

Graft Copolymerization of Acrylonitrile and Methacrylonitrile onto Gelatin by Mutual Irradiation Method

INDERJEET KAUR,* RAGHUVIR BARSOLA, ANITA GUPTA, and B. N. MISRA

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171005, India

SYNOPSIS

In order to improve upon certain properties of gelatin graft copolymerization of acrylonitrile (AN) and methacrylonitrile (MAN) onto gelatin has been studied in aqueous medium using γ rays as a source of initiation. Optimum conditions for affording maximum percentage of grafting have been evaluated as a function of various reaction parameters. The grafted polyacrylonitrile (PAN) was isolated from the graft copolymer by acid hydrolysis, and the average molecular weight (M_v) of the isolated polymer has been determined viscometrically. The graft copolymers were characterized by IR spectroscopic methods and thermogravimetric analysis (TGA). Acrylonitrile was found to be more reactive than methacrylonitrile toward graft copolymerization. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Gelatin consists of a mixture of water-soluble proteins of high average molecular weight and is capable of forming firm gel below 35–40°C. It is obtained by the selective hydrolysis of collagen involving denaturation and physical and chemical degradation. Due to its proteinaceous nature, it is used in food, gummed tape, abrasives, in adhesives, and also as a protective colloid for the prevention of coalescence. Because of various potential uses of gelatin, it was considered worthwhile to effect modification of gelatin to give materials with improved properties. Misra et al.¹ grafted ethyl acrylate, methyl acrylate, and butyl acrylate onto gelatin using ceric ammonium nitrate as redox initiator. Graft copolymerization of acrylonitrile on enzymatically degraded gelatin in the presence of $K_2S_2O_8$ was reported by Kazimierz and Weislawa.² Park and Park³ studied aqueous emulsion graft copolymerization of methyl methacrylate onto gelatin by $K_2S_2O_8$ with sodium decyl sulfate (SDS) emulsifier. Recently, Stejskal et al.⁴ observed that when methyl methacrylate is polymerized in aqueous medium in the presence of

gelatin, gelatin graft copolymer macromolecules are formed. Little work on radiation-induced grafting of vinyl monomers onto gelatin is reported. In the present study we report on graft copolymerization of acrylonitrile and methacrylonitrile onto gelatin by mutual irradiation method.

EXPERIMENTAL

Materials and Method

Gelatin (Oxoid, England) in the form of granules was used. Acrylonitrile (AN) (Ferak) and methacrylonitrile (MAN) (Merck) 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. After cooling, a definite amount of monomer (AN/MAN) was added to the reaction flask and the reaction mixture was irradiated from a Co^{60} γ -ray source for different time periods at a constant dose rate of 0.14 Mrad/h. After the completion of the reaction, an excess of methanol was added to completely precipitate gelatin, grafted

* To whom correspondence should be addressed.

gelatin, and the homopolymer polyacrylonitrile/polymethacrylonitrile (PAN/PMAN). The precipitates were filtered and extracted with dimethylformamide (DMF) and acetone for complete removal of the homopolymer PAN and PMAN, respectively. 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 weights of original gelatin and grafted gelatin after complete removal of the homopolymer, respectively.

Evidence of Grafting

Infrared (IR) spectra of gelatin-*g*-PAN and gelatin-*g*-PMAN showed an additional peak at 2230 cm^{-1} due to $-\text{C}\equiv\text{N}$ of PAN and PMAN, which suggests that AN and MAN are grafted onto gelatin.

The primary thermograms of gelatin and gelatin-*g*-PAN are presented in Figure 1. It is observed from the figure that initial decomposition and final decomposition temperature (IDT and FDT) values decrease upon grafting probably due to the degradation of the backbone upon irradiation. The IDT, FDT, and decomposition temperature (DT) at different percent weight loss of gelatin and gelatin-*g*-PAN are presented in Table I.

Hydrolysis of Gelatin-*g*-PAN and Determination of Molecular Weight of Grafted Branches

The grafted PAN was isolated from the graft copolymer by hydrolysis with 6*N* HCl. A known amount of gelatin-*g*-PAN sample was treated with 6*N* HCl, and the mixture was refluxed for 22 h when all the gelatin goes into solution. The residue left behind was filtered, washed with water, dried, and identified by IR spectroscopy as PAN. The solid mass was further dried in vacuum oven and the intrinsic viscosity of homopolymer was determined at 25°C in DMF by using a Ubbelohde viscometer. The molecular weight was calculated from

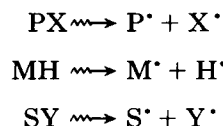
$$[\eta] = 3.4 \times 10^{-4} \times \bar{M}_n^{0.733}$$

The molecular weight determined as a function of percentage of grafting is presented in Table II.

