

Supporting Information

Synthesis and characterization of acrylic acid-g-(k-carrageenan) copolymer and study of its application

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Optimization of Reaction Conditions:

Effect of Peroxymonosulphate Concentration

The concentration of peroxymonosulphate has been varied from 8.0 to 22.0 $\times 10^{-3}$ mol dm^{-3} for studying its effect on grafting ratio, grafting efficiency, add on, conversion, homopolymer and rate of grafting and results are summarized in Table S1. It has been observed that the grafting parameters of acrylic acid on carrageenan increased on increasing the concentration of peroxymonosulphate upto 14.0 $\times 10^{-3}$ mol dm^{-3} after that these parameters decreased. The increment in grafting parameters is due to the progressive reduction of peroxymonosulphate by mercaptosuccinic acid producing large number of free radicals thereby enhance all the grafting parameters except homopolymer and decrement in grafting parameters are due to oxidative termination of growing grafted chains by free radicals.

Table- S1: Effect of Peroxy monosulphate Concentration

[MSA] = 32.0×10^{-4} mol dm^{-3} ; $[\text{H}^+] = 15.0 \times 10^{-4}$ mol dm^{-3} ; [Acrylic acid] = 18.0×10^{-2} mol dm^{-3} ; [CGN] = 1.0 g dm^{-3} ; Time = 120 min.; Temp. = 40°C.

[PMS] $\times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H	Rg $\times 10^6$ mol $\text{l}^{-1} \text{s}^{-1}$
8.0	106.0	43.8	51.5	18.7	56.2	2.1
11.0	120.0	47.2	54.5	19.6	52.9	2.4
14.0	510.4	81.8	83.6	48.1	18.2	10.2
16.0	480.0	80.8	82.6	45.8	19.2	9.6
18.0	320.0	53.9	76.2	45.7	46.1	6.4
20.0	284.2	69.6	74.0	31.5	30.4	5.7
22.0	261.8	67.3	72.3	30.0	32.7	5.2

Effect of Mercaptosuccinic acid Concentration

The effect of mercaptosuccinic acid on grafting Parameters has been studied by varying the concentration of mercaptosuccinic acid from 14 to 48 $\times 10^{-4}$ mol dm⁻³. From Table S2, it has been observed that all the grafting parameters increased on increasing the concentration of mercaptosuccinic acid up to 32 $\times 10^{-4}$ mol dm⁻³ except homopolymer, which showed the opposite trend after that it decreased. The increment in %G, %E, %A, %C and Rg might be due to the increase in number of free radicals production *in-situ* and decrement in grafting parameters might be due to much formation of homopolymer than graft copolymer, which increases the viscosity of the medium due to that movement of dormant chains of graft copolymer are restricted, ultimately, their formation decreases.

Table- S2: Effect of Mercaptosuccinic acid Concentration

[PMS] = 14.0 $\times 10^{-3}$ mol dm⁻³; [H⁺] = 15.0 $\times 10^{-4}$ mol dm⁻³; [Acrylic acid] = 18.0 $\times 10^{-2}$ mol dm⁻³; [CGN] = 1.0 g dm⁻³; Time = 120 min.; Temp. = 40°C.

[MSA] $\times 10^4$ mol dm ⁻³	%G	%E	%A	%C	%H	Rg $\times 10^6$ mol l ⁻¹ s ⁻¹
14.0	300.0	71.4	75.1	32.4	28.6	6.0
16.0	240.0	64.9	70.6	28.5	35.1	4.8
32.0	510.0	81.8	83.6	48.1	18.2	10.2
36.0	428.0	78.9	81.06	41.8	21.1	8.6
40.0	398.0	77.4	79.9	39.6	22.6	8.0
44.0	276.0	69.0	73.4	30.9	31.1	5.5
48.0	224.0	65.7	69.1	27.0	35.1	4.4

