2.1 INTRODUCTION

Vinyl graft copolymerization through chemical initiation is easier than thermal, photochemical and other initiation methods because the activation energy of the redox initiation is quite low in comparison with other methods [1]. However, the choice of the redox initiating system has a great influence on the grafting results.

KPS in combination with AA is an excellent redox initiating system for the polymerization of vinyl monomers [2] because of KPS is excellent oxidizing agent and Ascorbic Acid (AA) is excellent reducing agent in an aqueous solution.

(a) Peroxydisulphate (KPS) as an excellent oxidant property

The readily available peroxydisulphate ion (Fig. 2.1) has an excellent reduction potential and versatile oxidant for a variety of organic and inorganic compounds.

![Peroxydisulphate](image)

**Fig.2.1. Potassium Persulphate**

Potassium persulphate can be prepared by electrolysis of a mixture between potassium sulfate and hydrogen sulfate at a high current density.

\[ 2 \text{KH}_2\text{SO}_4 \rightarrow \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2 \quad (2.1) \]

It can also be prepared by adding potassium hydrogen sulfate (KH\textsubscript{2}SO\textsubscript{4}) to an electrolyzed solution of ammonium hydrogen sulfate (NH\textsubscript{4}HSO\textsubscript{4}).

Potassium persulfate (KPS) is a white crystalline, odourless salt with the density of 2.477. It can be decomposed at about 100 °C and can be dissolved in water, not in ethanol. It is used to produce detonator, bleacher, oxidant and initiator for the polymerization. It has the particular advantage of being almost non-hygroscopic of having good storage stability in normal temperature and of being easy and safe to handle. KPS is used as desizing agent and bleaching activating agent.

KPS is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation-reduction potential for the reaction:
Chapter 2

2SO₄⁻²(aq) → S₂O₈⁻²(aq) + 2e⁻ (2.2)

is estimated to be -2.01V. Reactions involving this ion, however, are generally slow at ordinary temperatures and many peroxydisulphate oxidations have been studied kinetically. The decomposition of persulphate and the activation by some reducing agents has been summarized by Bacon in his review [3]. The effect of various substances upon the thermal decomposition of persulphate in aqueous medium was studied by several workers [4-20]. The activation of persulphate by various reductants, viz. metals oxidizable metals, metal complexes, salts of various oxyacids of sulphur, hydroxylamine, hydrazine thiols, polyhydric phenols, etc., has been reported [3,5-8,11-16,20-24].

Persulphate such as ammonium persulphate (APS), sodium persulphate (NaPS) and potassium persulphate (KPS) are excellent free radical initiators, in aqueous medium. In analogy with H₂O₂ decomposition, their activity could be attributed to sulphate radical anions, formed by the homolytic fission:

\[(\text{OSO}_2\text{O-OSO}_2\text{O})^2 \rightarrow 2\text{(OSO}_2\text{O)}^· = 2\text{SO}_4^·\] (2.3)

The kinetics of persulphate decomposition in aqueous solution, which in absence of polymerizable substances, leading to oxygen evolution have been studied by several workers. Kolthoff and Miller [25] have shown that when heated, persulphate irons in aqueous solution decompose to produce sulphate ion-radicals:

\[\text{S}_2\text{O}_8^· \rightarrow \text{SO}_4^· ; \text{rate constat } k_0\] (2.4)

This is a first order reaction. The sulfate radical may react with water to produce hydroxyl radicals and finally oxygen:

\[\text{SO}_4^· + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \cdot\text{OH}\] (2.5)

\[2\cdot\text{OH} \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2\] (2.6)

In addition, a decomposition takes place that does not produce radicals, but the rate of this second process is very small compared with that of the first, when the \[p^H = 4.\]
Vinyl polymerization may thus be initiated by either the $\text{SO}_4^-$ radicals or by $\cdot \text{OH}$ radicals. That $\text{SO}_4^-$ radical take part in the initiation is shown by the fact that sulphur is present in the polymer [26].

(b) **Ascorbic acid (AA) as an excellent reductant property:**

The strong reducing properties of ascorbic acid (Fig. 2.2) and its subsequent use as an analytical reagent have been reviewed by Erdey and Svehla [27]. By mild oxidizing agents ascorbic acid is oxidized to dehydroascorbic acid (A) [28].

$$
\text{C}_6\text{H}_6\text{O}_6 \rightarrow \text{C}_6\text{H}_6\text{O}_6^+ + 2e^- + 2\text{H}^+ \quad (2.7)
$$

The structure ascorbic acid is shown below.

![Fig.2.2. Ascorbic Acid](image)

Several early publications have described the reductions by ascorbic acid from the kinetics standpoint, some of which have been directed towards the catalytic reduction [29]. Grinstead [30] has shown that the rate determining step during the EDTA Iron (III) chelate is the one electron oxidation of ascorbic acid to the ascorbate radical. In presence of hydrogen peroxide the reduction involved a chain process. Khan and Martell [31] investigated the kinetics of uncatalyzed, copper (II) and iron (III) catalysed oxidation of ascorbic acid by molecular oxygen in the $p^\text{H}$ range 2 to 5.5 and found the monoionic ascorbic acid as the main reacting species. The catalysed oxidation was explained on the basis of formation of complexes between catalyst and ascorbic acid. The reduction of palladium [32] and hexacyanoferrate (III) [33], by ascorbic acid has also been investigated.

The reduction of peroxydisulphate by ascorbic acid is a two electron transfer reaction in which ascorbic acid is oxidized to dehydroascorbic acid.
It has already been established by earlier workers that ascorbic acid exists as ascorbate ion in aqueous solution which are mainly responsible for the great reducing action. In an acidic medium the equation may be represented as:

\[
\text{AH}_2 \xrightleftharpoons[k_{1a}]{k_{1a}} \text{AH}^- + H^+ \tag{2.8}
\]

The primary step in all oxidations involving peroxydisulphate is its symmetrical decomposition into two sulphate radical ions \([34]\), followed by several consecutive reactions forming a chain. For the reduction of peroxydisulphate, by ascorbic acid following chain mechanism has been proposed, which involves the intermediate formation of ascorbate free radicals (AH') \([1, 2]\):

Initiator:

\[
\text{SO}_2\text{O}_8^{2-} \xrightarrow{k_{1b}} 2\text{SO}_4^{--} \tag{2.9}
\]

Propagation:

\[
\text{SO}_4^{--} + \text{H}_2\text{O} \xrightarrow{k_2} \text{SO}_4^{2-} + \text{H}^+ + \cdot \text{OH} \tag{2.10}
\]

\[
\cdot \text{OH} + \text{AH}^- \xrightarrow{k_3} \text{AH}^- + \text{OH}^- \tag{2.11}
\]

\[
\text{AH}^- + \text{SO}_2\text{O}_8^{2-} \xrightarrow{k_4} \text{A} + \text{SO}_4^{2-} + \text{SO}_4^{--} + \text{H}^+ \tag{2.12}
\]

Termination:

\[
\text{AH}^- + \text{SO}_4^{--} \xrightarrow{k_5} \text{A} + \text{SO}_4^{2-} + \text{H}^+ \tag{2.13}
\]

\[
\text{AH}^- + \cdot \text{OH} \xrightarrow{k_6} \text{A} + \text{OH}^- + \text{H}^+ \tag{2.14}
\]

Where A represents the product dehydroascorbic acid. Assuming steady-state conditions with respect to SO_4^{--}, 'AH and 'OH, the rate of decomposition of peroxydisulphate may be obtained as follows:

\[
-\frac{d}{dt}[\text{S}_2\text{O}_8^{2-}] = \left(\frac{k_{1b}k_2k_4}{k_5}\right)^{1/2}[\text{S}_2\text{O}_8^{2-}] \tag{2.15}
\]
The above rate law equation (2.15) clearly explains that the reduction of peroxydisulphate by ascorbic acid will follow first order disappearance in peroxydisulphate and will be independent of ascorbic acid concentration. Peroxydisulphate (KPS) in combination with ascorbic acid (AA) can be used as an excellent redox initiating system for carrying out grafting.

Table 2.1 represents the literature survey data indicating that modification of Tamarind Kernel Powder (TKP) has been carried out by grafting of various vinyl monomers onto it using different initiating systems and KPS / AA initiating system has been successfully used for modification of various natural, renewable polymers. However, the data regarding modification of Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder via grafting are found to be scanty [49, 50].

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2.2 EXPERIMENTAL

2.2.1 MATERIALS AND METHODS

(a) Materials

(i) The Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder
   (Na-PCMTKP)

   Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder
   (Na-PCMTKP, $\bar{\alpha}_S = 0.15$) was kindly supplied by Encore Natural Pvt. Ltd; Naroda,
   Ahmedabad (Gujarat). It was purified by re-precipitation method and the traces of salt
   were removed by washing the sample repeatedly with 95% aqueous methanol solution
   and finally with pure methanol and ether respectively. It was then dried in a vacuum
   oven at 35 °C.

(ii) Potassium Persulphate

   Potassium persulphate (KPS) (Qualigens, Glaxo India Ltd.) of analytical
   reagent grade was used as received.

