Effect of Temperature on Grafting

Temperature (°C)	% Yield	% Grafting	% Grafting efficiency	% Conversion
40	9.22	2.50	0.24	10.13
50	12.31	33.95	3.43	13.56
60	23.84	160.20	16.16	26.24

TABLE II
Effect of Reaction Time on Grafting

Time (min)	% Yield	% Grafting	% Grafting efficiency	% Conversion
60	10.45	13.83	1.4	11.51
120	23.84	160.20	16.16	26.24
180	31.12	241.58	24.21	34.24

241, which was observed at 180 min. The %G and %GE have increased with increase in reaction time from 60 to 180 min. In the present study, no leveling off effect of %G or %GE was observed over the range of reaction time studied (see Fig. 5.) Earlier,¹¹ it was reported that a leveling off of such parameters, could be attributed to a decrease in monomer and catalyst concentrations as well as reduction in the number of sites available for grafting.

Effect of initiator concentration

Effect of initiator concentration was studied by varying the concentration of PPS while keeping other reaction conditions constant. As shown in Figure 6, on increasing the concentration of PPS, % G and % GE initially increased, but any further increase in concentration showed a negative effect. The increase in % G may be due to an increase in macroradicals, since an increase in concentration facilitates more of PPS free radicals to attack the saccharide unit of GG. This would generate more GG macroradicals and more active sites to react with MAA. By further increasing the amount of PPS (>1.1 mmol), the concentration of OSO_3K radicals would increase, which could help to initiate the polymerization of MAA thus, resulting in a decrease of % G and % GE.

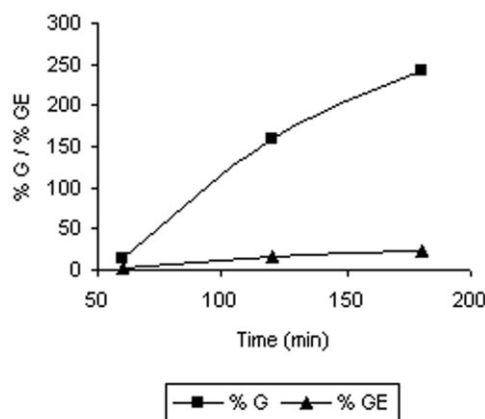


Figure 5 Effect of reaction time on grafting of MAA onto GG prepared by using PPS as initiator. Other reaction conditions: 0.5 g GG, 0.058 mol MAA, 1.14 mmol PPS, and 60°C reaction temperature.

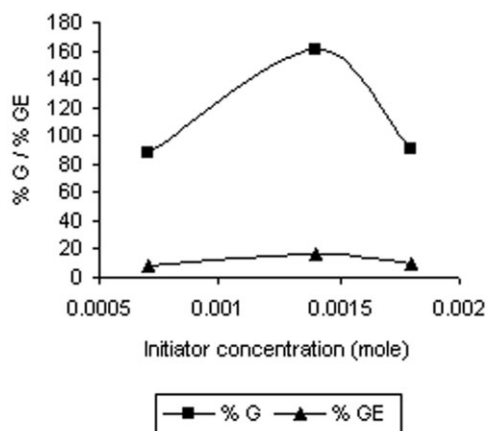


Figure 6 Effect of initiator concentration on the grafting of MAA onto GG prepared by using PPS as initiator. Other reaction conditions: 0.5 g GG, 0.058 mol MAA, 60°C reaction temperature, and 2 h reaction time.

In case of grafting initiated by a chemical initiator, the extent of grafting increases with initiator concentration up to a certain limit, beyond which grafting no longer increases. This could be ascribed to the decay of macroradicals.²⁵ Effect of PPS concentration on grafting was studied in the range of 0.07–1.84 mmol. The highest %G and %GE were obtained at 1.14 mmol, which attained maximum of 160 and 16, respectively. Above the 1.14 mmol PPS concentration, a decrease in grafting was observed. These results are summarized in Table III. This phenomenon may be due to the efficiency of PPS to participate in the termination reaction of the growing grafted chain as well as homopolymerization.²⁶

Initial increase in grafting with an increase in catalyst concentration may be due to catalyst exhaustion or an increase in the rate of grafting at low concentration.²⁷ The decrease in grafting parameters at higher initiator concentrations could be due to a decrease in the rate of polymerization. However, a higher persulfate ion concentration gives an increase in the number of GG radicals that terminate prior to monomer addition. Another factor contributing to the decrease in grafting levels at higher initiator concentration is the increase in homopolymer formation, which competes with the grafting reaction for the available monomer.

