

Radiation-Induced Grafting onto Wool. A Kinetic Analysis

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Synopsis

The radiation-induced graft copolymerization of styrene onto wool in aqueous methanol was studied over a temperature range of 0°C to 45°C and a radiation dose-rate range of 0.05 to 2.0 Mrad/hr. The rate of grafting was found to obey the classical polymerization equation. Chain transfer to wool was found to play an important role in the grafting process, and the molecular weight of the resulting graft copolymer was found to be independent of the irradiation dose. The activation energy of the graft process changed from a value of 4.7 kcal/mole below 19°C to a value of 18.7 kcal/mole above this temperature. This phenomenon is ascribed to the formation of hydrogen-bonded systems between the protic solvent molecules and the protein chain in the wool.

INTRODUCTION

One of the first reports on the chemical deposition of a synthetic polymeric substance in wool was published by Lipson and Speakman in 1949.¹ The generation of free radicals in gamma-irradiated wool was reported by Burke et al. in 1962.² These workers found that gamma irradiation of wool in vacuo produced stable free radicals and also demonstrated that acrylonitrile could be graft-copolymerized onto preirradiated wool.

To date, numerous reports have been published concerning the effect of grafting on the physical and mechanical properties of wool, and a review on this topic was published by Needles et al. in 1972.³ However, there have been only a few reports concerning investigations into the fundamental aspects of the grafting process. These investigations include a study on the location of the grafting in the wool fiber⁴ and studies on the kinetics of chemical grafting of methyl methacrylate onto wool,^{5,6} and radiation-induced grafting of styrene onto wool.^{7,8} In most of these investigations, the radiation-induced grafting processes were carried out under conditions of diffusion control, and considerable postpolymerization effects were observed. However, surprisingly little work has been done to elucidate the influence of the irradiation temperature on the grafting process.

In this report we wish to report in more detail on the kinetics of the radiation-induced graft copolymerization of styrene onto wool, with special reference to the influence of the irradiation temperature on the grafting process.

EXPERIMENTAL

White commercial-grade wool yarn was continuously extracted for 18-hr periods with methanol and petroleum ether prior to usage. Except where

otherwise stated, monomer solutions consisted of 25% styrene by volume, 70% methanol, and 5% water. Each experiment consisted of wool yarn and monomer solution in the ratio of 1 g to 10 ml, and was subjected to four degassing cycles and sealed in a glass ampoule in vacuo prior to irradiation.

Irradiations were carried out in both an AECL Gammabeam 650 (50 kCi) and a Gammacell 220 (10 kCi) irradiation source, both equipped with temperature control. After irradiation, the grafted wool samples were first washed with dioxane and then continuously extracted for 24 hr with benzene in a Soxhlet apparatus in order to remove all extractable homopolymer. The reported graft is given as percentage apparent graft.

Graft copolymer was isolated by digesting the wool of a grafted sample of yarn in 6*N* hydrochloric acid.⁹ Number-average molecular weights were determined by means of viscometry in toluene at 25°C, with the constants $a = 0.725$ and $K = 1.1 \times 10^{-4}$ according to Danuso and Moraglio.¹⁰

RESULTS AND DISCUSSION

Nature of the Propagating Species

Since all grafting experiments were carried out using monomer solutions containing 5% water, it would appear that the grafting process must proceed by means of a free-radical mechanism and that any ionic contribution must be negligible. A study of the influence of scavengers on the rate of graft copolymerization of styrene onto wool at 30°C and an irradiation dose rate of 0.36 Mrad/hr is indicated in Table I.

From this table, it clearly follows that the graft copolymerization of styrene onto wool in aqueous methanol by gamma irradiation proceeds by means of a free-radical pathway, in good agreement with earlier observations.⁸

Influence of Monomer Concentration

In order to ascertain the appropriate kinetic relationships for the grafting of styrene onto wool, the influence of monomer concentration was first determined. The radiation-induced graft copolymerization of styrene onto wool was carried out at 30°C and at a dose rate of 0.36 Mrad/hr. The styrene concentration in the monomer solution was varied over the range of 5% to 30% monomer by volume, controlled by adjusting the methanol concentration while maintaining the water concentration at a constant 5%.

TABLE I
Effect of Additives on the Polymerization^a

Additive	Additive concentration, % (w/w)	Percentage conversion to polymer, %
None	—	65.4
Benzoquinone	0.50	0.0
Air	saturated	59.3
Oxygen	saturated	31.3

^a Reaction conditions: temperature, 30°C; dose rate, 0.36 Mrad/hr; total dose, 0.36 Mrad.