(iii) Ascorbic Acid

   Ascorbic Acid (AA) (Samir Tech, Chem. Baroda, Gujarat) of analytical
   reagent grade was used as received.

(iv) Purification of Vinyl monomers

   Methyl Methacrylate (MMA) (Chiti-Chem Corporation, Baroda) was washed
   with 2% sodium hydroxide solution to remove the stabilizer and then was washed with
   distilled water, till it was freed from alkali and dried over anhydrous sodium sulphate.
   MMA was finally distilled at atmosphere pressure and the middle fraction of it was
   collected and used. Acrylonitrile (AN) (Chiti-Chem Corporation, Baroda) was distilled
   at atmosphere pressure and the middle fraction of it was collected and used.

(v) Solvents

   Methanol, acetone and dimethyl formamide were purified [90] prior to their use.
   Acetone free methanol of reagent grade was used throughout the study.
   Analytical reagent grade acetone was distilled at 56.5 – 57.5 °C and used.
   Dimethyl formamide was distilled at 152 – 154 °C and used.
   Analytical grade hydrochloric acid (Qualigents, Glaxo India Ltd.) was used as
   received.

   All the solutions were prepared in low conductivity water.
(b) Nitrogen Purification

Nitrogen gas (supplied by the Indian Oxygen Company Ltd. Ahmedabad) was purified by passing through freshly prepared alkaline solution of pyrogallol (15g pyrogallol dissolved in 100 mL of 50% NaOH solution).

(c) Determination of Optimum Reaction Conditions for Na-PCMTKP-g-PMMA

A 250 mL three necked flask equipped with mechanical stirrer, a reflux condenser and a gas inlet system was immersed in a constant temperature bath for grafting reactions. In a typical reaction, varying amount (0.25-3.00 g) of the Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder(Na-PCMTKP, $\overline{D_S} = 0.15$) was dissolved in low conductivity water (110 mL) with constant stirring and bubbling a slow stream of nitrogen for 1 h at the desired temperature ($20^0 - 80^0$C). The freshly distilled MMA (0.051 – 0.405 M) was then added to the charge. After 5 min., the freshly prepared 10 mL solution of AA ($10\times10^{-3}$ - $50\times10^{-3}$ mol/L) in low conductivity water was added. After 30 minutes, the freshly prepared 10 mL solution of KPS ($5\times10^{-3}$ - $45\times10^{-3}$ mol/L) in low conductivity water was added and stirred to it and this time was taken as zero time for reaction. The grafting reactions were carried out for different time intervals (0.5-10 h). During the course of the reaction, a slow stream of nitrogen was continuously passed to remove the dissolved oxygen. After completion of the reaction, the contents of the flask were poured immediately into excess of methanol to precipitate out the polymer. The crude copolymer product was then filtered, repeatedly washed with 95% methanol and finally with pure methanol. The crude sample thus obtained was dried under vacuum at $40^0$C.

(d) Determination of Optimum Reaction Conditions for Na-PCMTKP-g-PAN

In order to determine the optimum reaction conditions for grafting of acrylonitrile (AN) onto Na-PCMTKP ($\overline{D_S} = 0.15$), the grafting reactions were carried out in the similar manner as discussed above and the reaction conditions which were varied are:
The grafting reactions were carried out under nitrogen atmosphere in a 250 mL three-necked flask equipped with a reflux condenser, a stirrer and a gas inlet system, immersed in a constant temperature bath. Na-PCMTKP (\(D_{w}=0.15\)) sample (1.5 g, dry basis) was dispersed in 110 mL water/solvent mixtures (75:25, 50:50 and 25:75) with constant stirring and bubbling a slow stream of nitrogen, for 1 h at 35°C. The solvents include methanol, ethanol, n-propanol and n-Butanol. Nitrogen gas was continuously passed through this solution and freshly distilled acrylonitrile (AN) monomer (0.350 M) was added and the reaction mixture was stirred for 5 min. 10 mL of freshly prepared solution of AA (20 x 10^{-3} M) in conductivity water was added and the reaction mixture was stirred for 30 min. After that, 10 mL of freshly prepared solution of KPS (25 x 10^{-3} M) in conductivity water was added and nitrogen gas was continuously passed through this solution. The grafting reaction was carried out for 2.5 h at 35°C.

After completion of the reaction, the reaction mixture was immediately poured into the excess of methanol to precipitate out the polymer. The crude copolymer product was filtered, repeatedly washed with 95% ethanol and finally washed with pure methanol. The crude copolymer sample thus obtained was dried under vacuum at 40°C.

(f) Extraction of Homopolymers from Crude Graft Copolymers

The crude graft copolymers Na-PCMTKP-g-PMMA and Na-PCMTKP-g-PAN were freed from their respective ungrafted homopolymers (viz. PMMA and
PAN) by following Soxhlet extraction method [91] using acetone (in the case of PMMA) and DMF (in the case of PAN) as solvents for 48h.

After removal of the respective homopolymers, the residues were dried at 40°C under vacuum until constant weight was obtained.

(g) Evidence of Grafting

(i) Infrared Spectrometry

Infrared spectral study of Na-PCMTKP ($\bar{D}$s = 0.15) and its different graft copolymer (viz. Na-PCMTKP-g-PMMA, and Na-PCMTKP-g-PAN) and the corresponding homopolymers (PMMA and PAN) have been carried out with the point of view to:

(i) establish proof of grafting of different vinyl monomers onto Na-PCMTKP sample and
(ii) ensure complete removal of the non-grafted product, and to determine the structure of the grafted product.

Infrared (IR) spectra were scanned using potassium bromide disc method. According to the procedure of this method about 4 mg of polymer sample was mixed with 1 g of potassium bromide. An intimate mixture was obtained by grinding the sample and KBr in a pulverizer. The mixture was placed in a disc, which was then assembled and evacuated to 3 mm of Hg. A pressure of 18,000 psi was subjected to it for five minutes. For the blank set, standard disc was prepared under similar conditions without sample.

The IR spectra of Na-PCMTKP ($\bar{D}$s = 0.15), Na-PCMTKP-g-PMMA (% G = 146.25%), Na-PCMTKP-g-PAN (% G = 214.41%) as well as PMMA, PAN were taken in KBr pellets using Nicolet Impact 400D Fourier Transform Infrared Spectrophotometer.

(ii) Scanning Electron Microscopy (SEM)

Model ESEM THP + EDAX, Philips make has been used to obtain the micrographs of Na-PCMTKP ($\bar{D}$s = 0.15) and its different graft copolymers viz, Na-PCMTKP-g-PMMA (% G = 146.25) and Na-PCMTKP-g-PAN (% G = 214.41).

(iii) Isolation of Grafted Chains

All the grafted samples prepared in the present work were hydrolyzed by refluxing them for 12 h in 1 N HCl as suggested by Brockway [92]. After all the
Na-PCMTKP went into the solutions, resinous masses were obtained which were characterized by IR spectroscopy as PMMA and PAN.

(i) Calculations of Grafting Yields and Kinetic Parameters

The percentage of grafting, grafting efficiency, percentage of homopolymer and rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) were evaluated by the help of the following expressions [93].

(i) Percentage Grafting ($\% G$) = \[
\frac{\text{Weight of Polymer grafted}}{\text{Initial Weight of backbone}} \times 100
\]

(ii) Percentage grafting Efficiency ($\% GE$) = \[
\frac{\text{Weight of Polymer grafted}}{\text{Initial Weight of backbone}} \times 100
\]

(iii) % Homopolymer ($\% H_p$) = 100 - %GE

(iv) Rate of Polymerization = \[
\left( R_p \right) \left( \text{mol. L}^{-1} \cdot \text{s}^{-1} \right) = \frac{\text{Weight of Polymer grafted} + \text{Weight of homopolymer}}{\text{Mol. Wt. of monomer} \times \text{Reaction time (Sec)} \times \text{Volume of the reaction mix. (mL)}} \times 10^3
\]

(v) Rate of Graft Copolymerization = \[
\left( R_g \right) \left( \text{mol. L}^{-1} \cdot \text{s}^{-1} \right) = \frac{\text{Weight of Polymer grafted}}{\text{Mol. Wt. of monomer} \times \text{Reaction time (Sec)} \times \text{Volume of the reaction mix. (mL)}} \times 10^3
\]

(vi) Rate of Homopolymerization = \[
\left( R_h \right) \left( \text{mol. L}^{-1} \cdot \text{s}^{-1} \right) = \frac{\text{Weight of Homopolymer}}{\text{Mol. Wt. of monomer} \times \text{Reaction time (Sec)} \times \text{Volume of the reaction mix. (mL)}} \times 10^3
\]
2.3 RESULTS AND DISCUSSION

2.3.1 DETERMINATION OF OPTIMUM REACTION CONDITIONS

The optimal reaction conditions were established for studying the potassium persulfate (KPS) / ascorbic acid (AA) – redox initiator induced grafting of methyl methacrylate (MMA) and acrylonitrile (AN) onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\delta = 0.15$) by using various reaction parameters. The reaction parameters studied includes amount of backbone (Na-PCMTKP), concentrations of monomer (MMA or AN) and potassium persulphate (KPS), ascorbic acid (AA) and temperature as well as reaction time.

