CHAPTER - IV
GRAFT COPOLYMERIZATION OF BINARY MIXTURES

SECTION-A: GRAFT COPOLYMERIZATION OF (MA+AN) ONTO GELATIN

SECTION-B: GRAFT COPOLYMERIZATION OF (MA+MAN) ONTO GELATIN
SECTION-A

GRAFT COPOLYMERIZATION OF (MA+AN) ONTO GELATIN
Grafting provides a convenient method for tailoring material properties to specific end uses. In such studies the focus is generally on improvement of selective properties of backbone polymer without significantly affecting the bulk properties of polymers. Grafting of gelatin by attachment of various polymers has been studied with the objective of improving or modifying the properties of gelatin in an attempt to develop new materials by combining the properties of both natural and synthetic polymers (1,2). Moreover, grafting may play an important role in producing a material which will stabilize suspensions of polymer formed in the process of polymerization in aqueous medium (3). Gelatin also appears to provide a convenient substrate for basic studies of grafting phenomenon because grafted gelatin can be hydrolyzed easily, and the characterization of separated grafts may give a deeper insight into the grafting mechanism. The proper choice of polymer type is essential for optimum processibility and maximum property combination for the product and its intended end use. Graft copolymerization of MA, AN and MAN has been studied and discussed in previous chapters. In order to study the effect of MA on graft copolymerization of AN and MAN, an attempt has been made to graft copolymerize a binary mixture of MA with AN and MAN separately. Graft copolymerization of acrylate monomers such as methyl acrylate (4,5) ethylacrylate (6,7), methylmeth-
acrylate (8) and butylacrylate (9) onto gelatin has been studied using chemical initiators. Synthesis of graft copolymer of starch and acrylonitrile (10,11) afforded grafted starch which can be used in different fields. It was considered important to graft AN + MA onto gelatin for affording better product. Further AN shows a strong Trommsdorf's effect, and produces less percentage of grafting. Hence, it was considered relevant to study grafting of MA + AN onto gelatin. MA shows less tendency to gelling and produces much higher percentage of grafting. Hence, it will be interesting to study the effect of AN onto grafting of MA onto gelatin.

Methacrylonitrile having low polymerizability ($k_p/k_t^{1/2}$) as compared to MA, has been utilized for studying grafting of the binary mixture of MAN+MA onto gelatin. The present chapter has been divided into Section-'A' and Section-'B'. Section-'A' deals with the studies of grafting of MA+AN and Section-'B' describes grafting of MA+MAN onto gelatin. All the parameters that tend to influence grafting have been evaluated and the results are explained on the basis of the mechanism proposed earlier.
EXPERIMENTAL

Materials and Method

Gelatin (Oxoid, England) in the form of granules was used. Acrylonitrile AN (Ferak) and methyl acrylate (MA) (Sisco) were freshly distilled and the middle fractions were used. Distilled water was used as the reaction medium.

Graft Copolymerization

Gelatin (100 mg) was dissolved in a definite amount of water at 90°C in a conical flask and the temperature was brought to room temperature. To it a definite amount of mixed monomer (MA+AN) was added and the reaction mixture was irradiated from a Co\textsuperscript{60} source for different time periods at a constant dose rate of 0.092 Mrad/hour. After the completion of the reaction, the flask was removed from the chamber and 15 ml of chloroform was added (13). The mixture was left overnight. Excess of methanol was then added to completely precipitate gelatin, grafted gelatin, the homopolymers, polyacrylonitrile and polymethylacrylate and the copolymer of AN and MA. The product was extracted with excess of dimethylformamide for 24 hours for complete removal of the homopolymer and the copolymer. The homopolymer/copolymer free graft copolymer were dried at 50°C until constant weight was obtained. Percentage of grafting was calculated from the increase in the weight of gelatin as described in Chapter-II and Chapter-III.
Evidence of Grafting

I.R. Spectroscopy

I.R. spectra of gelatin and gelatin-g-Poly(AN)-co-
Poly(MA) were examined and it was observed that the peaks at
2230 cm\(^{-1}\) due to - C = N of AN and at 1725 cm\(^{-1}\) due to
\(\backslash C = O\) of MA were present in the grafted sample. This
suggests that both the monomers are grafted onto gelatin.