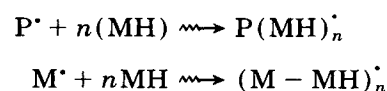
RESULTS AND DISCUSSION

Following mechanism is proposed to explain graft copolymerization of AN and MAN onto gelatin by mutual irradiation method:

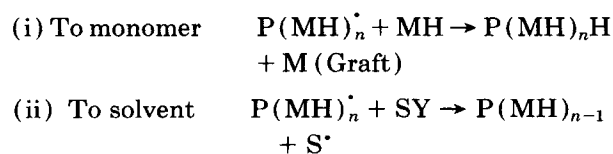
Initiation



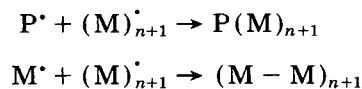
Propagation



Termination by Transfer



Termination by Coupling



where PX is a polymer backbone, MH is a monomer, and SY is a solvent.

Percentage of grafting of AN and MAN has been studied as a function of following reaction parameters, and the results are explained in the light of the above proposed mechanism.

Effect of Total Dose

Percentage of grafting of AN and MAN onto gelatin has been determined as a function of total dose, and the results are presented in Figures 1(a) and 1(b) respectively. Percentage of grafting of AN [Fig. 2(a)] increases with increasing total dose, reaches a maximum (96%) at 0.36 Mrad, and then decreases. However, maximum percentage of grafting of MAN (76%) is observed [Fig. 1(b)] at a much higher total dose of 3.26 Mrad. Both AN and MAN show gel effect during grafting.

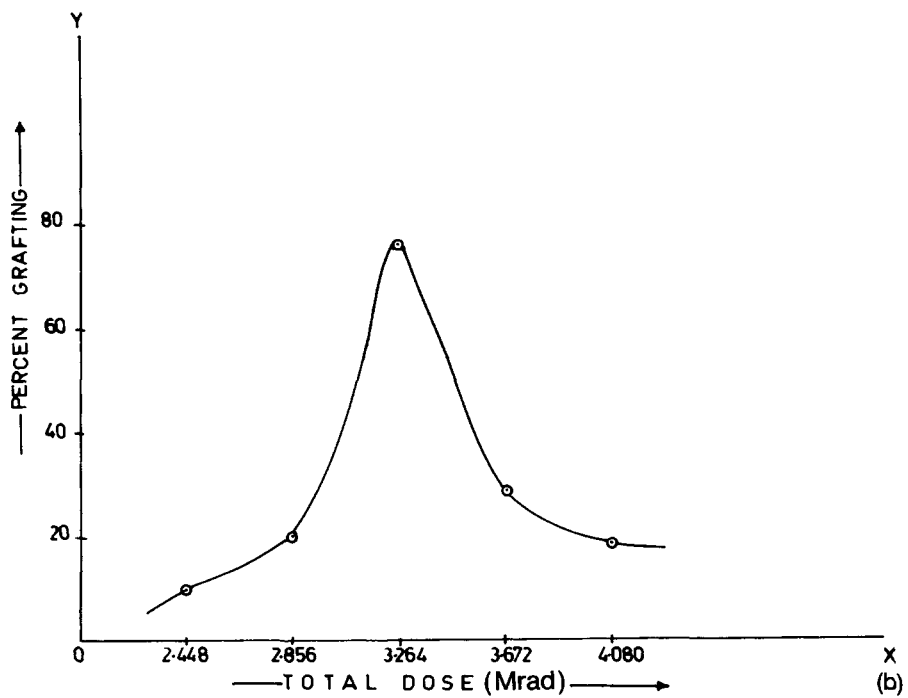
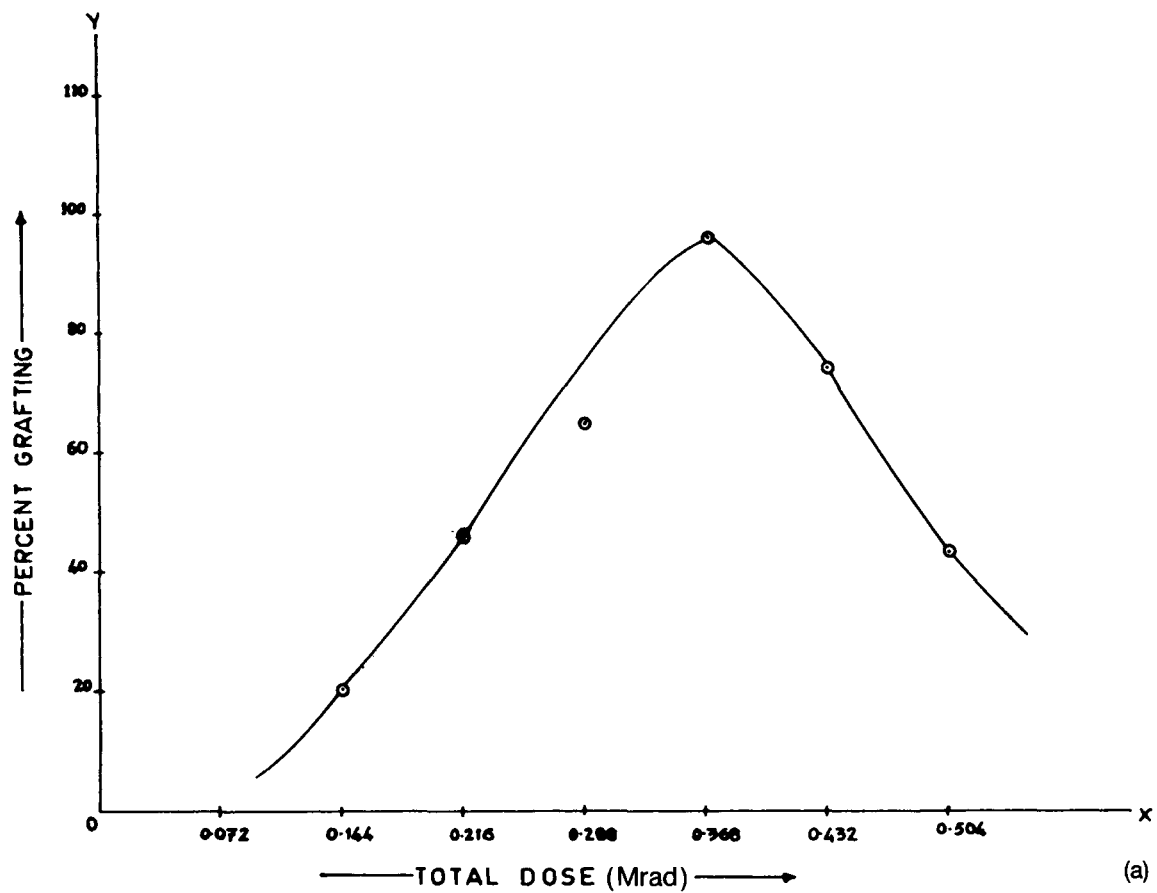