(a) Effect of Backbone Concentration

The results of the grafting yields [percentage grafting (%G) and percentage grafting efficiency (%GE)] as well as the rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) for grafting of Methyl methacrylate (MMA) and Acrylonitrile (AN) onto Na-PCMTKP ($\delta = 0.15$) are tabulated in Tables 2.1 and 2.2 respectively.

Figs. 2.1 and 2.2 show the dependence of percentage grafting (%G) as well as percentage grafting efficiency (%GE) on the backbone concentration in the case of MMA and AN respectively. It is observed from these figures that for both the monomers with increasing Na-PCMTKP concentration, the values of %G and %GE are found to be increased in the beginning up to optimum concentration i.e. Na-PCMTKP = 1.5 g. Beyond which they are decreased with future increase in the amount of backbone.

Thus, the observed initial increase in %G up to 1.5 g, in the case of both the monomers, is due to the fact that the reactive sites increase with increase in the concentration of Na-PCMTKP and after the optimum concentration, the observed decrease in %G is due to the destruction of radical activity backbone concentration soon after it is formed because of termination between backbone-backbone and backbone-primary radicals. This is in agreement with the results obtained in the grafting of acrylonitrile onto starch [94], carboxymethylated amylose [95], carboxymethylated starch [96], grafting of MA as well as AN onto sodium alginate [97] and grafting of methyl acrylate [98] and ethyl acrylate [99] onto gelatin. The results are also in agreement with the grafting of acrylonitrile onto sodium salt of
partially carboxymethylated tamarind kernel powder [50] as well as grafting of methyl acrylate [89] onto carboxymethyl starch.

The influence of amount of Na-PCMTKP onto \( R_p \), \( R_g \) and \( R_h \) in the case of grafting of MMA and AN is represented in Figs. 2.3 to 2.6. In both the cases, MMA and AN, the rate of polymerization (\( R_p \)) is found to be increased over the full range of amount of Na-PCMTKP studied (cf. Figs. 2.3 and 2.5). Thus, the observed increase in \( R_p \) may be due to increase either in the rate of graft copolymerization (\( R_g \)) or the rate of homopolymerization (\( R_h \)) or both. This is evidenced by the increase in \( R_g \) in case of MMA (Fig. 2.4) and AN (Fig. 2.6). However, the value of \( R_h \) in case of MMA (Fig. 2.3) is found to be decreased continuously. On the other hand in case of AN (Fig. 2.5) the value of \( R_h \) is found to be decreased initially up to Na-PCMTKP =1.5 g and beyond this value, the \( R_h \) value is found to be increased.

Similar results are also reported in the literature [39, 47, 66, 69, 100-116].

(b) Effect of Monomer Concentration

The results of the grafting yields and the values of \( R_p \), \( R_g \) and \( R_h \) for grafting of MMA and AN onto Na-PCMTKP (\( d_s = 0.15 \)) at various monomer concentrations are tabulated in Tables 2.3 and 2.4. Figs 2.7 and 2.8 represent the influence of monomer concentration on the grafting yields in the case of MMA and AN respectively. In the case of MMA (Fig. 2.7) the value of %G increases from 0.05 to 0.15 mol/L (or from 0.76 to 2.28 mL) and reaches a maximum value of %G = 121.27. Beyond [MMA] = 0.15 mol/L (or 2.28 mL) the value of %G is found to be decreased with further increase in the concentration. On the other hand %GE decreases continuously in the whole range of concentration of MMA studied. In case of AN (Fig. 2.8) the value of %G increases from 0.05 to 0.35 mol/L (or from 0.50 to 3.50 mL) and reaches a maximum value of %G = 307.49. However, beyond [AN] = 0.35 mol/L (or 3.50 mL), the values of %G and %GE are found to be decreased with further increase in the concentration. The enhancement of grafting by increasing monomer (MMA or AN) concentration could be associated with the greater availability of monomer molecules in the vicinity of Na-PCMTKP in particular and in the reaction medium in general [117-119]. It may also be noted that once the graft copolymer radicals are formed, the excess monomer will shield the graft copolymer, which may inhibit the rate of graft copolymerization. In addition to this the excess monomer will be available for
initiator radicals to initiate the homopolymerization reaction and thereby decrease the grafting efficiency (Figs. 2.7 and 2.8).

Figs. 2.9 to 2.12 represent the influence of monomer concentration onto \( R_p, R_g \) and \( R_h \) in the case of grafting of MMA and AN onto Na-PCMTKP \((\bar{\delta}_s = 0.15)\). It can be observed from these figures that an increase in monomer (MMA and AN) concentration in the reaction system, increases the rate of polymerization \( (R_p) \) (Figs. 2.9 and 2.11). Thus, the observed increase in \( R_p \) may be due to the innate either in the rate of graft copolymerization \( (R_g) \) or the rate of homopolymerization \( (R_h) \) or both. This is evidenced by the increase in the rate of graft copolymerization \( (R_g) \) as well as rate of homopolymerization \( (R_h) \) (cf. Figs. 2.11 and 2.12). However, on the other hand the observed increase in \( R_p \) in case of MMA is due to the increase in \( R_h \) over the whole range of monomer concentration studied (cf. Fig. 2.9).

Similar results are also reported in the literature [35, 37, 47, 67, 82, 86, 120-128].

(c) Effect of Potassium Persulphate concentration

The results of grafting yields (%G and %GE) as well as of \( R_p, R_g \) and \( R_h \) for the graft copolymerization of MMA and AN onto Na-PCMTKP \((\bar{\delta}_s = 0.15)\) at various initiator (KPS) concentrations are tabulated in Tables 2.5 and 2.6.

The influence of the potassium persulphate (KPS) on the grafting yields, in the case of MMA and AN onto Na-PCMTKP \((\bar{\delta}_s = 0.15)\) is shown in Figs. 2.13 and 2.14 respectively. It is evident from the figures that with increasing KPS concentration %G increases in the case of both the monomers and reaches a maximum value of 174.53% at \([\text{KPS}] = 15 \times 10^{-3} \text{ mol/L}\) for MMA, and a maximum value of 116.03% at \([\text{KPS}] = 25 \times 10^{-3} \text{ mol/L}\) for AN. With future increase in the concentration of initiator, the value of %G decreases as observed in the case of both the monomers. (Figs. 2.13 and 2.14). A similar situation is encounter with %GE in the case of MMA. However, in case of AN, the value of %GE remains almost constant over the whole range of KPS concentration studied.

Thus, the observed increase in %G as well as %GE within the KPS concentration range of \(5 \times 10^{-3} - 15 \times 10^{-3} \text{ mol/L}\) with MMA (Fig. 2.13) as well as \(5 \times 10^{-3} - 25 \times 10^{-3} \text{ mol/L}\) with AN (Fig. 2.14) indicate that the amount of polymer
grafted and its variation with KPS concentration determines the trends for both grafting and grafting efficiency. This observed increase in %G can be explained on the basis of the fact that as the concentration of initiator increases, more and more radicals are generated on the backbone as well as on the monomer (MMA or AN), which results in the increase in %G. After reaching the optimum values (174.53% for MMA and 116.03% for AN), %G decreases with future increase in initiator concentration. It may be due to the fact that with further increase in the initiator concentration, chain termination reactions dominate the graft copolymerization, which leads to decrease in %G.

Figs. 2.15 to 2.18 represent the influence of the initiator concentration on $R_p$, $R_g$ and $R_h$ in the case of both the monomers. It is evident that the values of $R_p$ as well as $R_g$ increase up to the respective optimum concentration of the initiator in the case of both the monomers but beyond the respective optimum concentration, values of $R_p$ and $R_g$ decrease with future increase in initiator concentration. The observed decrease in $R_p$ and $R_g$ may be due to annihilation of primary radicals formed in the system without being utilized for grafting and homopolymerization reactions and to termination of grafting radicals by the primary radicals.

Similar observations are reported in the literature [45, 60, 62, 66, 67, 70, 75, 125-130].

(d) Effect of Ascorbic Acid Concentration [Activator]

The results of grafting yields (%G and %GE) as well as of $R_p$, $R_g$ and $R_h$ for the graft copolymerization of MMA and AN onto Na-PCMTKP ($\bar{D_S} = 0.15$) at various activator (ascorbic acid) concentrations are tabulated in Tables 2.7 and 2.8.

The influence of ascorbic acid (AA) concentration on grafting yields in the case of grafting of MMA and AN onto Na-PCMTKP ($\bar{D_S} = 0.15$) is shown in Figs. 2.19 and 2.20 respectively. It is evident from these figures that with increasing ascorbic acid concentration the value of %G increases and reaches a maximum value of 124.99% at $[AA] = 20 \times 10^{-3}$ mol/L and a maximum value of 156.52% at $[AA] = 20 \times 10^{-3}$ mol/L for MMA and AN respectively. With further increase in the concentration of activator (ascorbic acid), the value of %G is found to be decreased in the case of both the monomers (Figs. 2.19 and 2.20).
Figs. 2.21 to 2.24 indicate the influence of the activator (ascorbic acid) concentration on the values of $R_p$, $R_g$, and $R_h$. The increase in values of $\%G$, $\%GE$ and $R_g$ with the ascorbic acid concentration, in the case of both the monomers within respective range, is attributed to the fact that in the presence of ascorbic acid, $\cdot \text{AH}$ and $\text{SO}_4^{-}$ radicals generated in the system as per the reaction [Eqns. 2.11 and 2.12], may attack the Na-PCMTKP molecules resulting in more active sites on Na-PCMTKP backbone followed by the addition of monomer (MMA or AN). Beyond the respective optimum concentration of the activator the observed decrease in percentage grafting and percentage grafting efficiency as well as $R_g$ is due to the increased formation of ascorbate radicals($\cdot \text{AH}$) which are mainly responsible for homopolymerization.