Effect of Acrylic acid Concentration

The effect of acrylic acid on grafting parameters has been studied by varying the concentration of acrylic acid from 8.0 to 24.0 $\times 10^{-2}$ mol dm⁻³ and results are summarized in Table S3. It is observed that on varying the concentration of acrylic acid from 8.0 to 24.0 $\times 10^{-2}$ mol dm⁻³ %G, %E, %A and Rg increased up to 18.0 $\times 10^{-2}$ mol dm⁻³ but %H decreased and beyond this concentration of acrylic acid %G, %E, %A and Rg have been found to decrease. However, conversion decreased continuously as the concentration of acrylic acid increases. The increment in %G, %E, %A and Rg might be due to greater availability of acrylic acid at the close proximity of the Carrageenan backbone. The monomer molecule at the close proximity of the reaction site becomes acceptor of the carrageenan radicals resulting in chain initiation. Thereafter, monomer molecule became free radical donor to the neighbouring molecules, in this way grafted chains grow. The decrease in %G, %E, %A and

R_g could be explained in terms of increase in the viscosity of the reaction medium due to preferential formation of polyacrylic acid at higher concentration of monomer.

Table- S3: Effect of Acrylic acid Concentration

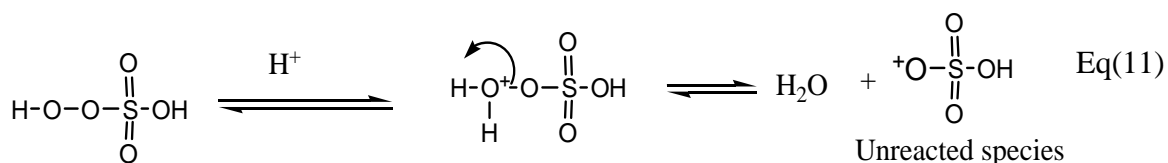
[PMS] = $14.0 \times 10^{-3} \text{ mol dm}^{-3}$; [MSA] = $32.0 \times 10^{-4} \text{ mol dm}^{-3}$; [H⁺] = $15.0 \times 10^{-4} \text{ mol dm}^{-3}$;

[CGN] = 1.0 g dm^{-3} ; Time = 120 min.; Temp = 40°C.

[Acrylic acid] $\times 10^2 \text{ mol dm}^{-3}$	%G	%E	%A	%C	%H	R _g $\times 10^6$ $\text{mol l}^{-1} \text{ s}^{-1}$
8.0	330.0	70.3	75.4	33.5	29.7	6.1
12.0	336.0	73.7	77.4	35.8	26.3	6.8
16.0	380.0	74.8	77.7	36.2	25.2	7.0
18.0	510.0	81.8	83.6	48.1	18.2	10.2
20.0	505.0	69.0	73.7	31.3	31.0	5.6
22.0	494.0	71.3	75.0	32.4	28.7	6.0
24.0	450.0	70.0	74.4	32.0	30.0	5.8

Effect of Hydrogen Ion Concentration

The graft copolymerization has been carried out at different concentration of hydrogen ion i.e. from 5.0 to $25.0 \times 10^{-4} \text{ mol dm}^{-3}$ and results are shown by Fig. S1 and S2. It has been observed that on increasing the hydrogen ion concentration from 5.0 to $15.0 \times 10^{-4} \text{ mol dm}^{-3}$ %G, %C, %E, %A and R_g increased. Thus, from the result it can be concluded that hydrogen ion play an important role with this redox pair in terms of grafting parameters. The increment in grafting parameters is due to the much formation of protonated species which accelerates the grafting. The decrement in grafting parameters beyond $15.0 \times 10^{-4} \text{ mol dm}^{-3}$ can be explained on the basis of fact that in the acidic medium peroxy monosulphate protonated to produce protonated species H_3SO_5^+ with increasing the hydrogen ion concentration (eq. 11). Thus on increasing the hydrogen ion concentration, much formation of protonated species took place due to which quantum of primary free radical decreased thereby %G, %E, %A, %C, R_g decreased and homopolymer increased.