Figure 1 Effect of total dose on percent grafting of (a) AN and (b) MAN.

Table I Thermogravimetric Analysis (TGA) of Gelatin and Gelatin-*g*-PAN

Sample No.	Sample	IDT (°C)	FDT (°C)	DT (°C) at Every 10% Weight Loss								
				10%	20%	30%	40%	50%	60%	70%	80%	90%
1	Gelatin	275	625	75	262.5	342.5	387.5	480	630	670	692.5	725
2	Gelatin- <i>g</i> -PAN	265.5	600	262.5	325	347	382	480	587	632.5	677.5	725

Effect of Monomer Concentration

Figures 3(a) and 3(b) represent the effect of concentration of AN and MAN on percentage of grafting, respectively. Percentage of grafting of AN [Fig. 3(a)] was found to increase with increasing monomer concentration upto $[AN] = 3.0 \times 10^{-2}$ mol while in case of MAN [Fig. 3(b)] maximum percentage of grafting (105%) is obtained at $[MAN] = 2.4 \times 10^{-2}$ mol, beyond which it decreases due to preferential formation of homopolymer at higher concentration.

Rate of grafting (R_g) as a function of total initial monomer concentration of AN and MAN has been evaluated from Figures 4(a) and 4(b), respectively. It is observed from Figure 4(a) that the rate of grafting of AN is maximum (8.81%/min) at $[AN] = 0.75 \times 10^{-2}$ mol. Further increase in AN concentration decreases the rate of grafting due to excessive gelation, which hinders the movement of the growing polymeric chains to the active sites. Rate of grafting of MAN, however, increases with increasing MAN concentration showing a maximum (0.44%/min) at $[MAN] = 3.0 \times 10^{-2}$ mol. Rate of grafting as determined from Figures 4(a) and 4(b) is presented in Table III.

Effect of Amount of Water

Percentage of grafting of AN and MAN has been studied as a function of amount of water, and the results are presented in Figures 2(a) and 2(b), re-

Table II Molecular Weight of PAN Isolated from Gelatin-*g*-PAN

Sample No.	% Grafting	Value of $[\eta]$	Molecular Weight (M_v)
1	437.1	0.56	23,930
2	522.8	1.0	53,810
3	840.0	1.4	85,150
4	940.7	1.6	102,300

spectively. Maximum percentage of grafting of AN and MAN is observed when 25 and 35 mL of water, respectively, is used under optimum conditions. Further increase in amount of water decreases percentage of grafting of both the monomers. This may be explained by assuming that, with increased amount of water beyond optimum, radiolysis of water occurs leading to the formation of too many hydroxyl radicals, which are mutually engaged in terminating the growing grafted chains leading to decrease in percentage of grafting.