Thermogravimetric Analysis

The primary thermogram of gelatin-g-poly(AN)-co-
poly(MA) is presented in Fig.1. The initial decomposition
temperature (IDT), final decomposition temperature (FDT) and
decomposition temperature (DT) at every 10% weight loss are
presented in Table-I.

The IDT of the grafted gelatin (390°C) is higher than
that of gelatin (275°C) but FDT (470°C) of the grafted
gelatin is much lower than that of the gelatin (625°C). This
suggests that grafting of mixed monomer (MA+AN) increases
the thermal resistance of gelatin during initial heating. It
is further observed that decomposition temperature (DT) at
every 10% weight loss of grafted gelatin are higher than
those of gelatin upto 40% weight loss beyond which (DT)
values of grafted gelatin decreases and are less than those
of gelatin. As discussed in Chapter-III, it is suggested
that during heating of the gelatin-g-poly(AN)-co-poly(MA),
the grafted gelatin, grafted polymeric chains of (MA+AN)
FIG I  PRIMARY THERMOGRAM OF GELATIN-g-POLY(AN)-CO-POLY(MA)
upon heating decompose with the formation of anhydride and amide like structures as follows:

In case of gelatin, during initial heating, different pendant groups such as -COOH, -NH₂, -OH etc. are affected producing anhydrides imides etc. and consequently IDT and DT values up to 40% weight loss are lower than grafted gelatins. Beyond 40% weight loss these anhydrides and amides, that are formed in case of gelatin, impart higher resistance to heating and therefore has higher DT values. In the grafted gelatin beyond 40% loss, the pendant groups of gelatin may now decompose and therefore has lower DT values for further weight loss as compared to gelatin. Further grafting also
affects the crystallinity of the gelatin and this will decrease the thermal stability of the grafted gelatin.

RESULTS AND DISCUSSION

Irradiation of aqueous solution of gelatin in the presence of monomer leads to the formation of graft copolymer and homopolymer. The mechanism of graft copolymerization by mutual method has been discussed in the previous chapters. In the present chapter, a binary mixture of acrylonitrile and methylacrylate has been used as the monomer for grafting and hence the copolymer of AN and MA is expected to be grafted onto gelatin and this has been observed in the IR spectra of the grafted samples. In addition, the homopolymers due to AN and MA and also the copolymer poly(AN-co-MA) is expected to be formed which have been removed by solvent extraction method. The graft copolymerization of binary mixture has been studied as a function of different reaction parameters and the results are explained in the light of the mechanism proposed in Chapter-III.

Effect of Total Dose:

Figure (II) presents the plot of percentage of grafting of binary mixture (AN+MA) as a function of total dose. It is observed from the figure that percentage of grafting increased with increasing total dose, reaches
FIG II  EFFECT OF TOTAL DOSE ON PERCENT GRAFTING OF (MA+AN)

GELATIN = 100 mg, H₂O = 20 ml, DOSE RATE = 0.088 Mrad/hr,

[MA+AN] = 0.005 to 0.007 moles
maximum (361%) at 1.936 Mrad and decreased thereafter. Increase in percentage of grafting with increasing total dose is explained by the fact that with increasing total dose, generation of active sites on gelatin are facilitated, where grafting of the monomer can take place. Decrease in percentage of grafting beyond optimum total dose may be due to mutual annihilation of growing grafted chain. Following three types of polymeric branches may be attached as 'grafts' to gelatin:

(i) Branches having only AN units i.e. poly(AN)
(ii) Branches having only MA units i.e. poly(MA)
(iii) Branches having both MA and AN units i.e. poly(MA-co-AN).

The growing grafted chains which are still active may attack the neighbouring grafted branches thus bringing in chain scission and chain termination of the grafted chains. This backbiting by the growing grafted chain reduces the length of the grafted chains and as a consequence the overall weight of the grafted polymer is decreased. This process of backbiting is depicted as follows:

\[ \text{Gelatin} \rightarrow \text{Gelatin} \]

\[ \begin{align*}
\text{H} - \text{C} - \text{H} & \quad \text{H} - \text{C} - \text{H} \\
\text{H} - \text{C} - \text{CN} & \quad \text{H} - \text{C} - \text{CN} \\
\text{H} - \text{C} - \text{H} & \quad \text{H} - \text{C} - \text{H} \\
\text{H} - \text{C} - \text{CN} & \quad \text{H} - \text{C} - \text{C} - \text{OCH}_3
\end{align*} \]
Also at higher total dose excessive homopolymer formation may lead to decrease in percentage of grafting.