Similar types of results have been reported in the literature [66, 86, 130-134].

(e) Effect of Reaction Temperature

The data given in Tables 2.9 and 2.10 represent the effect of temperature on the grafting yields ($\%G$ and $\%GE$) as well as on $R_p$, $R_g$ and $R_h$, in the case of grafting of MMA and AN onto Na-PCMTKP ($\overline{\delta} = 0.15$). All the grafting reactions were carried out at different temperatures ranging from $20^\circ C$ to $80^\circ C$, keeping the other variables constant. Figs. 2.25 and 2.26 represent the variation of $\%G$ and $\%GE$ as a function of temperature for MMA and AN respectively.

The results indicate that initially with increasing temperature, $\%G$ increases and reaches a maximum value ($\%G = 133.16$) at temperature $50^\circ C$ in case of MMA (Fig. 2.25) and a maximum value ($\%G = 168.91$) at temperature $35^\circ C$ in case of AN (Fig. 2.26). Beyond the respective optimum value of temperature, $\%G$ decreases with further increase in temperature in both the cases. Thus, the observed increase in percentage grafting with temperature can be interpreted in terms of favourable influence of temperature on: (a) the swelling of Na-PCMTKP (b) the solubility of monomer (MMA or AN) molecules, (c) the enhanced diffusion of monomer molecules (MMA or AN) from aqueous phase to the Na-PCMTKP backbone, (d) the increase in the mobility of the monomer (MMA or AN) molecules and their collision with Na-PCMTKP macroradicals, and (e) the rates of initiation and propagation of grafting. The observed decrease in $\%G$ beyond $50^\circ C$ in the case of MMA and beyond $35^\circ C$ in the case of AN can be ascribed to the fact that after attaining respective optimum temperature, graft copolymerization occurs with poor selectivity. In
addition, various hydrogen abstraction and chain transfer reactions also might be accelerated at higher temperature leading to decrease in percentage of grafting.

The influence of reaction temperature on $R_p$, $R_g$ and $R_h$ in the case of grafting of MMA and AN is shown in Figs. 2.27 to 2.30. The initial increase in temperature favours the activation of backbone radicals leading to an increase in the rate of graft copolymerization ($R_g$) and ultimately the rate and total conversion ($R_p$) (cf. Figs. 2.27, 2.29 and 2.30) in case of both monomers. Beyond the respective optimum temperature an increase in temperature favours the homopolymerization.

Similar results are also reported in the literature are [37, 39, 105, 109-112, 115-120, 125-127, 130, 131, 135-144].

(f) Effect of Reaction Time

The values of %G and %GE obtained in the case of graft copolymerization of MMA and AN onto Na-PCMTKP ($\bar{D}\bar{S} = 0.15$) at various reaction time are tabulated in Tables 2.11 and 2.12. The influence of reaction time on %G as well as %GE in the case of MMA and AN are represented in Figs. 2.31 and 2.32 respectively.

It is evident from these figures that the percentage grafting increases up to a maximum of 167.31% within 1.5 h and 203.48% within 2.5 h in case of MMA and AN respectively. The initial increase in %G in the case of both the monomers is due to the increase in number of grafting sites on the Na-PCMTKP backbone as reaction progresses. But beyond the optimum time, i.e. 1.5 h in case of MMA (Fig. 2.31) and 2.5 h in case of AN (Fig. 2.32), the value of %G decreases which is due to the depletion in monomer and initiator concentrations as well as shortage of the available grafting sites. The initial increase in the value of %GE, as observed in the case of MMA (Fig. 2.31) is attributed to the formation of more and more Na-PCMTKP grafted radicals, during the process of grafting reaction and beyond the optimum time the observed decrease in %GE is due to the homopolymer (PMMA) formation. However, in the case of AN (Fig. 2.32) the value of %GE remains almost constant over the time range studied.

The influence of reaction time on $R_p$, $R_g$ and $R_h$ in the case of grafting of MMA and AN onto Na-PCMTKP ($\bar{D}\bar{S} = 0.15$) is shown in Figs. 2.33 to 2.36. It is evident from these figures that the values of $R_p$, $R_g$ and $R_h$ are decreasing with increase in time in the case of both the monomers. This effect can be attributed to the fact that the relative increment in the total yield is very much less when compared to that of time and in the expression for $R_p$, the numerator becomes almost constant and
when the time for the reaction is raised, the denominator becomes larger and the value of \( R_p \) will get reduced accordingly. Since \( R_g \) and \( R_h \) are related to \( R_p \), the relative decrease of \( R_p \), as observed in the case of both the monomers as well as \( R_h \) with time can be understood. Their decrease may also be due to depletion of concentrations of initiator and monomer with reaction time.

Similar results have been reported in the literature \([35, 37, 38, 50, 66, 87, 89, 97, 104-106, 108, 126, 131, 136, 144-150]\).

Thus, from the above discussion, the optimized reaction conditions established in the graft copolymerization of

(a) MMA are

\[
\text{Na-PCMTKP} = 1.5 \text{ g; } [\text{KPS}] = 15 \times 10^{-3} \text{ M; } [\text{AA}] = 20 \times 10^{-3} \text{ M; } [\text{MMA}] = 0.150 \text{ mol/L; Time} = 1.5 \text{ h; Temperature} = 50^\circ \text{C; Volume of Water} = 147.7 \text{ mL and Total Volume} = 150 \text{ mL and}
\]

(b) AN are

\[
\text{Na-PCMTKP} = 1.5 \text{ g; } [\text{KPS}] = 25 \times 10^{-3} \text{ M; } [\text{AA}] = 20 \times 10^{-3} \text{ M; } [\text{AN}] = 0.350 \text{ mol/L; Time} = 2.5 \text{ h; Temperature} = 35^\circ \text{C; Volume of Water} = 146.5 \text{ mL; and Total Volume} = 150 \text{ mL}
\]

2.3.2 REACTION MECHANISM

The kinetics of the redox system containing ascorbic acid and peroxydisulfate was studied by Mehrotra and Mushran \([2]\) and a mechanism involving \( \text{SO}_4^{2-}, \text{AH} \) (ascorbate) and \( \cdot \text{OH} \) radicals which are known as chain carriers was proposed as represented by Eqns. 2.9 to 2.14. This redox system has been exploited for the polymerization of vinyl monomers by several workers \([2, 151]\).

Misra and Gupta \([152]\) reported the formation of a complex between the monomer and peroxydisulfate which later dissociates to liberate initiating primary free radicals, but the existence of such a complex was not verified by the authors. Roskin \([5]\) proposed that the hydroxyl radicals formed in the system [Eqn. 2.11] also take part in the initiation but this could not be verified on the basis of the end group analysis of homopolymers obtained by the system.
The proposed mechanism for graft copolymerization is:

**INITIATION**

\[
\text{Na-PCMTKP} - \text{OH} + \text{R}^* \rightarrow \text{Na-PCMTKP} - \text{O}^* + \text{RH} \tag{2.16}
\]

\[
\text{M} + \text{R}^* \rightarrow \text{RM}^* \text{ (or } \text{M}^*) \tag{2.17}
\]

**PROPAGATION**

\[
\text{Na-PCMTKP} - \text{OH} + \text{M}^* \rightarrow \text{Na-PCMTKP} - \text{O} - \text{M}^* \tag{2.18}
\]

\[
\text{Na-PCMTKP} - \text{O} - \text{M}^* + \text{nM} \rightarrow \text{Na-PCMTKP} - \text{O} - (\text{M})_n - \text{M}^* \tag{2.19}
\]

\[
\text{Na-PCMTKP} - \text{O}^* + \text{nM} \rightarrow \text{Na-PCMTKP} - \text{O} - (\text{M})_n - \text{M}^* \tag{2.20}
\]

\[
\text{RM}^* + \text{nM} \rightarrow \text{R} - (\text{M})_n - \text{M}^* \tag{2.21}
\]

**TERMINATION**

\[
\text{Na-PCMTKP} - \text{O} - (\text{M})_n - \text{M}^* + \text{M} - (\text{M})_n - \text{O} - \text{Na-PCMTKP} \rightarrow
\]

\[
\text{Na-PCMTKP} - \text{O} - (\text{M})_n - \text{M}_2 - (\text{M})_n - \text{Na-PCMTKP} \tag{2.22}
\]

Graft Copolymer

\[
\text{Na-PCMTKP} - \text{O} - (\text{M})_{n-1} - \text{M}^* + \text{M} - (\text{M})_{n-1} - \text{O} - \text{Na-PCMTKP} \rightarrow
\]

\[
\text{Na-PCMTKP} - \text{O} - (\text{M})_{n-1} - \text{M}_2 - (\text{M})_{n-1} - \text{Na-PCMTKP} \tag{2.23}
\]

\[
\text{R} - (\text{M})_n - \text{M}^* + \text{R} - (\text{M})_n - \text{M}^* \rightarrow \text{R} - (\text{M})_n - \text{M}_2 - (\text{M})_n - \text{R} \tag{2.24}
\]

Homopolymer
2.3.3 Reactivity of Vinyl Monomers

In order to understand the reactivity of the vinyl monomers, the grafting of MMA and AN onto Na-PCMTKP \((\bar{D}S = 0.15)\) has been carried out using KPS/ascorbic acid as a redox initiator and the optimized reaction conditions were determined for affording maximum percentage of grafting, as described in the previous sections 2.2 (c) and 2.2 (d).