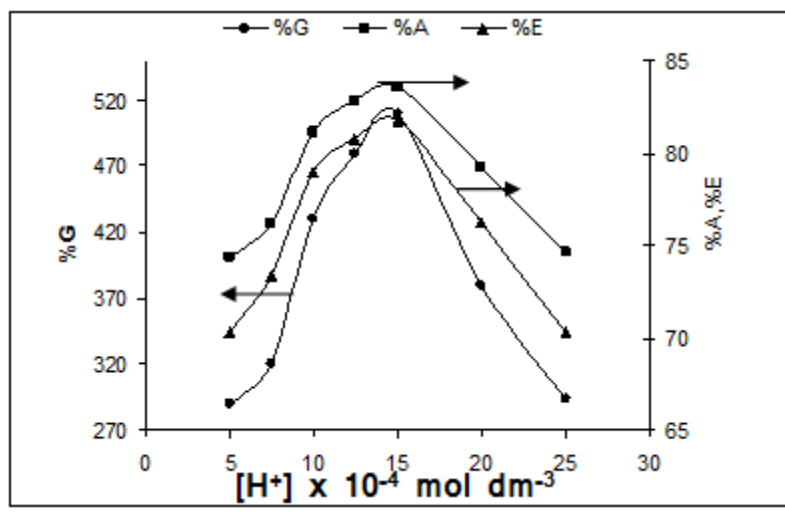


Figure S1 Effect of Hydrogen ion concentration on grafting parameters (%A, %E & %G,)

[MSA] = 32.0×10^{-4} mol dm⁻³; [PMS] = 14.0×10^{-3} mol dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; [CGN] = 1.0 g dm⁻³; Time = 120 min.; Temp. = 40°C.

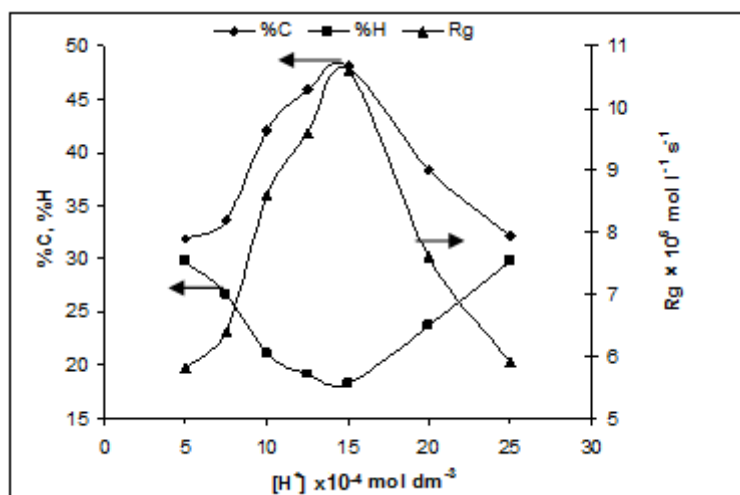


Figure S2 Effect of Hydrogen ion concentration on grafting parameters (%C, %H & Rg,)

[MSA] = 32.0×10^{-4} mol dm⁻³; [PMS] = 14.0×10^{-3} mol dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; [CGN] = 1.0 g dm⁻³; Time = 120 min.; Temp. = 40°C.

Effect of Carrageenan Concentration

From the Fig. S3 & S4 it is clear that %G, %C, %E, %A and Rg increased on increasing the concentration of carrageenan from 0.6 to 1.0 g dm⁻³ and this increment might be due to the availability of more grafting sites, where polyacrylic acid can be grafted while further increase of concentration i.e. from 1.0 to 2.2 g dm⁻³ shows the decrement in above grafting

Parameters. This behavior can be explained on the ground that viscosity of the reaction medium increases on increasing the carrageenan concentration which hinders the movement of free radicals, therefore, decrement in the grafting ratio, efficiency, add on, conversion and rate of grafting have been observed.

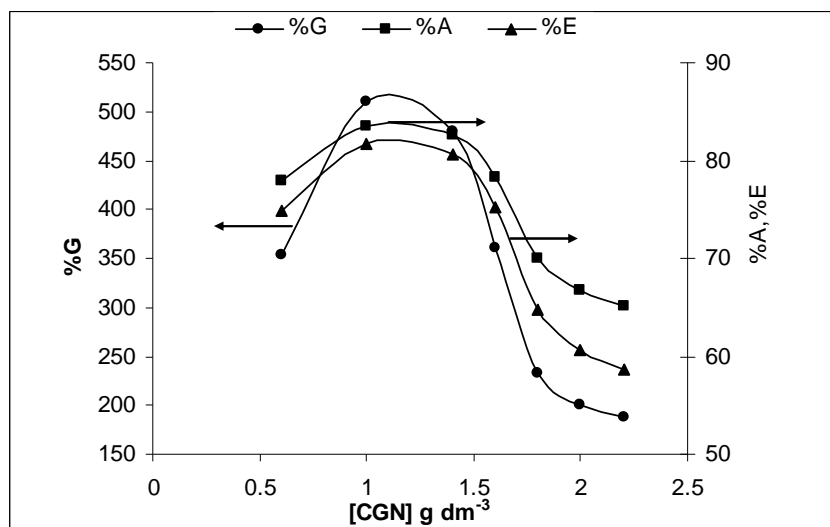


Figure S3 Effect of Carrageenan concentration on grafting parameters (%A, %E, & %G)