On comparison of the results of grafting of binary mixture (AN+MA) with that of grafting of AN onto gelatin, it is observed that maximum grafting of AN (96%) was obtained at a very low total dose of 0.6 Mrad. Although the grafting of binary mixture (AN+MA) is quite high (361%), but it is obtained at a higher total dose i.e. at 1.936 Mrad. With MA alone as the monomer, maximum percentage of grafting (641%) was obtained at a much higher total dose of 2.69 Mrad. These observations suggest that the addition of MA to AN changes the behaviour of grafting. Acrylonitrile is well known to show Trommfrof's effect and this affects the accessibility of the growing polymeric chains to the active sites because of restricted movements of the growing grafted chains and hence low percentage of grafting at low total dose is obtained. Although MA also shows Trommfrof's effect but this effect is mild in comparison with AN. The $k_p$ and $k_e$ value of AN are much higher ($k_p = 14500$ l/mole sec., $k_e = 2000 \times$
$10^6$ l/mole sec. at 25°C) than that of MA ($k_p = 1580$ l/mole sec. $k_c = 55 \times 10^6$ l/mole sec. at 25°C) and the radiation chemical yields per 100 eV energy absorbed [(GR) values] (for AN = 2.4-5.6 and for MA = 6.3-7.5) also suggests that MA should be more reactive towards polymerization than AN. The polymerizability ($k_p / k_c^{1/2}$) value of MA = 0.2164 is also less than that of AN ($k_p / k_c^{1/2} = 0.322$). Hence, MA will graft copolymerize more selectively than AN affording higher grafting. In the binary mixture, addition of MA to AN, increases both the percentage of grafting and the total dose required for optimum grafting of AN.

**Effect of Amount of Water**

Percentage of grafting of mixed monomer (AN+MA) system has been studied as a function of amount of water. Water is the best medium for graft copolymerization since wastage reaction due to chain transfer in water is minimum as water has zero chain transfer constant value. Results are presented in Fig. (III). It is observed from the figure that the percentage of grafting of the mixed monomer does not change appreciably with change in amount of water from 5 ml to 10 ml. But upon increasing the amount of water to 20 ml percentage of grafting increases to give maximum (361%) and then suddenly decreases. Maximum percentage of grafting of
FIG III EFFECT OF AMOUNT OF H₂O ON PERCENT GRAFTING OF (MA+AN)

GELATIN = 100 mg, TOTAL DOSE = 1.93 Mrad,

[MA+AN] = 0.005 ± 0.007 moles
MA (641%) alone and AN (96%) alone onto gelatin was obtained in 15 ml and 25 ml of water respectively. Thus it seems that the amount of water required for different monomers to give maximum percentage of grafting varies. This can be explained by considering the solubility of the monomers in water. MA being insoluble in water, produces maximum percentage of grafting in 15 ml water while AN having some solubility in water produces maximum percentage of grafting in 25 ml water indicating that in the presence of increased amount of water more AN is brought to the active sites. The mixed monomer (AN+MA) produces maximum grafting with 20 ml water.

The decrease in percentage of grafting with increasing amount of water beyond optimum is due to the reason that excess of hydroxyl radicals (OH) are produced during the radiolysis of water leading to preferential formation of homopolymer.