The values of the maximum percentage of grafting of MMA and AN onto Na-PCMTKP \((\bar{D}S = 0.15)\) obtained, under the optimum reaction conditions, are tabulated in Table 2.13. This table reveals that both vinyl monomers are not equally reactive towards graft copolymerization.

The comparison of the results of Table 2.13 clearly shows that following reactivity order of monomers:

\[
\text{AN} > \text{MMA}
\]

This difference in monomer reactivity might depends on solubility, polarity, molecular size, chemical nature etc.

The higher reactivity of AN towards grafting compared to MMA may be attributed to the lower electro-negativity of nitrogen when compared with oxygen. Because of higher electro-negativity of oxygen the \(\pi\) electron of C=C will be attracted towards oxygen whereas this attraction is less in AN. This will make C=C \(\pi\) bond comparatively more localized in AN, thus making it prone to be opened more easily during graft copolymerization [153, 154].

2.3.4 Effect of Reaction Medium

The grafting of acrylonitrile (AN) onto Na-PCMTKP \((\bar{D}S = 0.15)\) using KPS/AA as a redox initiator was studied in water/solvent mixtures. The solvents used include methanol, ethanol, n-propanol and b-butanol. The results obtained are summarized in Table 2.14.

Water soluble organic solvents might affect the swelling properties of Na-PCMTKP. Any change in Na-PCMTKP swellability would be reflected on the behavior of Na-PCMTKP towards grafting, since diffusion of monomer and initiator, availability of functional groups (sites of grafting) propagation and termination of the
graft etc. would depend to a considerable extent on the swelling properties of Na-PCMTKP.

It is clear (Table 2.14) that regardless of the water/solvent mixture employed, the substantial amount of grafting is obtained. A regular decrease in percentage grafting occurs with increasing the solvent ratio in the water solvent mixture. It can be further seen from this table that the reaction medium plays an important role in graft copolymerization reaction.

From the perusal of this table a regular decrease in % grafting can be observed with increasing the solvent ratio in the water/solvent mixture. This could be interpreted in terms of the adverse effect of the solvent on the swelling properties of Na-PCMTKP in water.

It is important to note from the result of Table 2.14 that of the water/solvent mixtures used, water/ethanol at a ratio of 75/25 constitutes the most favourable medium for polymerization of AN with Na-PCMTKP ($\bar{D_S}$=0.15) using KPS/AA as an initiator giving rise to highest value of %G. Increasing the molecular weight of the alcohol, the graft yield decreases very slowly from Methanol to n-Butanol, except ethanol. The lower graft yields could be ascribed to its adverse effect on the swelling of Na-PCMTKP by water. Associated with this factor is the hydrophobic character of the alcohols which decreases from n-Butanol to Methanol. These effects seriously hinder a monomer access to reactive sites on Na-PCMTKP. However, the difference in capability of these solvents as terminators for the graft copolymer radicals and the Na-PCMTKP macroradical via chain transfer reaction cannot also be ruled out.

Differences in % grafting obtained with water/solvent mixtures as polymerization medium could be attributed to differences in (i) miscibility with monomer (AN), (ii) ability to swell Na-PCMTKP, (iii) compatibility with KPS/AA and (iv) termination of the graft chain radical and Na-PCMTKP macroradical via chain transfer. While the first three factors enhance grafting by simplifying the access and diffusion of the monomer, the last factor adversely effects grafting by lowering the molecular size of the graft.

Similar results have been also reported in literature [155-158].
2.3.5. EVIDENCE OF GRAFTING

(a) IR-spectra of Na-PCMTKP (DS=0.15) and its graft copolymers

Fig.2.37 shows the IR spectrum of Na-PCMTKP (DS=0.15). The presence of a very strong and broad absorption band at ~ 3428 cm⁻¹ is assigned to -OH stretching. Reasonably sharp absorption band at ~ 2927 cm⁻¹ may be attributed to the - CH stretching. The asymmetric and symmetric vibrations due to (-CO-) moiety are assigned to ~ 1640 cm⁻¹ and ~ 1424 cm⁻¹ respectively. This can be attributed to the incorporation of carboxymethylated groups in Tamarind Kernel Powder.

The IR spectrum of the copolymer Na-PCMTKP-g-PMMA (Fig.2.38) showed absorption bands of Na-PCMTKP as well as an additional strong absorption band at about ~ 1737.06 cm⁻¹ which can be assigned to C=O stretching of ester group (-COOCH₃), characteristics of methacrylates. Moreover, this graft copolymer (namely Na-PCMTKP-g-PMMA) was hydrolyzed in order to isolate the grafted chains i.e. PMMA. The infrared spectrum of PMMA (Fig. 2.40) shows the presence of -C=O stretching at about ~ 1730 cm⁻¹. This may be attributed to the fact that the hydrolysis of the graft copolymer gives back the grafted chain PMMA. Thus, the results of Figs. 2.38 and 2.40 provide a substantial evidence of grafting of MMA onto Na-PCMTKP (DS=0.15).

Figs. 2.39 and 2.41 represent the IR spectra of Na-PCMTKP-g-PAN and PAN (isolated by hydrolysis) sample respectively. The spectrum of graft copolymer (Fig. 2.39) showed absorption bands of Na-PCMTKP (DS=0.15) as well as an additional absorption bands at ~2228.78 cm⁻¹, which has been attributed to -C≡N stretching mode, characteristics of the spectra of PAN (Fig.2.41). Thus, the presence of addition band at ~2228 cm⁻¹ in the graft copolymer i.e. Na-PCMTKP-g-PAN indicates beyond doubt that grafting of AN onto Na-PCMTKP has taken place.

(b) Scanning Electron Microscopy (SEM)

The SEM technique is considered to be an effective tool to study the surface topology of different kinds of polymers. The comparison of Scanning Electron Micrographs of Na-PCMTKP and its graft copolymers viz. Na-PCMTKP-g-PMMA and Na-PCMTKP-g-PAN as discussed in section 3.3.5 of Chapter-3, constitutes further additional evidence of grafting.
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Table 2.1

Grafting yields for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\bar{D}S = 0.15$) at various backbone concentrations.\(^a\)

<table>
<thead>
<tr>
<th>Weight of backbone (g)</th>
<th>%Grafting (%G)</th>
<th>%Grafting Efficiency (%GE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
</tr>
<tr>
<td>0.25</td>
<td>42.56</td>
<td>82.87</td>
</tr>
<tr>
<td>0.50</td>
<td>78.84</td>
<td>149.69</td>
</tr>
<tr>
<td>1.00</td>
<td>99.91</td>
<td>157.63</td>
</tr>
<tr>
<td>1.50</td>
<td>160.65</td>
<td>160.81</td>
</tr>
<tr>
<td>2.00</td>
<td>150.13</td>
<td>131.80</td>
</tr>
<tr>
<td>2.50</td>
<td>146.20</td>
<td>108.33</td>
</tr>
<tr>
<td>3.00</td>
<td>151.32</td>
<td>109.21</td>
</tr>
</tbody>
</table>

\(a\) Reaction Conditions

Na-PCMTKP : Varied as shown (dry basis)

[Monomer] : 0.200 m\(\text{c}-\text{l}/\text{L}\)

[KPS] : 20 \times 10^{-2} \text{m}\(\text{ol}/\text{L}\)

[AA] : 20 \times 10^{-3} \text{m}\(\text{ol}/\text{L}\)

Time : 3 h

Temperature : 45°\(\text{C}\)

Volume of Water : 146.5mL (AN) and 147.0mL (MMA)

Total volume : 150 mL
Table 2.2

The Rates of polymerization ($R_p$), graft copolymerization ($R_g$), and homopolymerization ($R_h$), for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-FCMTKP, $\overline{D_S} = 0.15$) at various backbone concentrations.\(^a\)

