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The Graft Polymerization of Acrylamide onto Paper Preirradiated with High Energy Electrons

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Synopsis

The graft polymerization of acrylamide onto filter paper preirradiated in air with electrons from a 200-keV accelerator has been shown to lead to weight increases of up to 210%. The degree of grafting depends on the radiation dose, the moisture content of the paper, and the time interval between irradiation and grafting, but is independent of the radiation dose rate. The degree of grafting increases with the monomer concentration of the reaction medium, and increases as the grafting temperature is reduced. Irradiations in the presence of O_2 or N_2 and the effect of ferrous ions in the grafting solution indicated that peroxides derived from cellulose do not contribute significantly to the initiation reactions up to 60°C. The results are consistent with the degree of grafting depending primarily on the concentration of trapped radicals present in the paper at the time of copolymerization. The cellulose in the grafted material was degraded and the grafted acrylamide was isolated and its molecular weight measured and compared with a calculated value. The moisture regain characteristics of the grafted material are reported.

INTRODUCTION

The interaction of ionizing radiation with cellulose leads to the formation of free radicals which are trapped in the polymer matrix and are long-lived at ambient temperature.[1,2] These radicals are polymeric species, since they are formed on the cellulose molecule,[1,2] and can therefore be used to initiate a graft copolymerization reaction with vinyl monomers under conditions where the monomer can diffuse into the polymer matrix and reach trapped radical sites.[1]

If the monomer is present during irradiation, then initiation will also result from radicals produced in the monomer phase so that homopolymer will be formed in addition to the grafted material. This method of grafting to cellulose has been widely studied[3] and has been used to graft vinyl monomers onto paper.[4,5] Alternatively, the cellulose may be irradiated before being brought into contact with the monomer. This preirradiation technique has also been extensively applied to cellulose.[3] The method leads to considerably less homopolymer than the simultaneous process since the only sources

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of radicals to initiate its formation are from the decomposition of peroxides and chain transfer reactions, both of which make very little contribution at temperatures below 50°C.

There are very few studies of the grafting onto paper by the preirradiation method. Cramer et al.[6] compared the two methods for a range of monomers, and Moore[7] made a more detailed comparison for the case of styrene. These authors used ^{60}Co γ-radiation and 1 MeV electrons, the maximum dose rates being 10 or 360 Mrad/hr, respectively.

This report presents a study of the graft copolymerization of acrylamide with paper preirradiated at the high dose rates ($\sim 5 \times 10^4$ Mrad/hr) available in electron beams in the 200-keV energy region. These high dose rates enable the radical concentration required for grafting to be reached in a very short period compared with that required at the dose rates delivered by γ-radiation sources. This should enhance the possibility of industrial application of radiation-induced grafting to paper.

EXPERIMENTAL

Materials

The cellulose was Whatman No. 41 filter paper used in the form of 12.5-cm-diameter sheets. These were 0.22 mm (8.8 mil) thick and had a mean density of 8.68 mg/cm^2 after drying under vacuum.

Acrylamide was Koch-Light Laboratories Ltd. pure grade, and was used as received. All other chemicals were of A.R. grade.

Irradiation Procedure and Dosimetry

The paper samples were irradiated in polyethylene bags (heat-sealed, lay-flat tubing) having a wall thickness of 2.4 ± 0.1 mil. These bags were attached to plates on a variable-speed conveyor which passed through the 15-cm-wide beam of electrons emerging from a 200-keV accelerator.[8]

The radiation dose delivered to each batch of samples was monitored by means of the radiation-induced bleaching of cellophane film containing a blue dye. Blue Rayophane film (supplied by British Sidac Ltd.), 1 mil thick (3.5 mg/cm^2) was irradiated in a polyethylene bag under identical conditions to the paper samples, and the change in the absorbance of the film at 625 nm was measured. This was related to the absolute energy deposition in the film by a calorimetric technique.[9]

The doses measured with the cellophane film give the dose received by the top 3.5 mil of the filter paper samples. Irradiation of a stack of three layers of the cellophane film, which is approximately equivalent to the thickness of the filter paper, showed that the relative doses received in each $^1/_3$ of the thickness of the paper from the top were 1.0:0.88:0.72.

