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Grafting Onto Wool

22. Radiation Induced Graft Copolymerization of Methyl Methacrylate in Water-Methanol System

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Graft copolymerization of MMA onto Himachali wool fiber has been studied by using gamma-irradiation from a Co^{60} source in water-methanol system. Percentage of grafting and percent efficiency have been determined as function of total dose and composition of solvent mixtures. The maximum graft yield (52%) occurred at a total dose of 2.56 Mrad, when the composition of solvent mixture consisted of 1:3 water-methanol. In 1:1 water-methanol medium at the total dose of 2.56 Mrad, a maximum of 38% grafting was obtained. An attempt has been made to explain the role of methanol in gamma-irradiation induced grafting of MMA onto wool fiber.

INTRODUCTION:

Modification of natural polymers such as starch (MINO & KAIZERMAN, 1958), cellulose (RICHARDS, 1961) and natural rubber has been studied extensively. Comparatively less attention has been paid to the modification of proteins in general and wool fiber in particular, by graft copolymerization techniques. Initiation of graft copolymerization can be effected by a variety of methods which include (a) chemical (b) mechanical and (c) irradiation. Among chemical methods initiation of grafting by redox initiator has been successfully attempted onto a variety of backbone polymers. With the availability of irradiation facilities attempts are being made to effect grafting by either low or high energy irradiation. Ultra-violet light in conjunction with sensitizers has been employed for initiation of graft copolymerization onto cellulose. Gamma radiation induced grafting of acrylic acid onto starch by pre-irradiation technique has been reported (REYES et al., 1968). Radiation grafting of acrylic acid onto polypropylene fiber has also been attempted (M.H. RAO et al., 1979). Little work, however, has been reported on gamma-irradiation induced graft copolymerization of vinyl monomers onto wool fiber. In recent years, polymer chemists have shown interest in carrying out graft copolymerization by gamma-irradiation, because it was found that radiation methods for the preparation of graft are often easier to handle than most conventional chemical methods. It has been found that considerable amount of styrene was grafted to wool in air and that the percentage of grafting was dependent upon the

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nature of swelling agent. Moreover, the radiation grafting methods are very general, owing to the unselective absorption of radiation in matter and can in principle be used to prepare any desired combination of polymers. Recently STANNETT et al. (1966) have been able to effect grafting of styrene onto wool fiber by using gamma-irradiation technique. A comprehensive research programme on graft copolymerization of vinyl monomers onto a variety of natural backbone polymers by chemical and radiation methods has been initiated in our laboratory (MISRA et al., 1978, 79, 80). In this preliminary investigation, we report studies on graft copolymerization of MMA onto wool fiber by use of gamma-irradiation from a Co^{60} source as a function of total dose and composition of reaction medium.

EXPERIMENTAL:

Purification of Himachali wool fiber has been described earlier (MISRA et al., 1977). Methyl methacrylate was washed with 5% NaOH and then dried over anhydrous sodium sulfate. The dried monomer was distilled and the middle fraction was used. Nitrogen was purified by passing through an alkaline pyrogallol solution for removing traces of oxygen. Methanol was distilled over sodium metal.

Graft Copolymerization:- 100 mg of the purified wool was immersed in 20 ml of water-methanol system in a 50 ml conical flask equipped with two standard joints with hollow stopcocks. Definite amount of monomer was added to the reaction flask and nitrogen was passed through the reaction flask prior to irradiation for twenty minutes. Both the stopcocks were closed and nitrogen atmosphere was maintained inside the reaction flask. Irradiation of reaction mixture was carried out in a 2500 curie cobalt-60 source at room temperature and the graft copolymerization by mutual technique was carried out at different doses. After completion of graft copolymerization, homopolymer was removed from the graft by solvent extraction. The percentage of grafting and percent efficiency were calculated from increase in weight of original wool after grafting in the following manner:

$$\% \text{ Grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

$$\% \text{ Efficiency} = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1, W_2 and W_3 denote respectively the weight of the original wool, weight of the grafted wool and weight of the monomer added.

RESULTS AND DISCUSSION:

Primary interaction of radiation with matter leads to the formation of positive ions and excited molecules. In the present investigation, grafting of MMA onto wool fiber was effected by gamma irradiation by the mutual technique in the absence of air. The wool fiber was dispersed in varying amounts of water-methanol mixture and to the reaction mixture monomer (MMA) was added. The resulting reaction mixture was subjected to gamma irradiation. The following primary events appear to have taken place:

$$WH \rightsquigarrow WH^{*} \longrightarrow W^{\bullet} + H^{\bullet} \qquad (1)$$

$$M \rightsquigarrow M^{*} \longrightarrow M^{\bullet} + e \qquad (2)$$

$$CH_3OH \rightsquigarrow CH_3OH^{*} \longrightarrow \dot{C}H_3 + \dot{O}H \qquad (3)$$

$$H_2O \rightsquigarrow H_2O^{*} \longrightarrow H^{\bullet} + \dot{O}H \qquad (4)$$

Upon irradiation the backbone polymer (WH) and other species afford excited molecules which then undergo dissociation into free radicals. Other reaction involving formation of ions may also occur, but these are of little significance for grafting. Once the formation of various free radical species is rationalized then it is easier to explain grafting by analogy with the mechanism of radical initiated grafting onto wool fiber by chemical methods.