<table>
<thead>
<tr>
<th>Weight of backbone (g)</th>
<th>$R_p \times 10^6$ (mol.L(^{-1}).s(^{-1}))</th>
<th>$R_g \times 10^6$ (mol.L(^{-1}).s(^{-1}))</th>
<th>$R_h \times 10^6$ (mol.L(^{-1}).s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
</tr>
<tr>
<td>0.25</td>
<td>14.65</td>
<td>2.08</td>
<td>0.66</td>
</tr>
<tr>
<td>0.50</td>
<td>15.80</td>
<td>11.85</td>
<td>2.42</td>
</tr>
<tr>
<td>1.00</td>
<td>17.41</td>
<td>19.57</td>
<td>6.16</td>
</tr>
<tr>
<td>1.50</td>
<td>21.48</td>
<td>28.20</td>
<td>14.86</td>
</tr>
<tr>
<td>2.00</td>
<td>25.20</td>
<td>33.26</td>
<td>18.51</td>
</tr>
<tr>
<td>2.50</td>
<td>27.61</td>
<td>34.61</td>
<td>22.53</td>
</tr>
<tr>
<td>3.00</td>
<td>30.78</td>
<td>39.50</td>
<td>27.99</td>
</tr>
</tbody>
</table>

\(a\). Reaction Conditions

- **Na-PCMTKP**: Varied as shown (dry basis)
- **[Monomer]**: 0.200 mcl/L
- **[KPS]**: $20 \times 10^{-3}$ mol/L
- **[AA]**: $20 \times 10^{-5}$ mol/L
- **Time**: 3 h
- **Temperature**: 45$^\circ$C
- **Volume of Water**: 146.5mL (AN) and 147.0mL (MMA)
- **Total volume**: 150 mL
Table 2.3

Grafting yields for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-FCMTKP, $\overline{D_S} = 0.15$) at various monomer concentrations.

<table>
<thead>
<tr>
<th>Monomer (mol/L)</th>
<th>Monomer mL</th>
<th>%Grafting (%G)</th>
<th>%Grafting Efficiency (%GE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
</tr>
<tr>
<td>0.05</td>
<td>0.76</td>
<td>0.50</td>
<td>109.29</td>
</tr>
<tr>
<td>0.10</td>
<td>1.52</td>
<td>1.00</td>
<td>118.93</td>
</tr>
<tr>
<td>0.15</td>
<td>2.28</td>
<td>1.50</td>
<td>121.27</td>
</tr>
<tr>
<td>0.20</td>
<td>3.04</td>
<td>2.00</td>
<td>116.93</td>
</tr>
<tr>
<td>0.25</td>
<td>3.80</td>
<td>2.50</td>
<td>113.03</td>
</tr>
<tr>
<td>0.30</td>
<td>4.56</td>
<td>3.00</td>
<td>108.56</td>
</tr>
<tr>
<td>0.35</td>
<td>5.32</td>
<td>3.50</td>
<td>89.35</td>
</tr>
<tr>
<td>0.40</td>
<td>6.08</td>
<td>4.00</td>
<td>82.83</td>
</tr>
</tbody>
</table>

a. Reaction Conditions

Na-PCMTKP : 1.00 g (cry basis)
[Monomer] : Varied as shown
[KPS] : $20 \times 10^{-3}$ mol/L
[AA] : $20 \times 10^{-3}$ mol/L
Time : 3 h
Temperature : $45^\circ$C
Volume of Water : 146.5 mL (AN) and 147.0 mL (MMA)
Total volume : 150 mL
Table 2.4
The rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\bar{D_S} = 0.15$) at various monomer concentrations.

<table>
<thead>
<tr>
<th>Monomer (mol/L)</th>
<th>Monomer mL</th>
<th>$R_p \times 10^6$ (mol.L⁻¹.s⁻¹)</th>
<th>$R_g \times 10^6$ (mol.L⁻¹.s⁻¹)</th>
<th>$R_h \times 10^6$ (mol.L⁻¹.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
<td>AN</td>
</tr>
<tr>
<td>0.05</td>
<td>0.76</td>
<td>0.50</td>
<td>6.75</td>
<td>10.27</td>
</tr>
<tr>
<td>0.10</td>
<td>1.52</td>
<td>1.00</td>
<td>10.57</td>
<td>11.59</td>
</tr>
<tr>
<td>0.15</td>
<td>2.28</td>
<td>1.50</td>
<td>14.72</td>
<td>12.83</td>
</tr>
<tr>
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<td>3.04</td>
<td>2.00</td>
<td>18.40</td>
<td>19.74</td>
</tr>
<tr>
<td>0.25</td>
<td>3.80</td>
<td>2.50</td>
<td>18.76</td>
<td>23.53</td>
</tr>
<tr>
<td>0.30</td>
<td>4.56</td>
<td>3.00</td>
<td>24.71</td>
<td>29.55</td>
</tr>
<tr>
<td>0.35</td>
<td>5.32</td>
<td>3.50</td>
<td>28.18</td>
<td>37.07</td>
</tr>
<tr>
<td>0.40</td>
<td>6.08</td>
<td>4.00</td>
<td>32.46</td>
<td>33.82</td>
</tr>
</tbody>
</table>

**a. Reaction Conditions**

- Na-PCMTKP : 1.00 g (dry basis)
- [Monomer] : Varied as shown
- [KPS] : $20 \times 10^{-5}$ mol/L
- [AA] : $20 \times 10^{-5}$ mol/L
- Time : 3 h
- Temperature : 45°C
- Volume of Water : 146.5mL (AN) and 147.0mL (MMA)
- Total volume : 150 mL
Table 2.5
Grafting yields for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\overline{DS} = 0.15$) at various potassium persulphate (KPS) concentrations.a

<table>
<thead>
<tr>
<th>[KPS]$\times 10^3$</th>
<th>%Grafting (G)</th>
<th>%Grafting Efficiency (GE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
</tr>
<tr>
<td>5</td>
<td>140.84</td>
<td>105.57</td>
</tr>
<tr>
<td>10</td>
<td>149.86</td>
<td>107.41</td>
</tr>
<tr>
<td>15</td>
<td>174.53</td>
<td>109.30</td>
</tr>
<tr>
<td>20</td>
<td>133.73</td>
<td>113.32</td>
</tr>
<tr>
<td>25</td>
<td>120.52</td>
<td>116.03</td>
</tr>
<tr>
<td>30</td>
<td>110.73</td>
<td>114.22</td>
</tr>
<tr>
<td>35</td>
<td>100.78</td>
<td>111.26</td>
</tr>
<tr>
<td>40</td>
<td>101.88</td>
<td>110.34</td>
</tr>
<tr>
<td>45</td>
<td>109.33</td>
<td>109.70</td>
</tr>
</tbody>
</table>

a. Reaction Conditions

- Na-PCMTKP: 1.00gm (dry basis)
- [Monomer]: 0.200 mol/L
- [KPS]: Varied as shown
- [AA]: $20 \times 10^{-2}$ mol/L
- Time: 3 h
- Temperature: 45°C
- Volume of Water: 146.5mL (AN) and 147.0mL (MMA)
- Total volume: 150 mL
Table 2.6
The rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $D_S = 0.15$) at various potassium persulphate (KPS) concentrations.3

<table>
<thead>
<tr>
<th>[KPS]$\times 10^3$</th>
<th>$R_p \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
<th>$R_g \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
<th>$R_h \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
<td>AN</td>
</tr>
<tr>
<td>5</td>
<td>19.69</td>
<td>12.51</td>
<td>8.68</td>
</tr>
<tr>
<td>10</td>
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</tr>
<tr>
<td>15</td>
<td>22.11</td>
<td>13.11</td>
<td>10.76</td>
</tr>
<tr>
<td>20</td>
<td>21.19</td>
<td>13.44</td>
<td>8.24</td>
</tr>
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<td>25</td>
<td>19.55</td>
<td>13.81</td>
<td>7.43</td>
</tr>
<tr>
<td>30</td>
<td>17.55</td>
<td>13.72</td>
<td>6.83</td>
</tr>
<tr>
<td>35</td>
<td>17.60</td>
<td>13.43</td>
<td>6.21</td>
</tr>
<tr>
<td>40</td>
<td>17.61</td>
<td>13.30</td>
<td>6.28</td>
</tr>
<tr>
<td>45</td>
<td>17.94</td>
<td>13.22</td>
<td>6.74</td>
</tr>
</tbody>
</table>

a. Reaction conditions

Na-PCMTKP : 1.00gm (dry basis)
[Monomer] : 0.200 mol/L
[KPS] : Varied as shown
[AA] : $20 \times 10^{-3}$ mol/L
Time : 3 h
Temperature : 45°C
Volume of Water : 146.5mL (AN) and 147.0mL (MMA)
Total volume : 150 mL
Table 2.7

Grafting yields for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, DS = 0.15) at various ascorbic acid (AA) concentrations.a