[MSA] = 32.0×10^{-4} mol dm⁻³; [PMS] = 14.0×10^{-3} mol dm⁻³; [H⁺] = 15.0×10^{-4} mol dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; Time = 120 min; Temp. = 40°C.

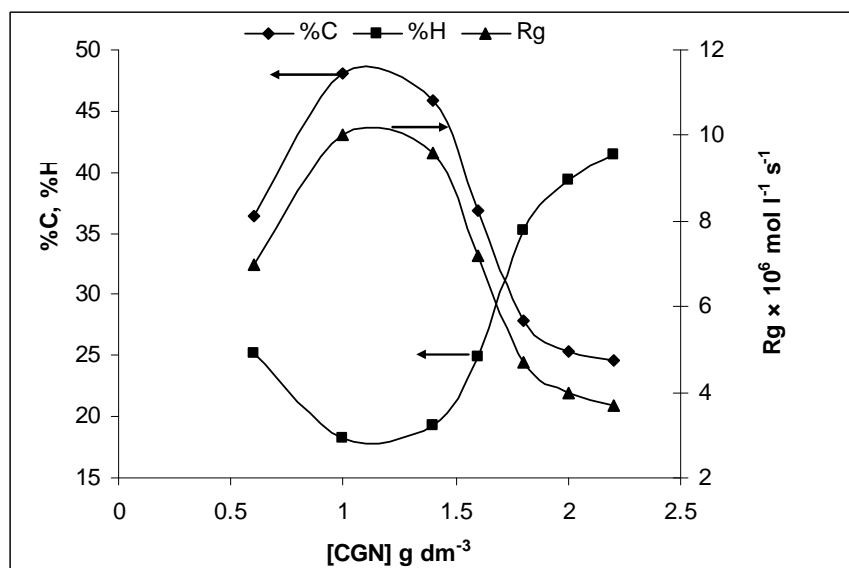


Figure S4 Effect of Carrageenan concentration on grafting parameters (%C, %H, & Rg)

[MSA] = 32.0×10^{-4} mol dm⁻³; [PMS] = 14.0×10^{-3} mol dm⁻³; [H⁺] = 15.0×10^{-4} mol dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; Time = 120 min; Temp. = 40°C.

Effect of Time

The graft copolymerization reaction has been conducted on intervals of time i.e. from 60 to 240 minutes for studying the effect of the duration of the reaction on grafting Parameters and rate of grafting and results are shown by Fig. S5 & S6. It has been observed that the grafting ratio, add on, efficiency and conversion increased but homopolymer decreased as the time period of the reaction increases up to 120 minutes. The increase in grafting parameters might be due to more and more addition of monomer molecules to the growing grafted chains. But on further increasing time period grafting ratio, add on, efficiency, conversion has been decreased and homopolymer increased while rate of grafting increases continuously upto 240 minute. This behaviour can be explained that, all the active sites have been exhausted after 120 min. and beyond this time period the mutual annihilation of the growing grafted chains occurred, which resulted in the formation of homopolymer.