Effect of Methanol in Water-Methanol Solvent System

Effect of mole fraction of methanol in water-methanol solvent system on percentage of grafting of AN and MAN has been studied, and the results are presented in Figures 5(a) and 5(b), respectively. It is observed that maximum percentage of grafting with both the monomers is obtained when water alone is used as the reaction medium. As the amount of methanol is increased in the reaction medium, percentage of grafting decreases with both the monomers. This is explained by the fact that methanol promotes various chain transfer reactions leading to wastage of monomers.

Reactivity of AN and MAN Toward Grafting

It is evident from the foregoing discussions that AN is more reactive toward grafting than MAN since AN affords higher percentage of grafting (96%) at a lower optimum total dose (0.36 Mrad) as compared to MAN, which produces 76% as maximum percentage of grafting at a much higher optimum total dose (3.26 Mrad). The observed reactivity can be rationalized by the fact that AN, being soluble in water, shows greater accessibility to the active sites of the backbone polymer, thereby producing higher percentage of grafting than MAN, which is insoluble in water. Further, the growing polymeric chains of MAN are more resonance stabilized and therefore less reactive than those of AN as shown below:

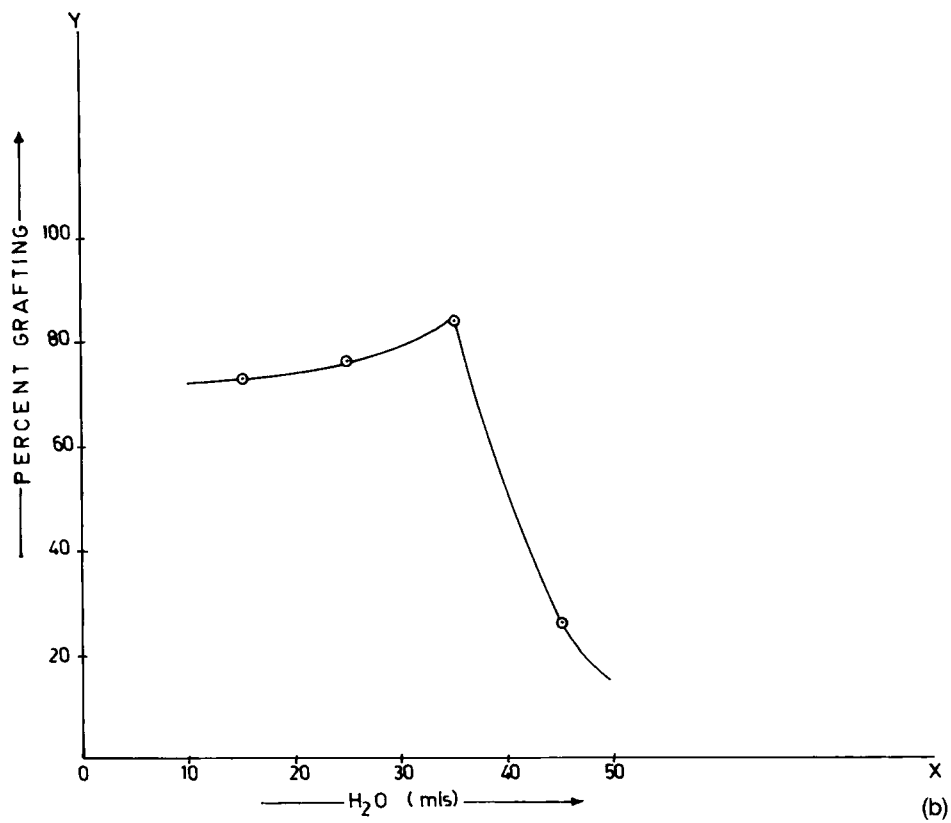
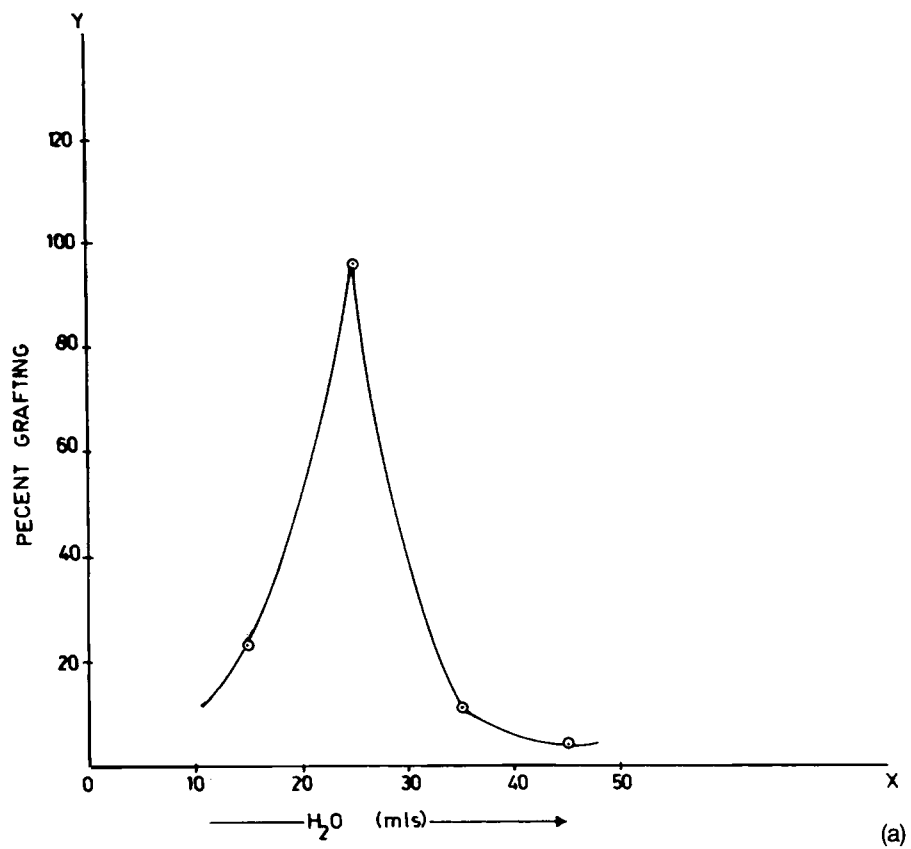