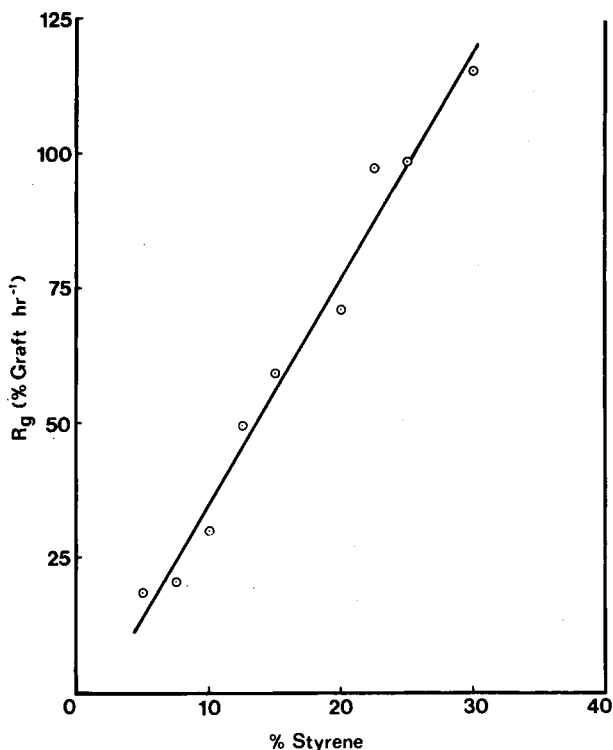


Fig. 1. Influence of the styrene concentration on the rate of grafting at a dose rate of 0.36 Mrad/hr and an irradiation temperature of 30°C.

As seen in Figure 1, a straight-line fit is obtained for a plot of the rate of grafting R_g as a function of styrene concentration. This indicates that the rate of grafting is directly proportional to the concentration of styrene in the monomer solution. While the concentration of styrene within a wool fiber need not be precisely the same as in the monomer solution, we may reasonably assume that a linear relationship will exist between the two.

In the present investigation, it was observed that very high linear grafting rates (74%/hr at 30°C and over 100%/hr at 40°C) could be maintained up to conversions of at least 400%. Notwithstanding these high grafting rates, no tailing-off effects resulting from monomer depletion in the fiber, were observed, in contrast to what most earlier investigators observed. Such high rates of grafting can be maintained only if high rates of diffusion both through the fiber surface and throughout the fiber interior are attained. This can be attributed in particular to the presence of water which acts together with methanol as a very effective swelling agent. In contrast to most earlier observations, we have to conclude that the radiation-induced grafting of styrene onto wool is not a diffusion-controlled process when carried out in aqueous methanol.

Thus, we may conclude that the rate of grafting of styrene onto wool in aqueous methanol is directly proportional to the concentration of styrene within the wool fiber. This is in agreement with the observation by Odian et

al. that the rate of grafting of styrene onto nylon in methanol is directly proportional to the monomer concentration.¹¹

Influence of Radiation Intensity

The rate of grafting was determined as a function of radiation intensity at 30°C over a dose-rate range of 0.05 to 2.0 Mrad/hr. The results of the dose-rate study are presented in Figure 2. As can be seen from this figure, a 0.5-order dependence of R_g on radiation intensity was found. This indicates that a bimolecular termination process is predominant in the graft copolymerization of styrene onto wool.

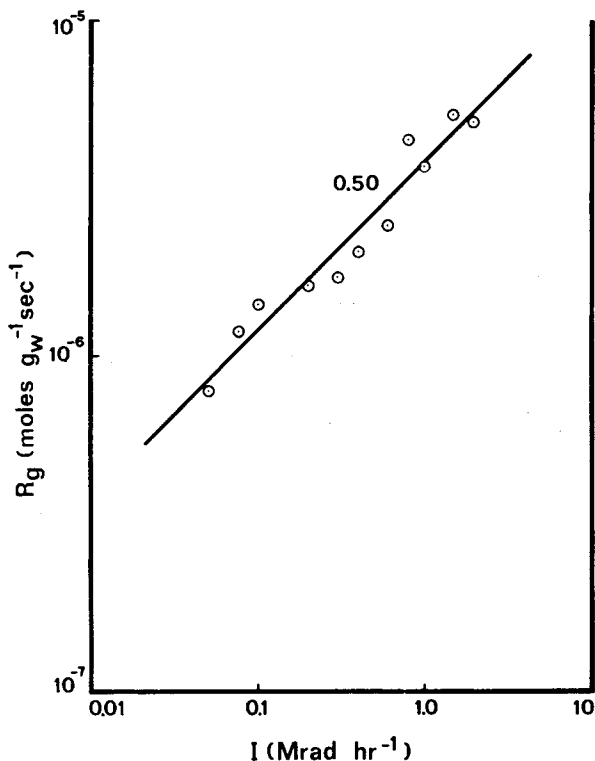
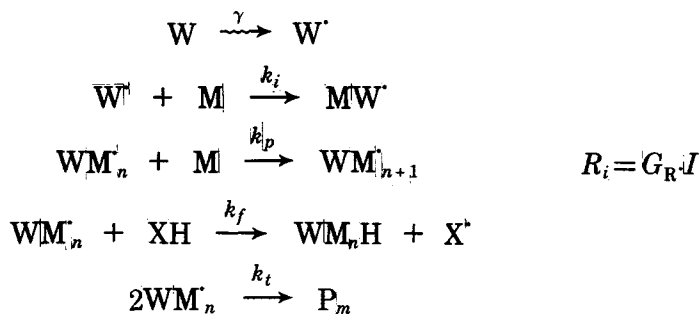