$$WH \rightsquigarrow WH^{*} \longrightarrow W^{\bullet} + H^{\bullet} \qquad (5)$$

$$M \rightsquigarrow M \longrightarrow M^{\bullet} \xrightarrow{nM} (M)^{\bullet}_{n+1} \qquad (6)$$

$$WH + M^{\bullet}_{n+1} \longrightarrow W^{\bullet} + M_{n+1} - H \qquad (7)$$

$$WH + (R^{\bullet}) \longrightarrow W^{\bullet} + RH \qquad (8)$$

$$W^{\bullet} \xrightarrow{M} WM^{\bullet} \xrightarrow{nM} W - (M)^{\bullet}_{n+1} \qquad (9)$$

$$W - (M)^{\bullet}_{n+1} + M^{\bullet}_{n+1} \longrightarrow W - (M)_{2n+2} \qquad (10)$$

where WH represents the wool fiber, $(R^{\bullet})$ represents various radical species arising from the irradiation of solvent molecules. Termination of growing grafted chain may occur by process (10). It is apparent from the above mechanism that the formation of various radical species $(R^{\bullet})$ will generate more active sites onto polymeric backbone (WH) by hydrogen abstraction process. Thus both methanol and water molecules upon irradiation produce radical species $(R^{\bullet})$ which participate in the generation of active sites onto wool fiber. It is observed from Table I and II that as the amount of CH_3OH increases percent grafting also increases and a maximum of 52% grafting was obtained when grafting is performed in 1:3 (water-methanol) system.

TABLE-I

Effect of gamma-irradiation in mutual grafting of PMMA on wool fiber in 1:1 water-methanol system

S.No.	MMA x 10^2 moles/L	MeOH:H_2O	Dose rate	Total dose	% G	% E
1.	47.0	1:1	.16MR	0.32MR	26	2.76
2.	47.0	1:1	.16MR	0.48MR	36	3.82
3.	47.0	1:1	.16MR	0.80MR	41	4.36
4.	47.0	1:1	.16MR	2.56MR	38	4.04
5.	47.0	1:1	.16MR	3.68MR	35	3.72
6.	47.0	1:1	.16MR	4.00MR	31	3.29
7.	47.0	1:1	.16MR	6.84MR	25	2.65
8.	47.0	1:1	.16MR	10.00MR	24	2.55

Wool = 100 mg; Temp. = room temperature.

TABLE-II

Effect of gamma-irradiation in mutual grafting of PMMA on wool fiber in 1:3 water-methanol system

S.No.	MMA x 10^2 moles/L	H_2O:CH_3OH	Dose rate	Total dose	% G	% E
1.	47.0	1:3	.16MR	0.32MR	6	0.63
2.	47.0	1:3	.16MR	0.48MR	40	4.25
3.	47.0	1:3	.16MR	0.80MR	45	4.78
4.	47.0	1:3	.16MR	2.56MR	52	5.53
5.	47.0	1:3	.16MR	4.00MR	52	5.53
6.	47.0	1:3	.16MR	10.00MR	50	5.32

Wool = 100 mg; Temp. = room temperature.

Methanol is known to facilitate swelling of wool fiber and with the swollen wool fiber penetration of monomer becomes easier. This would afford enhanced grafting. It is also observed from Table I and II that total dose at the initial stages exert profound effect on percent grafting. The percent grafting increases with increase in dose and reaches a maximum value when the total dose is 0.80 Mrad and 2.56 Mrad in 1:1 and 1:3 water-methanol mixture respectively.

With further increase in dose, percentage of grafting essentially remains constant (Fig. 1).

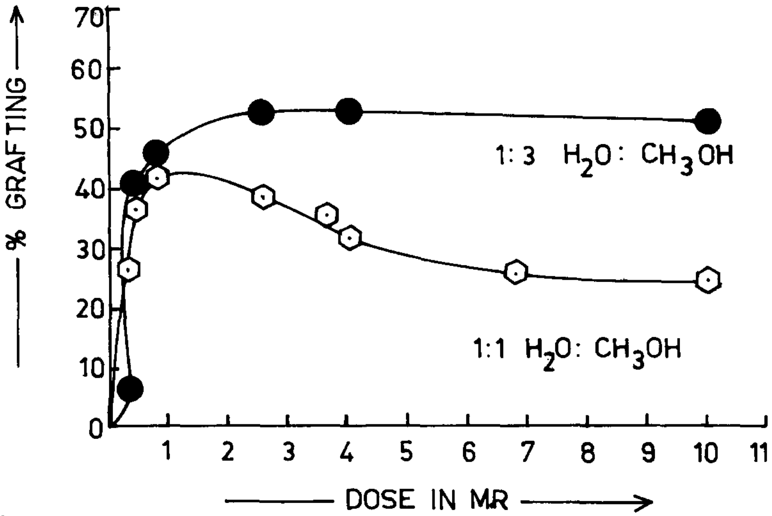

Fig. 1:- Effect of total dose on percont grafting of MMA onto wool

This indicates that at higher doses, various radical species that are formed, are engaged in mutual termination of grafted chains and homopolymerization becomes the preferred process.

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