**Effect of Monomer Concentration:**

Figure (IV) represents the effect of mole fraction of MA in the binary mixture (MA+AN) of different concentration of the mixed monomers on percentage of grafting. It is observed from the figure that percentage of grafting of the mixed monomer (AN+MA) increases with increase in the mole fraction of MA giving maximum 115% at $N_{MA} = 1$ when total amount of binary mixture is 0.5 ml i.e. (0.009 moles of MA +
FIG IV  EFFECT OF MOLE FRACTION OF MA ON PERCENT GRAFTING OF (MA + AN)

GELATIN = 100 mg, \( \text{H}_2\text{O} = 20 \text{ml} \), TOTAL DOSE = 1.93 Mrad
When the total amount of the mixed monomer system was increased to 1 ml i.e. [0.005 moles of MA + 0.007 moles of AN] and 1.5 ml [0.01 moles of MA + 0.009 moles of AN] the percentage of grafting increases with increasing mole fraction of MA giving (622%) Curve-II and (681%) (Curve-III) at N_{MA}=1. These observations indicates that the addition of MA to AN increases the percentage of grafting of AN. The decrease in the Pg observed beyond maximum percentage of grafting may be due to the onset of Trommsdorff's effect shown by AN.

An attempt has been made to determine the rate of grafting, Rg, of (MA+AN) as a function of total initial monomer concentration from the slopes of curves presented in Fig.(V). The Rg values are reported in Table (II). It is observed from the table that maximum rate of grafting of (MA+AN) (2.273%/min.) is obtained with 1 ml of binary mixture having the composition (0.005 moles of MA + 0.007 moles of AN). With further increase in the monomer concentration of the binary mixture to 1.5 ml (0.009 moles of MA + 0.010 moles of AN) the rate decreases to 0.266%/min. which may be due to preferential homopolymer formation and gelling effect shown by AN.

**Effect of Methanol in Water-Methanol Solvent System**

Effect of amount of methanol in water-methanol system on percentage of grafting of (MA+AN) has been studied and the results are presented as a function of mole fraction of
IMA* AN 

\[0.005 \times 0.007 \text{ moles} = 0.003 \times 0.003 \text{ moles} = 0.009 \times 0.010 \text{ moles} =\]

FIG V PERCENTAGE OF GRAFTING AS A FUNCTION OF TIME AT DIFFERENT MONOMER CONCENTRATIONS

\(\text{GELATIN} = 100 \text{ mg, } H_2O = 20 \text{ ml, DOSE RATE} = 0.10 \text{ Mrad/hr}\)
methanol in water-methanol system. The total amount of mixed solvent system, water-methanol, was kept constant (20 ml) but the ratio of the water-methanol mixture was varied. It is observed from the (Fig.VI) that with increase in the mole fraction of methanol in mixed solvent system, percentage of grafting of (MA+AN) decreases. Decrease in percentage of grafting is attributed to various chain transfer reactions occurring in methanol leading to wastage reactions. Also gelatin is associated in water due to formation of hydrogen bonds involving various functional groups of gelatin and water. Upon addition of methanol, hydrogen bonds between water and gelatin are broken. This will decrease the accessibility of the monomer to the active sites and consequently grafting in methanol will decrease.
FIG VI  EFFECT OF MOLE FRACTION OF MeOH IN H₂O-METHANOL
SYSTEM ON PERCENT GRAFTING OF (MA+AN)

GELATIN = 100 mg, [MA+AN] = 0.005 ± 0.007 moles,
TOTAL DOSE = 1.93 Mrad
SECTION-B

GRAFT COPOLYMERIZATION OF (MA+MAN) ONTO GELATIN
EXPERIMENTAL

Materials and Methods

Gelatin (Oxoid, England) in the form of granules was used. Methacrylonitrile (Merck) and methylacrylate (MA) (Sisco) were freshly distilled and the middle fraction were used. Distilled water was used as the reaction medium.

Graft Copolymerization

Gelatin (100 mg) was dissolved in a definite amount of water at 90°C in a conical flask. After cooling, a definite amount of mixed monomer (MA+MAN) was added to the reaction flask and reaction mixture was irradiated from a Co60 γ-rays source for different time periods at a constant dose rate of 0.092 Mrad/hour. After the completion of specific reaction, the flask was removed from the chamber and an excess of methanol was added to completely precipitate gelatin, grafted gelatin, the homopolymer polymethylene acrylonitrile/polymethylacrylate and the copolymer Poly(MA -co- MAN). The precipitates were filtered and extracted with acetone for complete removal of PMAN, PMA and Poly(MAN -co- MA). The graft copolymer was then dried at 50°C until constant weight was obtained and percentage of grafting was calculated from the increase in the weight of gelatin as follows:

\[
\% \text{ Grafting} = \frac{W_2 - W_1}{W_1} \times 100
\]
where $W_1$ and $W_2$ are the weight of original gelatin and grafted gelatin after complete removal of homopolymer respectively.