Fig. 2. Influence of dose rate on the rate of grafting at an irradiation temperature of 30°C.

Although earlier investigators observed that the conversion curves become progressively nonlinear with an increase in the dose rate, even the high dose rates used in this investigation failed to bring about this effect. This observation gives further support to our contention that the grafting process is not diffusion controlled in aqueous methanol.

Kinetics of the Graft Process

We may now consider the following kinetic scheme which represents the radiation grafting onto the polypeptide wool molecule W by the styrene monomer M :



In this scheme the grafting process is initiated by the addition of a monomer molecule to a free-radical site formed on the polypeptide chain by irradiating the wool. According to Campbell et al.,⁸ the production of free radicals on wool in solution (30/70 styrene-dioxane + 18% methanol) is $G_R = 0.37$. Furthermore, regenerative chain-transfer processes involving monomer, solvent, or polypeptide molecules are also taken into account. In addition, only termination through recombination is considered as this is known to be the predominant process by means of which styryl radicals terminate.¹²

According to Odian, chain-transfer processes between the growing graft styryl radical and both the monomer itself and primary alcohols are negligible.¹¹ Working on this assumption, we take into account only chain transfer between the styryl radical and the polypeptide molecule, a process which will lead to further grafting. Based on the above scheme, the rate of grafting R_g can then be expressed as follows:

$$R_g = k_p k_t^{-1/2} R_i^{1/2} [M] \quad (1)$$

Clearly, our experimental derived relationships between the rate of grafting, monomer concentration, and radiation intensity are in accord with eq. (1).

Based on the observation that the molecular weight of the graft copolymer obtained in the case of cellulose is an order higher than is the case for wool, Campbell concluded that heavy chain transfer plays an important role in the case of wool compared with cellulose. The results of this investigation support this conclusion, notwithstanding the fact that the molecular weight of the graft polymer is indeed much higher than that of the homopolymer formed in solution, for example, the number-average molecular weights of the graft copolymer and the homopolymer formed in the monomer solution are, at 40°C, 161,000 and 4,800, respectively. The importance of chain-transfer reactions can be gauged from the absolute magnitude of $G(-m)/\overline{DP}_n$ for the polymer formed. Where this quantity exceeds 10 for a radical reaction, it is fairly safe to assume that chain transfer is important in determining the molecular weight.¹³ As follows from Table II, we notice that for the graft process, chain transfer does indeed play an important role over the entire temperature range investigated. However, in the case of the homopolymer, negligible chain transfer takes place. This is in agreement with Odian's assumptions concerning the importance of a chain-transfer process between the growing styryl radical and the styrene-alcohol system. It is also apparent from Table II that chain transfer becomes increasingly important with an increase in temperature.

TABLE II
The Effect of Irradiation Temperature on Regenerative Chain Transfer on the Formation of Graft Copolymer and Homopolymer at a Dose Rate of 0.20 Mrad/hr

Temperature, °C	Graft copolymer		Homopolymer	
	$G(-m)/\overline{DP}_n$	N_t^a	$G(-m)/\overline{DP}_n$	N_t^a
0	3.2	7		
5	6.8	16		
10	9.2	22		
15	13.0	31		
20	13.6	33	4.2	0
30	15.5	38		
40	20.8	51	2.5	0
45	23.7	58	1.7	0

^a $N_t = (G(-m)/\overline{DP}_n)/G_R - 1$ where G_R in the case of the graft copolymer was taken to be 0.4, and in the case of the monomer solution a value of 4.5 was used, a weighted average of the free-radical production of styrene¹⁵ and methanol.¹⁶ The fact that N_t can be less than unity in the case of homopolymer indicates that not every free radical generated in the monomer solution leads to the formation of a polymer chain.