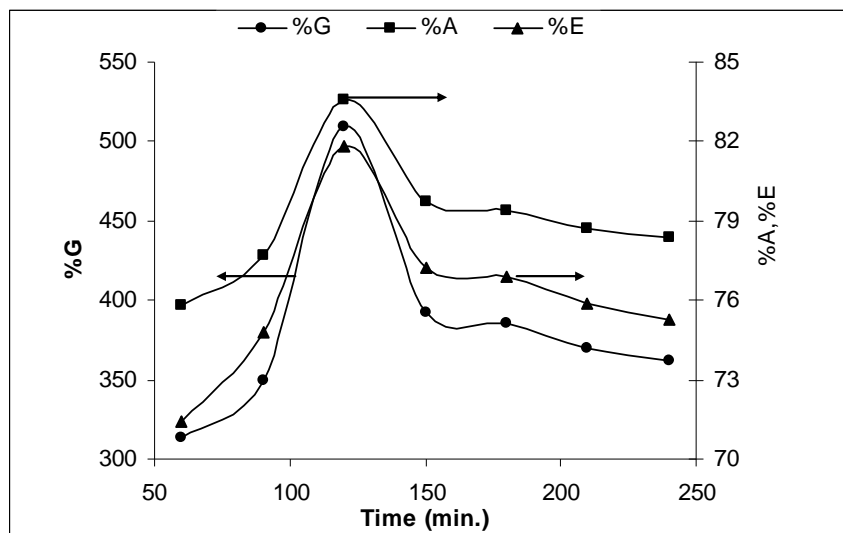


Figure S5 Effect of time duration on grafting parameters(%A, %E & %G,)

[MSA] = 32.0×10^{-4} mol dm⁻³; [PMS] = 14.0×10^{-3} mol dm⁻³; [H⁺] = 15.0×10^{-4} mol dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; [CGN] = 1.0 g dm⁻³;
Temp. = 40°C.

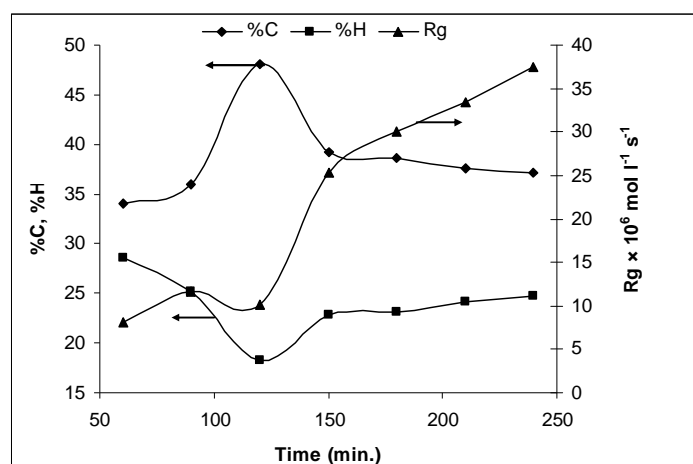


Figure S6 Effect of time duration on grafting parameters(%A, %E & %G,)

[MSA] = 32.0×10^{-4} mol dm⁻³; [PMS] = 14.0×10^{-3} mol dm⁻³; [H⁺] = 15.0×10^{-4} mol dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; [CGN] = 1.0 g dm⁻³; Temp. = 40°C.

Effect of Temperature

The grafting reaction has been carried out at various temperatures ranging from 30°C to 55°C (Table S4). On increasing the temperature up to 40°C grafting ratio, add on, conversion, efficiency and rate of grafting have been found to increase but homopolymer decrease. This effect might be due to (I) the rate of production of primary free radicals increased, (II) the rate of diffusion of acrylic acid onto carrageenan matrix increased on increasing temperature. But on further increasing the temperature of reaction, it has been observed that the grafting Parameters decreased and it might be due to the decomposition of PMS into HSO₄⁻, H₂O and O₂, since O₂ act as scavenger, thereby lowering the concentration of free radicals.

Table S4: Effect of Temperature on grafting parameters

[PMS] = 14.0×10^{-3} mol dm⁻³; [MSA] = 32.0×10^{-4} mol dm⁻³; [H⁺] = 15.0×10^{-4} mol dm⁻³; [CGN] = 1.0 g dm⁻³; [Acrylic acid] = 18.0×10^{-2} mol dm⁻³; Time = 120 min.

Temp. (°C)	%G	%E	%A	%C	%H	Rg × 10 ⁶ mol l ⁻¹ s ⁻¹
30	342.0	73.7	77.4	35.8	26.3	6.8
35	350.0	74.8	77.7	36.2	25.2	7.0
40	510.0	81.8	83.6	48.1	18.2	10.2
44	306.0	70.3	75.4	33.5	29.7	6.1
48	300.0	69.0	73.7	31.3	31.0	5.6
52	291.0	71.3	75.0	32.4	28.7	6.0
55	280.0	70.0	74.4	32.0	30.0	5.8