TABLE III
Effect of Initiator Concentration on Grafting

Initiator concentration (mmol)	% Yield	% Grafting	% Grafting efficiency	% Conversion
0.73	17.25	88.50	8.91	18.99
1.14	23.84	160.20	16.16	26.24
1.8	17.40	91.22	9.13	19.14

TABLE IV
Effect of Monomer Concentration on Grafting

Monomer (mol)	% Yield	% Grafting	% Grafting efficiency	% Conversion
0.029	20.77	23.62	4.77	24.97
0.058	23.84	160.20	16.16	26.24
0.08	15.12	135.01	9.28	16.16

Effect of monomer concentration

It is well known that the initiation of graft copolymerization by free radical mechanism involves the formation of free radicals, which can react with the monomer to initiate graft copolymerization. However, its efficiency depends upon the concentration of monomer present, i.e., larger the concentration of monomer, more favored will be the reaction between free radicals and the monomer, which triggers the grafting process. Another important parameter to assess the effect of monomer concentration on grafting is the gel effect, which arises from the solubility of homopolymer in the monomer itself. A consequence of this gel effect is a higher monomer concentration. As a result of this effect, termination rate would decrease. Besides this, the gel effect helps in swelling the GG, which ultimately facilitates the diffusion of monomer to the active sites on GG, thereby enhancing the grafting reaction. Even though grafting increases with increase in concentration of monomer, there is always a limitation beyond which grafting is not favored. One of the reasons could be that swelling of the base polymer at a higher monomer concentration is not favorable for grafting.²⁶

The effect of monomer concentration on grafting is presented in Table IV. The % grafting and grafting efficiency increased with an increase in monomer con-

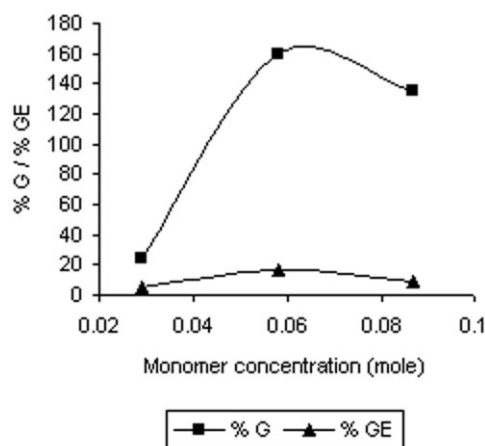


Figure 7 Effect of monomer concentration on the grafting of MAA onto GG prepared by using PPS as initiator. Other reaction conditions: 0.5 g of GG, 60°C reaction temperature, 1.14 mmol PPS, and 2 h reaction time.

TABLE V
Effect of Initiator Type on Grafting

Initiator	Concentration (mmol)	% Yield	% Grafting	% Grafting efficiency	% Conversion
CAN	1.14	10.86	21.0	2.06	11.94
PPS	1.14	23.84	160.20	16.16	26.24

centration from 0.029–0.058 mol of MAA. The %grafting and grafting efficiency reached the maximum values of 160 and 16, respectively, at the monomer concentration of 0.058 mol, as shown in Figure 7. This effect is more pronounced at higher monomer concentration, thus termination rate is decreased. However, at higher concentration of the monomer (i.e. beyond 0.058 mol), % grafting and grafting efficiency decreased due to the formation of higher percentage of the homopolymer in the growing grafted chain. It is expected that swelling of the base polymer at higher monomer concentrations is not favorable for grafting.

Effect of initiator

Two different initiators, viz., PPS and CAN, were chosen to study their effect on grafting. Experiment was conducted at the same molar concentration of initiators by keeping other reaction conditions constant. These results are presented in Table V. It was observed that in case of PPS, % was 160, while for CAN it was only 21. This implied that PPS was a more efficient initiator than CAN in grafting MAA onto GG.

CONCLUSIONS

In the present study, guar gum was successfully grafted by methacrylic acid using PPS and CAN initiators. Reaction conditions such as temperature, time, initiator concentration, and monomer concentration have shown an influence on grafting. The % grafting up to 160 and 21 were achieved by using PPS and CAN, respectively. The maximum % grafting was possible by using PPS at 60°C, 3 h of reaction time, 1.1 mmol of PPS, and 0.058 mol of MAA. It was also proved that PPS was the most efficient initiator than CAN in the formation of graft copolymer, i.e. MAA-g-GG.

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