TABLE III
The Influence of Dose on the Number-Average Molecular Weight of the Graft Copolymer at 40°C and a Dose Rate of 0.20 Mrad/hr

% Graft	$\overline{M}_n \times 10^{-5}$
73	1.89
129	1.61
181	1.59
213	1.39
249	1.58

The importance of the chain-transfer process in determining the molecular weight of the graft copolymer is also demonstrated by the observation that the number-average molecular weight is independent of the degree of grafting (dose), as follows from Table III. This observation is in disagreement with earlier findings.⁸ This independence of the graft copolymer molecular weight with respect to dose was observed over the entire temperature range studied.

The above conclusions were arrived at by making the assumption that all chain transfer in the wool can lead only to the formation of new graft polymer. We thus conclude that the graft copolymer obtained experimentally contained little homopolymer. This is in agreement with an earlier observation of Arai.⁹

Influence of Temperature

The effect of temperature on the grafting process was determined at a dose rate of 0.20 Mrad/hr over the temperature range of 0°C to 45°C. Over this temperature range, the rate of grafting was found to be linear with respect to dose. An Arrhenius plot of these rate data, together with that for the homo-

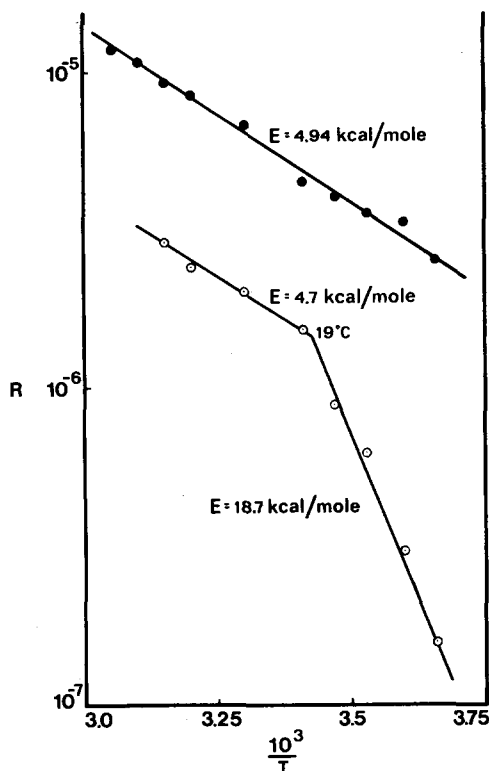


Fig. 3. Influence of irradiation temperature on the rates of grafting and homopolymerization at a dose rate of 0.20 Mrad/hr: (○) graft copolymerization; (●) homopolymerization.

polymerization process, is shown in Figure 3. Over the temperature range from 0°C to 19°C, an activation energy of 18.7 kcal/mole was determined. The activation energy then changes abruptly at 19°C to a value of 4.7 kcal/mole from 19°C to 45°C. By way of comparison, the activation energy of the homopolymerization process in the monomer solution is shown to be 4.9 kcal/mole over the entire temperature range investigated.

It follows from Figure 3 that above 19°C the graft copolymerization process proceeds with an activation energy almost identical to that of the homopolymerization process in the monomer solution. Thus, it would appear that below 19°C the structure of the wool exerts a marked influence on the growth of the polymer in the wool. In addition to the change in rate, there is also an abrupt increase in the number-average molecular weight of the graft polymer as the irradiation temperature exceeds 19°C. In each of the two temperature ranges, the molecular weight of the graft polymer remains relatively constant, averaging 96,000 over the temperature range of 0°C to 19°C and increasing abruptly to an average value of 166,000 above 19°C. From both the rate and molecular weight data, we can conclude that the rate of change of chain propagation increases abruptly as the irradiation temperature exceeds 19°C. Although the rate of chain transfer also increases with an increase in temperature, as follows from Table II, the relative increase in the rate of propagation predominates in the grafting process.

Two possible explanations for the observed apparent increase in the rate of grafting which takes place above 19°C can be forwarded. In the first, the protic nature of the monomer-solvent system can lead to pronounced hydrogen bonding of the swelling agent with the polypeptide molecules in the wool fiber, to impede the rate of grafting. However, the observed 14 kcal/mole change in activation energy that occurs at 19°C is somewhat larger than the energy generally associated with a hydrogen-bonded system of this type.¹⁴ The second explanation, forwarded by Chapiro,¹⁷ requires that the observed change in activation energy can be associated with a change in the energy of diffusion of the monomer into the wool, a process which requires an energy in agreement with the observed change in activation energy. However, thermal analysis (DSC) of the wool fiber wetted with monomer solution revealed no change in state at temperatures close to the point of the observed change in activation energy.

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