Evidence of Grafting

I.R. Spectra

Gelatin-g-Poly(MAN-co-MA) shows two additional peaks, one at 1735 cm$^{-1}$ due to $\equiv C = O$ group of PMA and another at 2230 cm$^{-1}$ due to $- C \equiv N$ of PMAN indicating that MA and MAN are grafted onto gelatin.

RESULTS AND DISCUSSIONS

When graft copolymerization of a suitable monomer is carried out on a particular backbone via radical mechanism two basic types of grafting are usually recognized. In grafting 'from' method, radicals are generated on a polymer backbone and they start the polymerization of a monomer, which form grafts. The 'grafting onto' method consists in the generation, termination or transfer reaction of the growing graft macroradical to the backbone. In both cases the formation of comb-like structures, obeying the definition of graft copolymers, (12) is anticipated.

The simple concept can hardly be expected to reflect reality fully, because mutual interaction of the radical species present in the polymerization mixture is more complex. In response to the initiation process
(decomposition of initiators, irradiation etc.) radicals of at least one of the following types are created.

(a) Growing graft macroradical, when the initiation step starts the homopolymerization of monomer,

(b) backbone fragment, originated by degradation of the backbone in response to the attack by primary radicals,

(c) macroradical created on backbone by a transfer reaction or by reaction of functional groups; and

(d) macroradical formed by a similar mechanism on a graft polymer chain.

In the latter two cases, a radical is localized on a polymer chain but not necessarily at its end, as in the first two cases.

Grafting is supposed to take place during the polymerization of monomers in the presence of gelatin. No macroscopic precipitate is formed, even though the homopolymers PMA, PMAN and the copolymer PMA-co-PMAN are insoluble in water. If, alternatively, the polymerization is carried out under similar conditions in the absence of gelatin, the polymer separated as a sticky solid precipitate.

In the first step, some of the growing polymeric chains are attached to gelatin macromolecules by a transfer or termination reaction. Alternatively, the growth of a graft may be started by a radical localized on the backbone. On this basis the following radiochemical mechanism is proposed to explain the graft copolymerization of the binary mixture of (MA + MAN).
Gel - H → Gel' + H'
H₂O → OH' + H'

M₁ + OH → M₁' - OH → nM₁ → (M₁)ⁿ⁺₁ OH

M₂ + OH → M₂' - OH → nM₂ → (M₂)ⁿ⁺₁ OH

M₁' - OH + M₂ → M₂' - M₁ - OH

M₂' - OH + M₁ → M₁' - M₂ - OH

Gel + M₁ → Gel - M₁
Gel + M₂ → Gel - M₂

Gel + growing polymer chain → Graft

(I, II, III, IV)

All the reaction parameters that seem to affect graft copolymerization have been evaluated to produce maximum percentage of grafting and the results are discussed in the light of proposed mechanism.

Effect of Total Dose

Percentage of grafting of (MAN+MA) onto gelatin has been determined as a function of total dose and the results are presented in Fig. (I). It is observed from the figure that percentage of grafting increase with increasing total dose, reaches maximum (265%) at an optimum dose of 1.92 Mrad and decreases thereafter. Increase in percentage of grafting with increasing total dose is due to the generation of active sites on the polymeric backbone. The decrease in percent grafting beyond optimum total dose (1.92 Mrad) may be due to the chain termination of the growing polymeric
FIG I  EFFECT OF TOTAL DOSE ON PERCENT GRAFTING OF (MA+MAN)

GELATIN = 100 mg, H₂O = 15 ml, DOSE RATE = 0.092 Mrad/hr,

\([\text{MA+MAN}] = 1.10 \pm 0.01\) moles
chains. At higher total doses, homopolymer formation becomes the preferred process. Also the backbiting of the growing grafted chains and the polymeric backbone leads to chain scission thereby decreasing the overall percentage of grafting. Following three types of polymeric chains may be grafted onto gelatin:

(a) Branches having only MAN units as Poly(MAN).*
(b) Branches having only MA units as Poly(MA).*
(c) Branches having both MA + MAN units as Poly(MA-co-MAN)*

Diagrammatically these can be represented as:

The growing grafted chains which are still active may attack the neighbouring grafted chain thus bringing the chain scission and chain termination as well. This backbiting of the chain brings down the length of the grafted chain and as such decreases the percentage of grafting.
When the effect of total dose on grafting of MAN and MA individually onto gelatin is compared with that of the mixed monomer system (MA+MAN), it is observed that methacrylonitrile, produces maximum percentage of grafting (76%) at a much higher total dose of 3.26 Mrad, MA produces maximum (641%) at an optimum dose of 2.69 Mrad while with mixed monomer system the maximum percentage (265%) is obtained at a lower dose of 1.92 Mrad. From the result it is observed that the addition of MA to MAN in mixed monomer system increases the percentage of grafting of MAN from 76% to 265%. This is attributed to the fact that the rate of propagation ($k_p$) and rate of termination ($k_t$) values of MAN ($k_p = 26$ l/mole sec; $k_t = 21 \times 10^{-6}$ l/mole sec) are much less than those of MA ($k_p = 1580$ l/mole sec, $k_t = 55 \times 10^{-6}$ l/mole sec) suggesting that the propagation and termination of MAN is very slow while the propagation of MA being fast, growing polymeric chains are generated which are terminated at a lower rate. Also, the homopolymer, poly(MAN), is soluble in the reaction medium i.e. water and as such the viscosity of the medium increases which restricts the mobility of the growing grafted chain to the active sites consequently low percentage of grafting is observed with MAN. Therefore, the addition of MA changes the reactivity of MAN towards grafting.
Effect of Amount of Water

Percentage of grafting of mixed monomers (MAN+MA) onto gelatin has been studied as a function of amount of water and the results are presented in Fig.II. It is observed from the figure that percentage of grafting of mixed monomer increases with increasing amount of water giving maximum (590%) in 10 ml of water beyond which it decreases and becomes constant after 20 ml of water. Water also has the tendency to form hydrogen bonds with the functional groups such as hydroxy, carboxyl, amino, hydroperoxide of gelatin. The growing polymeric chain thus have an easy accessibility to the backbone to produce the graft copolymer. However, with increase in the amount of water beyond optimum (10 ml), the decrease in percentage of grafting may be attributed to the fact that with the increase in the amount of water, there is an increase in the amount of hydroxyl radical produced as a result of radiolysis of water. Excess of hydroxyl radicals produced terminate the growing grafted chain leading to decreased grafting.

Effect of Monomer Concentration

In order to study the effect of MA on the percentage of grafting MAN, graft copolymerization of a binary mixture of (MA+MAN) has been studied. Figure (III) represents the mole fraction of MA in a binary mixture (MA+MAN) of
FIG II  EFFECT OF AMOUNT OF WATER ON PERCENT GRAFTING
OF (MA+MAN)

GELATIN = 100 mg, DOSE RATE = 0.92 Mrad/hr,
TOTAL DOSE = 1.92 Mrad, \([\text{MA+MAN}] = 0.016 + 0.005\) moles
(MA + MAN)

0.005 + 0.005 moles =

0.016 + 0.005 moles =

0.027 + 0.005 moles =

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FIG III EFFECT OF MOLE FRACTION OF (MA + MAN)

GELATIN = 100mg, H2O = 15ml, TOTAL DOSE = 1.92 Mrad
different concentrations of the mixed monomers. It is observed from the curves-I, II and III, that there is constant increase in the percentage of grafting with increasing mole fraction of MA in the binary mixture.

When 1 ml (1:1 v/v) binary mixture of (MA+MAN) was used using 0.005 moles each of MA and MAN, maximum percentage of grafting (753%) was obtained (Curve-I). But when the amount of binary mixture was increased to either 2 ml or 3 ml, the 1:1 v/v ratio of the two monomers MA and MAN did not afford maximum percentage of grafting. Maximum percentage of grafting (371% and 1490%) was obtained in 2 ml (0.016 moles MA + 0.005 moles MAN) and 3 ml (0.027 moles of MA + 0.005 moles MAN) respectively. Further increase in the mole fraction of methylacrylate in the binary mixture produces excessive homopolymer and separation of the graft copolymer becomes difficult.