Graft Copolymerization Technique

Paper samples were suspended in a hygrostat containing saturated NH_4NO_3 solution, giving a relative humidity of 63% at 20°C. After 4 hr,

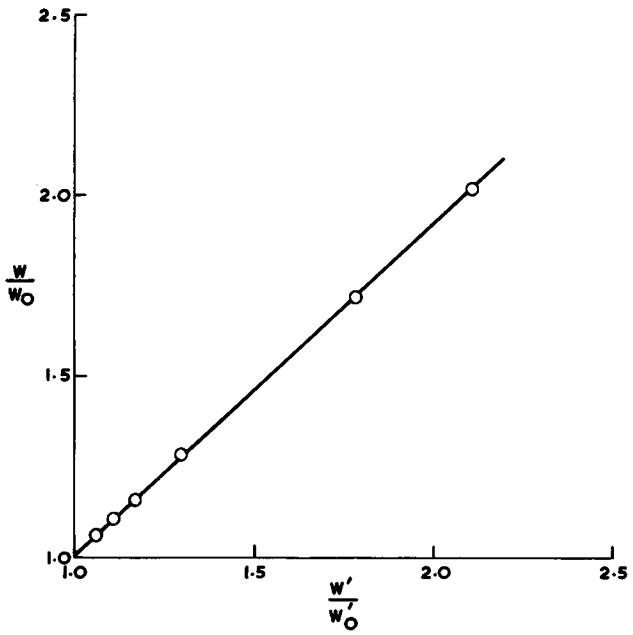

Fig. 1. Comparison of "wet" and "dry" weights of cellulose grafted with polyacrylamide. W and W_0 are weights of grafted and ungrafted samples after drying in vacuum; W' and W_0' are corresponding weights after equilibration in hygrostat.

when equilibrium had been reached, the paper was weighed and transferred into a polyethylene bag which was held open while it was heated at 80°C in a vacuum oven for at least 3 hr to ensure complete drying. The bag was then removed from the oven and immediately sealed. This enabled the paper to be irradiated in the dry state.

After irradiation, the paper was removed from the polyethylene bag and immersed in aqueous acrylamide solution at constant temperature for a measured period. The interval between irradiation and grafting was normally 3 ± 1 min. When the grafting reaction had been completed, the paper was washed six times with distilled water to remove excess monomer and then extracted with water in a Soxhlet apparatus for 4 hr to remove homopolymer. The samples were dried in a vacuum oven at 80°C and then left overnight in the hygrostat to equilibrate before being weighed.

Since the water content of papers containing different amounts of grafted polyacrylamide may vary, it is important that the degree of grafting should be measured by a comparison of the weights of dry samples. To facilitate the experimental procedure, a calibration curve was constructed by weighing a series of grafted filter paper samples after equilibration in the hygrostat and reweighing them after 24 hr in a vacuum oven at 80°C. The data were plotted (Fig. 1) as ratios relative to the corresponding weights of ungrafted paper, and the graph enabled all subsequent measurements of the degree of grafting to be evaluated from weights measured, after equilibra-

tion at 63% relative humidity, thus avoiding the need to dry every sample. The data are reported as the ratio W/W_0 of the weight of the dry grafted and homopolymer-free material to that of the dry untreated paper.

Blank Experiments

The following tests were carried out to determine whether the experimental procedures influenced the measured degree of grafting:

(a) Dried paper samples were irradiated to doses up to 6.2×10^{20} eV/g (10 Mrad) and immediately extracted, the grafting stage being omitted. Since no significant decrease (<0.2%) in weight occurred, the production of soluble radiolytic degradation products from the cellulose was negligible.

(b) Unirradiated, dry paper samples were immersed in 2.81 mole/l. (200 g/l.) aqueous acrylamide solution at 20°C for 2 hr. They were then washed six times with distilled water and extracted with water in a Soxhlet apparatus for 4 hr. No significant change (<0.2%) in weight of the paper occurred, thus demonstrating the efficiency of removal of monomer and also that no thermally induced grafting took place.

(c) In order to check the efficiency of removal of homopolymer, which in principle should only be formed in small quantities, grafted papers which had been extracted for 4 hr, were extracted for a further 24 hr. There was no change in the observed degree of grafting (W/W_0) when the results were compared with ungrafted samples extracted for the same period.