<table>
<thead>
<tr>
<th>[AA]×10³</th>
<th>%Grafting (%G)</th>
<th>%Grafting Efficiency (%GE)</th>
</tr>
</thead>
<tbody>
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<td>MMA</td>
<td>AN</td>
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<td>85.29</td>
</tr>
<tr>
<td>15</td>
<td>110.51</td>
<td>135.81</td>
</tr>
<tr>
<td>20</td>
<td>124.99</td>
<td>156.52</td>
</tr>
<tr>
<td>25</td>
<td>106.62</td>
<td>120.34</td>
</tr>
<tr>
<td>30</td>
<td>100.30</td>
<td>104.10</td>
</tr>
<tr>
<td>35</td>
<td>95.62</td>
<td>92.41</td>
</tr>
<tr>
<td>40</td>
<td>96.72</td>
<td>87.29</td>
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<tr>
<td>45</td>
<td>93.17</td>
<td>81.60</td>
</tr>
<tr>
<td>50</td>
<td>92.80</td>
<td>-</td>
</tr>
</tbody>
</table>

a. Reaction Conditions

Na-PCMTKP : 1.00gm (dry basis)
[Monomer] : 0.200 mcl/L
[KPS] : $20 \times 10^{-3}$ mol/L
[AA] : Varied as shown
Time : 3 h
Temperature : 45°C
Volume of Water : 146.5mL (AN) and 147.0mL (MMA)
Total volume : 150 mL
Table 2.8

The rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\overline{D_S} = 0.15$) at various Ascorbic acid (AA) concentrations.\(^a\)

<table>
<thead>
<tr>
<th>[AA]×10(^3)</th>
<th>$R_p \times 10^6$ (mol.L(^{-1}).s(^{-1}))</th>
<th>$R_g \times 10^6$ (mol.L(^{-1}).s(^{-1}))</th>
<th>$R_h \times 10^6$ (mol.L(^{-1}).s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
</tr>
<tr>
<td>10</td>
<td>18.05</td>
<td>10.17</td>
<td>6.51</td>
</tr>
<tr>
<td>15</td>
<td>18.57</td>
<td>15.92</td>
<td>6.81</td>
</tr>
<tr>
<td>20</td>
<td>21.07</td>
<td>18.37</td>
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<td>19.11</td>
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<td>18.51</td>
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<td>5.74</td>
</tr>
<tr>
<td>50</td>
<td>16.85</td>
<td>-</td>
<td>5.72</td>
</tr>
</tbody>
</table>

\(\text{a. Reaction Conditions}\)

Na-PCMTKP : 1.00gm (dry basis)

[Monomer] : 0.200 mol/L

[KPS] : $20 \times 10^{-3}$ mol/L

[AA] : Varied as shown

Time : 3 h

Temperature : 45\(^o\)C

Volume of Water : 146.5mL (AN) and 147.0mL (MMA)

Total volume : 150 mL
Table 2.9

Grafting yields for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, DS = 0.15) at various reaction temperature.\(^a\)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>%Grafting (%G)</th>
<th>%Grafting Efficiency (%GE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
</tr>
<tr>
<td>293.15</td>
<td>98.14</td>
<td>84.32</td>
</tr>
<tr>
<td>298.15</td>
<td>107.14</td>
<td>121.45</td>
</tr>
<tr>
<td>303.15</td>
<td>111.52</td>
<td>167.61</td>
</tr>
<tr>
<td>308.15</td>
<td>121.02</td>
<td>168.91</td>
</tr>
<tr>
<td>313.15</td>
<td>125.90</td>
<td>163.78</td>
</tr>
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<td>318.15</td>
<td>126.99</td>
<td>156.60</td>
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<td>323.15</td>
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<td>141.67</td>
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<td>333.15</td>
<td>103.46</td>
<td>120.76</td>
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<td>343.15</td>
<td>101.50</td>
<td>101.45</td>
</tr>
<tr>
<td>353.15</td>
<td>82.66</td>
<td>97.81</td>
</tr>
</tbody>
</table>

\(^a\) Reaction Conditions

Na-PCMTKP : 1.00gm (dry basis)

[Monomer] : 0.200 mol/L

[KPS] : 20 × 10\(^{-3}\) mol/L

[AA] : 20 × 10\(^{-3}\) mol/L

Time : 3 h

Temperature : Varied as shown

Volume of Water : 146.5mL (AN) and 147.0mL (MMA)

Total volume : 150 mL
Table 2.10

The rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\overline{D}$S = 0.15) at various reaction temperature.4

<table>
<thead>
<tr>
<th>Temp. ($^\circ$K)</th>
<th>$R_p \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
<th>$R_g \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
<th>$R_h \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
</tr>
<tr>
<td>293.15</td>
<td>18.05</td>
<td>10.25</td>
<td>6.05</td>
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<tr>
<td>298.15</td>
<td>18.48</td>
<td>14.51</td>
<td>6.61</td>
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<tr>
<td>303.15</td>
<td>19.00</td>
<td>19.90</td>
<td>6.88</td>
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<td>7.52</td>
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<td>19.94</td>
<td>19.40</td>
<td>7.71</td>
</tr>
<tr>
<td>318.15</td>
<td>20.43</td>
<td>18.63</td>
<td>7.83</td>
</tr>
<tr>
<td>323.15</td>
<td>20.50</td>
<td>16.82</td>
<td>8.21</td>
</tr>
<tr>
<td>333.15</td>
<td>16.85</td>
<td>14.38</td>
<td>6.38</td>
</tr>
<tr>
<td>343.15</td>
<td>16.22</td>
<td>13.08</td>
<td>6.26</td>
</tr>
<tr>
<td>353.15</td>
<td>16.11</td>
<td>11.56</td>
<td>5.10</td>
</tr>
</tbody>
</table>

**a. Reaction conditions**

- **Na-PCMTKP** : 1.00gm (dry basis)
- **[Monomer]** : 0.200 mol/L
- **[KPS]** : $20 \times 10^{-3}$ mol/L
- **[AA]** : $20 \times 10^{-3}$ mol/L
- **Time** : 3 h
- **Temperature** : Varied as shown
- **Volume of Water** : 146.5mL (AN) and 147.0mL (MMA)
- **Total volume** : 150 mL
Table 2.11

Grafting yields for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, DS =0.15) at various reaction times.a

<table>
<thead>
<tr>
<th>Reaction Time (h)</th>
<th>%Grafting (%)</th>
<th>%Grafting Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
</tr>
<tr>
<td>0.5</td>
<td>112.59</td>
<td>143.82</td>
</tr>
<tr>
<td>1.0</td>
<td>145.08</td>
<td>160.79</td>
</tr>
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<td>1.5</td>
<td>167.31</td>
<td>171.51</td>
</tr>
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<td>2.0</td>
<td>139.17</td>
<td>181.44</td>
</tr>
<tr>
<td>2.5</td>
<td>135.51</td>
<td>203.48</td>
</tr>
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<td>3.0</td>
<td>134.25</td>
<td>179.56</td>
</tr>
<tr>
<td>4.0</td>
<td>133.10</td>
<td>163.03</td>
</tr>
<tr>
<td>6.0</td>
<td>132.22</td>
<td>130.03</td>
</tr>
<tr>
<td>8.0</td>
<td>130.53</td>
<td>131.42</td>
</tr>
<tr>
<td>10.0</td>
<td>131.61</td>
<td>150.24</td>
</tr>
</tbody>
</table>

a. Reaction Conditions

Na-PCMTKP : 1.00gm (dry basis)
[Monomer] : 0.200 mol/L
[KPS] : 20 × 10⁻³ mol/L
[AA] : 20 × 10⁻³ mol/L
Time : Varied as shown
Temperature : 45°C
Volume of Water : 146.5mL (AN) and 147.0mL (MMA)
Total volume : 150 mL
Table 2.12
The rates of polymerization ($R_p$), graft copolymerization ($R_g$) and homopolymerization ($R_h$) for grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\bar{D}S = 0.15$) at various reaction times.

<table>
<thead>
<tr>
<th>Reaction Time (h)</th>
<th>$R_p \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
<th>$R_g \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
<th>$R_h \times 10^6$ (mol.L$^{-1}$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>AN</td>
<td>MMA</td>
</tr>
<tr>
<td>0.5</td>
<td>117.64</td>
<td>103.77</td>
<td>41.65</td>
</tr>
<tr>
<td>1.0</td>
<td>60.93</td>
<td>58.34</td>
<td>26.83</td>
</tr>
<tr>
<td>1.5</td>
<td>41.97</td>
<td>40.57</td>
<td>20.63</td>
</tr>
<tr>
<td>2.0</td>
<td>29.22</td>
<td>32.45</td>
<td>12.87</td>
</tr>
<tr>
<td>2.5</td>
<td>23.65</td>
<td>30.31</td>
<td>10.03</td>
</tr>
<tr>
<td>3.0</td>
<td>19.33</td>
<td>21.24</td>
<td>8.28</td>
</tr>
<tr>
<td>4.0</td>
<td>14.54</td>
<td>14.64</td>
<td>6.15</td>
</tr>
<tr>
<td>6.0</td>
<td>9.34</td>
<td>7.93</td>
<td>4.08</td>
</tr>
<tr>
<td>8.0</td>
<td>7.57</td>
<td>5.87</td>
<td>3.02</td>
</tr>
<tr>
<td>10.0</td>
<td>5.62</td>
<td>5.50</td>
<td>2.43</td>
</tr>
</tbody>
</table>

a. Reaction conditions

Na-PCMTKP : 1.00gm (dry basis)
[Monomer] : 0.200 mol/L
[KPS] : $20 \times 10^{-3}$ mol/L
[AA] : $20 \times 10^{-3}$ mol/L
Time : Varied as shown
Temperature : $45^\circ$C
Volume of Water : 146.5mL (AN) and 147.0mL (MMA)
Total volume : 150 mL
Table 2.13