Figure 2 Effect of amount of water or percent grafting of (a) AN and (b) MAN.

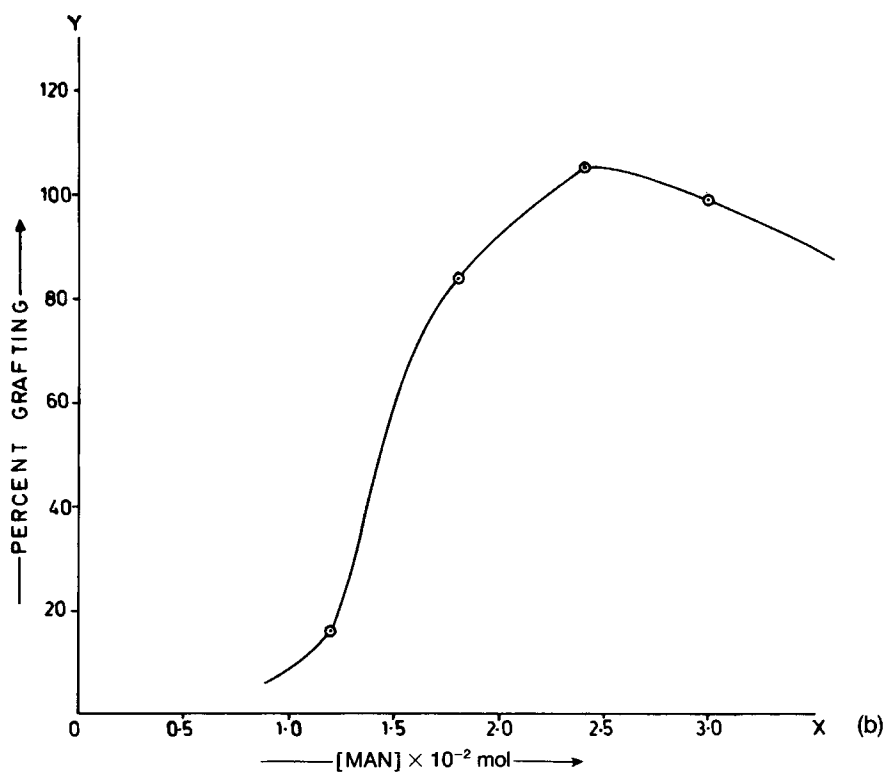
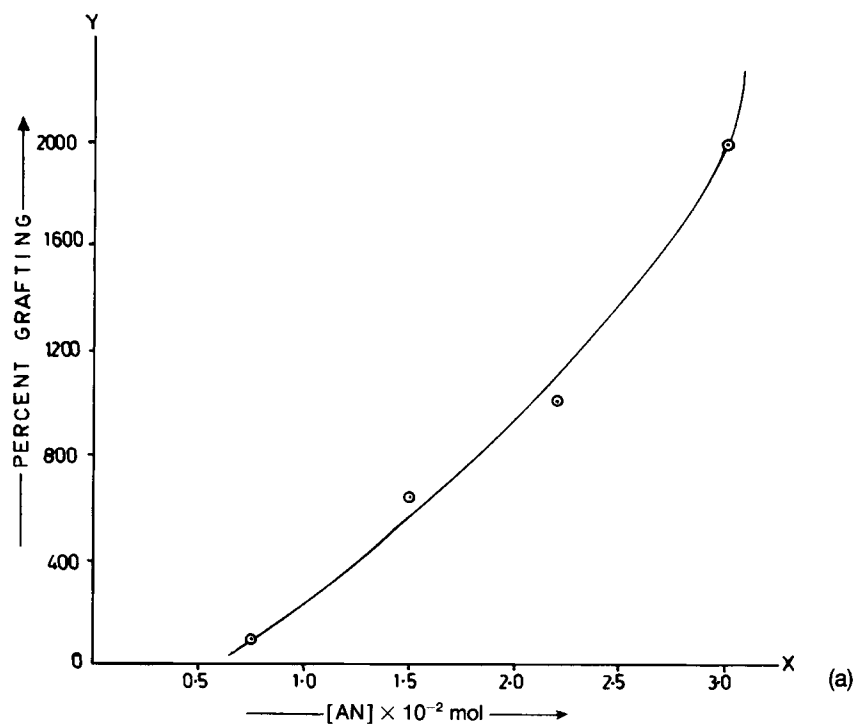