An attempt has been made to determine the rate of grafting, Rg, of (MA+MAN) as a function of total initial monomer concentrations. Rg has been determined from the slope of the curves presented in Fig. (IV) and the results are reported in Table-III. It is observed from the table that maximum rate of grafting of binary mixture (MA+MAN) 3.83%/min. is obtained when 3 ml of binary mixture (0.027 moles of MA + 0.005 moles of MAN) is used. Minimum rate of grafting 0.616%/min. occurs when 1 ml of binary mixture is used (0.005 moles of MA + 0.005 moles of MAN). Thus with
FIG IV  PERCENTAGE OF GRAFTING AS A FUNCTION OF TIME AT
DIFFERENT MONOMER CONCENTRATIONS

GELATIN = 100 mg, H₂O = 10 ml, DOSE RATE = 0.092 Mrad/hr
increasing monomer concentration of MA in (MA+MAN) there is constant increase in the rate of grafting. Hence MA is a better monomer which enhances the reactivity of the MAN thereby increasing the rate of grafting.

On the comparison of the effect of monomer concentration of MAN on Pg and rate of grafting of MAN as a function of initial monomer concentration with that those of mixed monomer system, it is observed that maximum percentage of grafting of MAN (105%) obtained at \([\text{MAN}] = 2.4 \times 10^{-2}\) moles is much less than that obtained (1490%) for mixed monomer system while the rate of grafting of MAN 0.44%/min. at \([\text{MAN}] = 3.0 \times 10^{-2}\) moles is also much less than that (3.83%/min.) observed with (MA+MAN) monomer mixture. Thus it seems that addition of MA to MAN produces higher percentage of grafting and enhances the rate of grafting to a larger extent. Thus MA is a better monomer as compared to MAN alone. Monomer transfer constant of MA \((C_M \text{ at } 55^\circ C = 0.275 \times 10^{-4})\) is much lower than that of MAN \((C_M \text{ at } 25^\circ C = 2.08 \times 10^{-4})\) and hence the wastage reaction are minimum with MA and consequently addition of MA enhances the Pg of the binary mixture of MA+MAN.
<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT (°C)</th>
<th>FDT (°C)</th>
<th>DT (°C) at every 10% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>Gelatin</td>
<td>275</td>
<td>625</td>
<td>75</td>
</tr>
<tr>
<td>Gelatin-g-Poly(MA-co-AN)</td>
<td>390</td>
<td>470</td>
<td>388</td>
</tr>
</tbody>
</table>
### Table-II

**Rate of Grafting [Rg] of MA+AN**

Determined as a Function of Initial Monomer Concentration

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Composition</th>
<th>Rg% /min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA + AN</td>
<td>0.005 moles of MA + 0.007 moles of AN</td>
<td>2.273</td>
</tr>
<tr>
<td>MA + AN</td>
<td>0.003 moles of MA + 0.003 moles of AN</td>
<td>0.337</td>
</tr>
<tr>
<td>MA + AN</td>
<td>0.009 moles of MA + 0.010 moles of AN</td>
<td>0.266</td>
</tr>
</tbody>
</table>

(i) Gelatin=100 mg; H₂O = 20 ml, Dose = 1.936 Mrad/hour
Table-III

Rate of Grafting \([R_g]\) of MA+MAN

Determined as a Function of Initial Monomer Concentration

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Composition</th>
<th>(R_g) %/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA + MAN</td>
<td>0.005 moles of MA + 0.005 moles of MAN</td>
<td>0.616</td>
</tr>
<tr>
<td>MA + MAN</td>
<td>0.016 moles of MA + 0.005 moles of MAN</td>
<td>1.58</td>
</tr>
<tr>
<td>MA + MAN</td>
<td>0.027 moles of MA + 0.005 moles of MAN</td>
<td>3.38</td>
</tr>
</tbody>
</table>

Gelatin = 100 mg, \(H_2O\) = 15 ml, Dose = 1.92 Mrad/hour
REFERENCES