Maximum values of the grafting yields obtained in the case of grafting of MMA and AN onto Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $DS = 0.15$) under optimum conditions$^{a,b}$.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>%Grafting (%G)</th>
<th>% Grafting Efficiency (%GE)</th>
<th>% Homopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>146.25</td>
<td>75.24</td>
<td>33.73</td>
</tr>
<tr>
<td>AN</td>
<td>214.41</td>
<td>98.85</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Optimum reaction conditions for

(a) MMA are:

Na-PCMTKP = 1.5 g (dry basis); [KPS] = $15 \times 10^{-3}$ M; [AA] = $20 \times 10^{-3}$ M; [MMA] = 0.15 mol. L$^{-1}$; Time = 1.5 h; Temperature = 50°C; Volume of Water = 147.7 mL and Total Volume = 150 mL

(b) AN are:

Na-PCMTKP = 1.5 g (dry basis); [KPS] = $25 \times 10^{-3}$ M; [AA] = $20 \times 10^{-3}$ M; [AN] = 0.35 mol. L$^{-1}$; Time = 2.5 h; Temperature = 35°C; Volume of Water = 146.5 mL; and Total Volume = 150 mL
Table 2.14
Influence of reaction medium on graft copolymerization of acrylonitrile (AN) onto Sodium Salt of Carboxymethylated Tamarind Kernel Powder Na-PCMTKP \((\text{DS}=0.15)\) using KPS-AA as a redox initiator.\(^a\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Water/Solvent ratio (V/V)</th>
<th>%Grafting (%)</th>
<th>%Grafting Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100:00</td>
<td>214.41</td>
<td>98.85</td>
</tr>
<tr>
<td>Methanol</td>
<td>75:25</td>
<td>121.16</td>
<td>93.96</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
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<td>90.31</td>
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<td>25:75</td>
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<td></td>
<td>00:100</td>
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<td>Ethanol</td>
<td>100:00</td>
<td>214.41</td>
<td>98.85</td>
</tr>
<tr>
<td></td>
<td>75:25</td>
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<td>97.46</td>
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<td>50:50</td>
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<td>25:75</td>
<td>104.27</td>
<td>92.39</td>
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<td>00:100</td>
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<td>88.47</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>100:00</td>
<td>214.41</td>
<td>98.85</td>
</tr>
<tr>
<td></td>
<td>75:25</td>
<td>98.06</td>
<td>81.55</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>83.88</td>
<td>79.83</td>
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<tr>
<td></td>
<td>25:75</td>
<td>68.27</td>
<td>68.12</td>
</tr>
<tr>
<td></td>
<td>00:100</td>
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<td>71.45</td>
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<td></td>
<td>25:75</td>
<td>51.15</td>
<td>48.34</td>
</tr>
<tr>
<td></td>
<td>00:100</td>
<td>42.46</td>
<td>42.34</td>
</tr>
</tbody>
</table>

**a. Reaction conditions**

Na-PCMTKP = 1.5 g (dry basis); [KPS] = \(25 \times 10^{-3}\) M; [AA] = \(20 \times 10^{-3}\) M; [AN] = 0.35 mol/L; Time = 2.5 h; Temperature = 35\(^\circ\)C; Volume of Water = 146.5 mL; and Total Volume = 150 mL.
Fig. 2.1: Effect of amount of Na-PCMTKP on: (\(\bullet\)) - %G; or (\(\blacksquare\)) - %GE in the case of MMA.

Fig. 2.2: Effect of amount of Na-PCMTKP on: (\(\bullet\)) - %G; or (\(\blacksquare\)) - %GE in the case of AN.
Fig. 2.3: Effect of amount of Na-PCMTKP on: (●) – $R_p \times 10^6$; or (▲) – $R_h \times 10^6$ in the case of MMA.

Fig. 2.4: Effect of amount of Na-PCMTKP on: (■) – $R_g \times 10^6$ in the case of MMA.
Fig. 2.5: Effect of amount of Na-PCMTKP on: (•) $R_p \times 10^6$; or (△) $R_h \times 10^6$ in the case of AN.

Fig. 2.6: Effect of amount of Na-PCMTKP on: (■) $R_g \times 10^6$ in the case of AN.
Fig. 2.7: Effect of Methyl methacrylate concentration on: (●) - %G; or (■) - %GE.

Fig. 2.8: Effect of Acrylonitrile concentration on: (●) - %G; or (■) - %GE.
Fig. 2.9: Effect of Methyl methacrylate concentration on: (●) $R_p \times 10^6$; or (△) $R_h \times 10^6$.

Fig. 2.10: Effect of Methyl methacrylate concentration on: (■) $R_g \times 10^6$. 

$R_p \times 10^6$ (mol.L$^{-1}$s$^{-1}$)

$R_g \times 10^6$ (mol.L$^{-1}$s$^{-1}$)

MMA (ml)

MMA (ml)
Fig. 2.11: Effect of Acrylonitrile concentration on: (●) $- R_p \times 10^6$; or (▲) $- R_h \times 10^6$.

Fig. 2.12: Effect of Acrylonitrile concentration on: (■) $- R_g \times 10^6$. 
Fig. 2.13: Effect of Potassium Persulfate (KPS) concentration on: (●) - %G; or (■) - %GE in the case of MMA.

Fig. 2.14: Effect of Potassium Persulfate (KPS) concentration on: (●) - %G; or (■) - %GE in case of AN.
Fig. 2.15: Effect of Potassium Persulphate (KPS) concentration on: (•) – $R_p \times 10^6$; or (▲) – $R_h \times 10^6$ in the case of MMA.

Fig. 2.16: Effect of Potassium Persulphate (KPS) concentration on: (■) – $R_g \times 10^6$ in the case of MMA.
Fig. 2.17: Effect of Potassium Persulfate (KPS) concentration on: (●) $R_p \times 10^6$; or (▲) $R_h \times 10^6$ in the case of AN.

Fig. 2.18: Effect of Potassium Persulfate (KPS) concentration on: (■) $R_g \times 10^6$ AN.

Fig. 2.17: Effect of Potassium Persulfate (KPS) concentration on: (●) $R_p \times 10^6$; or (▲) $R_h \times 10^6$ in the case of AN.

Fig. 2.18: Effect of Potassium Persulfate (KPS) concentration on: (■) $R_g \times 10^6$ AN.
Fig. 2.19: Ascorbic Acid (AA) concentration on: (●) - %G; or (■) - %GE in the case of MMA.

Fig. 2.20: Ascorbic Acid (AA) concentration on: (●) - %G; or (■) - %GE in the case of AN.
Fig. 2.21: Ascorbic Acid (AA) concentration on: (●) – $R_p \times 10^6$; or (▲) – $R_h \times 10^6$ in the case of MMA.

Fig. 2.22: Ascorbic Acid (AA) concentration on: (■) – $R_g \times 10^6$ in the case of MMA.
Fig. 2.23: Ascorbic Acid (AA) concentration on: (●) \( R_p \times 10^6 \); or (▲) \( R_h \times 10^6 \) in the case of AN.

Fig. 2.24: Ascorbic Acid (AA) concentration on: (■) \( R_g \times 10^6 \) in the case of AN.
Fig. 2.25: Plot of (•) - %G; or (■) - %GE versus temperature in the case of MMA.

Fig. 2.26: Plot of (•) - %G; or (■) - %GE versus temperature in the case of AN.
Fig. 2.27: Plot of (●) – $R_p \times 10^6$; or (■) – $R_g \times 10^6$; versus temperature in the case of MMA.

Fig. 2.28: Plot of (▲) – $R_h \times 10^6$ versus temperature in the case of MMA.
Fig. 2.29: Plot of (●) – $R_p \times 10^6$; or (▲) – $R_n \times 10^6$ versus temperature in the case of AN.

Fig. 2.30: Plot of (■) – $R_g \times 10^6$ versus temperature in the case of AN.
Fig. 2.31: Influence of reaction time on: (●) - %G; or (■) - %GE in the case of MMA.

Fig. 2.32: Influence of reaction time on: (●) - %G; or (■) - %GE in the case of AN.
Fig. 2.33: Influence of reaction time on: (●) – $R_p \times 10^6$; or (▲) – $R_h \times 10^6$ in the case of MMA.

Fig. 2.34: Influence of reaction time on: (■) – $R_g \times 10^6$ in the case of MMA.
Fig. 2.35: Influence of reaction time on: (•) – $R_p \times 10^6$; or (▲) – $R_h \times 10^6$ in the case of AN.

Fig. 2.36: Influence of reaction time on: (■) – $R_g \times 10^6$ in the case of AN.
Fig. 2.37: IR spectra of Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, DS = 0.15) sample.

Fig. 2.38: IR spectra of Na-PCMTKP-g-PMMA sample.
Fig. 2.39: IR spectra of Na-PCMTKP-g-PAN sample.

Fig. 2.40: IR spectra of Polymethyl methacrylate (PMMA) sample.
Fig. 2.41: IR spectra of Polyacrylonitrile (PAN) sample.