Figure 3 Effect of concentration of (a) AN and (b) MAN in ($\times 10^{-2} \text{ mol}$) on percent grafting.

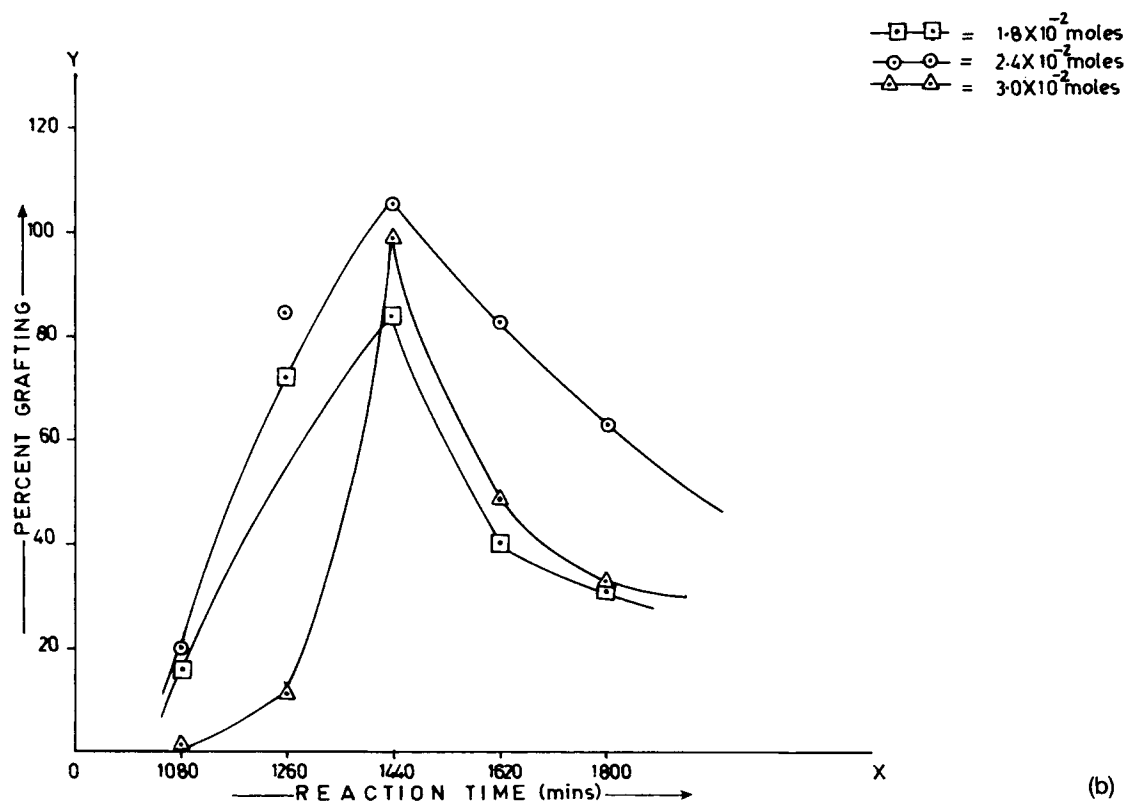
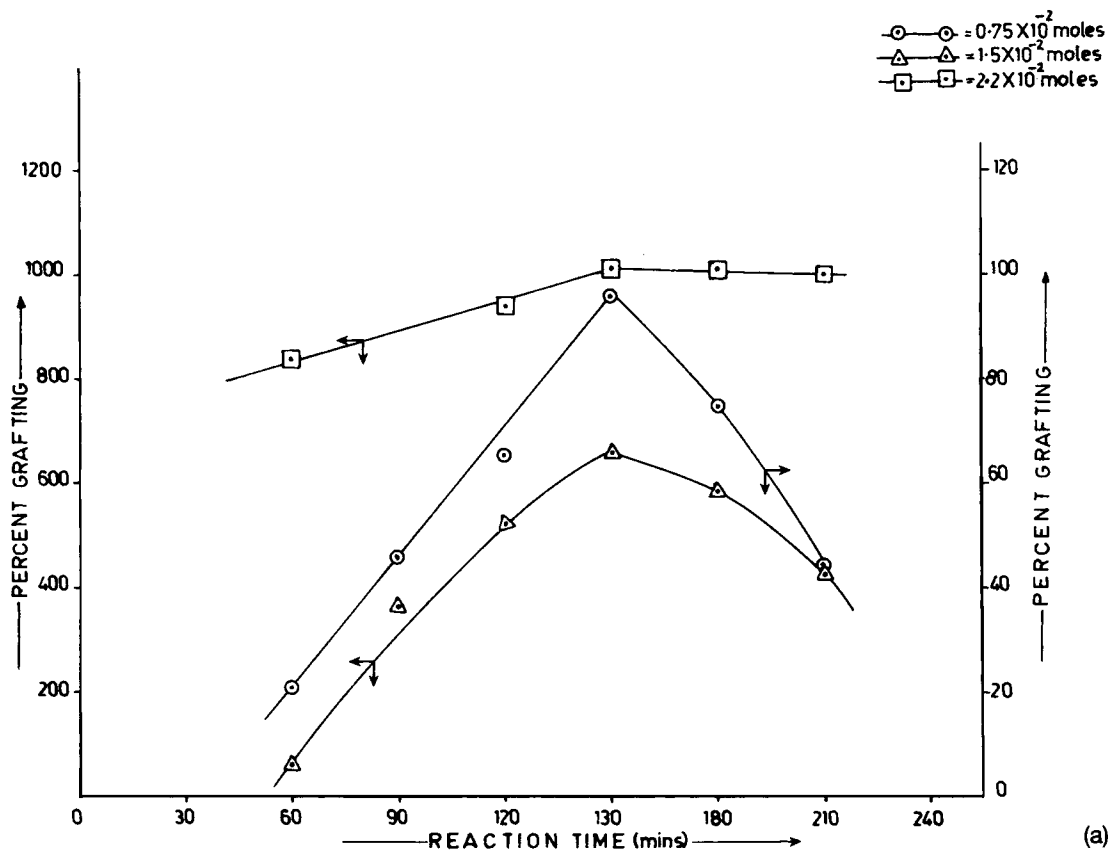


Figure 4 Determination of rate of grafting R_g of (a) AN and (b) MAN as a function of initial monomer concentration.

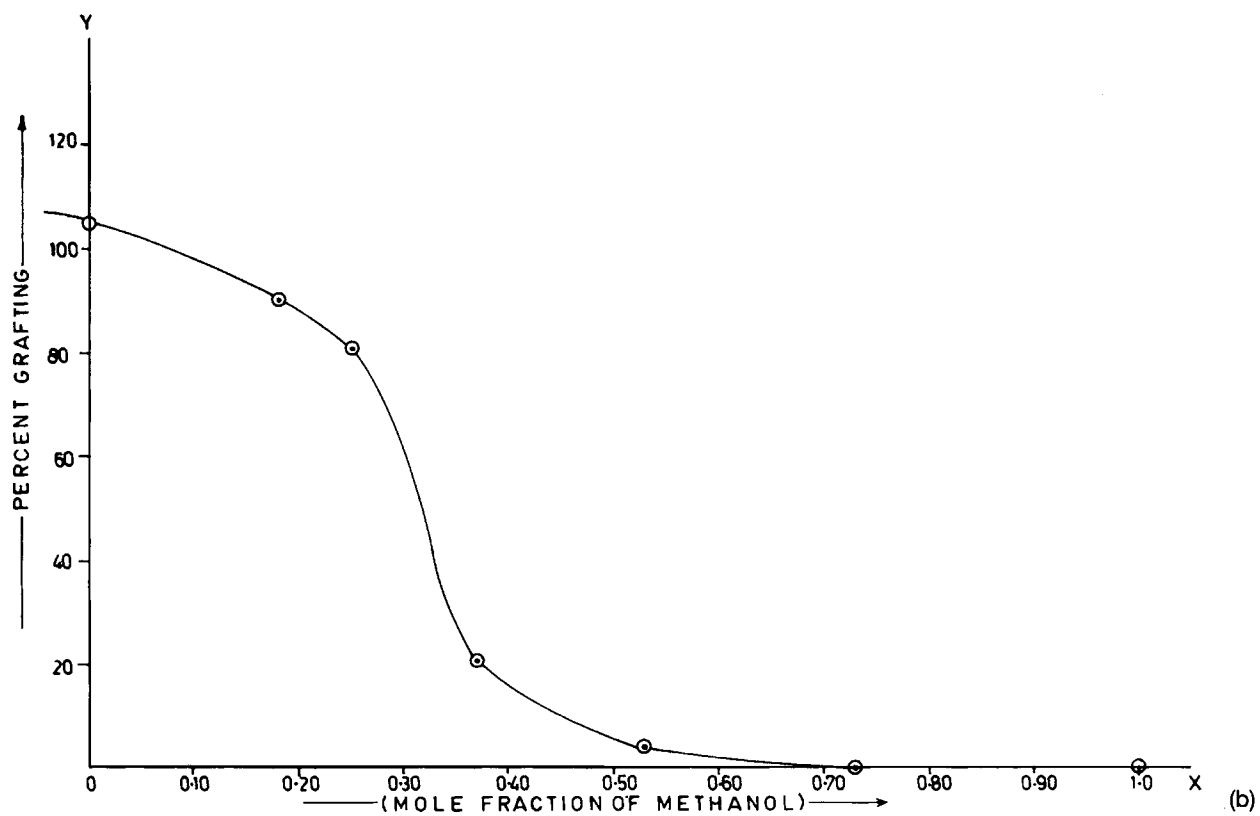
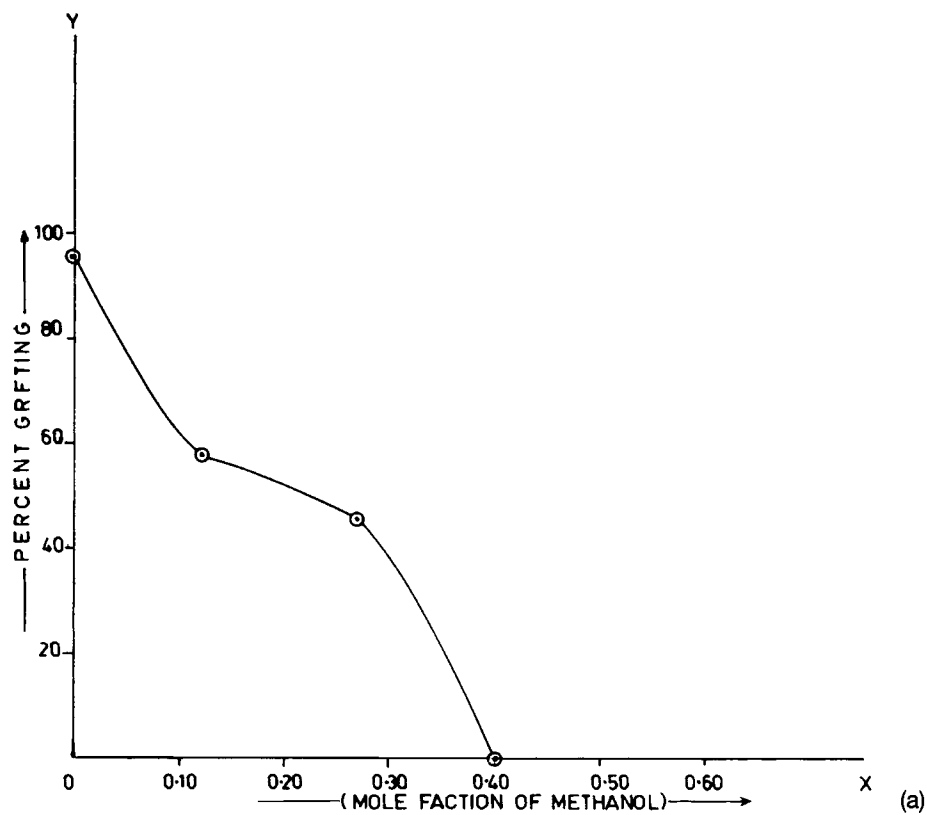


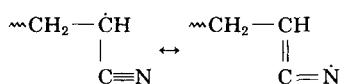
Figure 5 Effect of mole fraction of methanol in water-methanol system on percentage of grafting of (a) AN and (b) MAN.

Table III Rate of Grafting (R_g) of AN and MAN as a Function of Initial Monomer Concentration

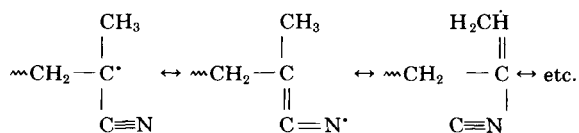
Sample No.	Monomer	$[M] \times 10^{-2}$ mol	R_g (%/min)
1	AN ^a	0.75	8.81
2	AN ^a	1.5	7.97
3	AN ^a	2.2	2.18
4	MAN ^b	1.8	0.19
5	MAN ^b	2.4	0.24
6	MAN ^b	3.0	0.44

^a Gelatin = 100 mg; H₂O = 25 mL; dose rate = 0.14 Mrad/h.

^b Gelatin = 100 mg; H₂O = 35 mL; dose rate = 0.136 Mrad/h.



Growing AN Chain



Growing MAN Chain

Finally, MAN has a high value of monomer transfer constant (C_M at 25°C = 2.08×10^{-4})⁵ as compared to AN (C_M at 25°C = 0.105×10^{-4})⁶ leading to wastage reactions and hence decrease in percentage of grafting.

One of us (R.B.) is thankful to CSIR, New Delhi, for providing financial assistance in the form of SRF.

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Received August 18, 1993

Accepted May 6, 1994