RESULTS AND DISCUSSION

Variation of Grafting Time and Monomer Concentration

Samples of dried paper were irradiated to a dose of 3.1×10^{20} eV/g and grafted in solutions of aqueous acrylamide (2.81 mole/l.) at 20°C for varying times up to 2 hr. The degree of grafting was found to reach its maximum value within 5 min of immersion. For all subsequent experiments the reaction period was 20 min. Cramer et al.[6] have also reported that acrylamide in aqueous solution rapidly grafts to irradiated filter paper and that a weight increase of 100% on grafting at 50°C can be achieved in 10 min. These results contrast with the long periods (50 hr) required to attain maximum grafting of styrene to preirradiated filter paper at 30°C.[7] The high rate of grafting in the present case presumably results from very rapid swelling of the cellulose matrix by water and fast diffusion of the monomer to the trapped radical sites.

Paper samples irradiated as above were grafted at 20°C in acrylamide solutions of various concentrations, the maximum being limited by the solubility of acrylamide in water. The results (Fig. 2) show that weight increases up to 210% were achieved when a 5.62 mole/l. acrylamide solution was employed. As the monomer concentration is increased in the grafting mixture, its enhanced rate of diffusion will lead to a higher concentration

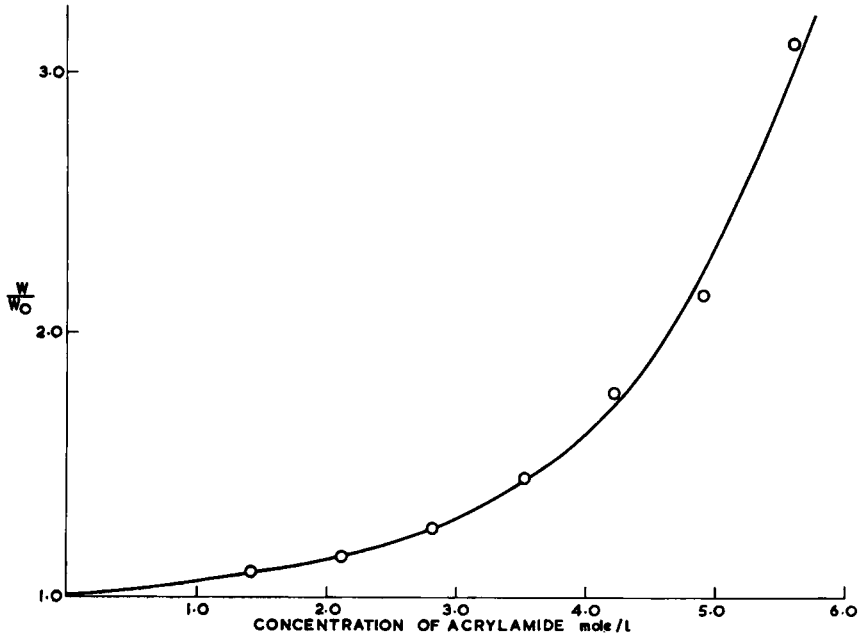

Fig. 2. Effect of monomer concentration on degree of grafting.

in the region of the growing chains in the polymer matrix. This will increase the propagation rate relative to the rate of termination, and consequently give an increased degree of grafting as a result of the formation of longer chains since the number of initiating radicals will be unchanged. Moore[7] also observed an increase in the degree of grafting of styrene as the monomer content of the reaction medium was increased up to 60%.

Effect of Dose and Dose Rate on the Degree of Grafting

Paper samples were irradiated to various doses at a constant election beam current of 0.26 ± 0.04 mA, i.e., at a constant dose rate. They were then reacted with a 2.81 mole/l. solution of acrylamide at 20°C. From Figure 3 it is seen that the grafting yield increases linearly with the dose. Since Dilli et al.[2] have demonstrated that in the γ-irradiation of paper, the production of trapped radicals is proportional to the dose over the range of doses used here, it appears that the degree of grafting is proportional to the concentration of trapped radicals.

A total dose of (3.1 ± 0.3) × 10^{20} eV/g was delivered to samples at different dose rates and they were then grafted at 20°C in a 2.81 mole/l. solution of acrylamide. From Table I it is seen that the degree of grafting is independent of the dose rate over an eight-fold range. Since for a given dose it is expected that the concentration of trapped radicals produced will not depend on the dose rate,[2] the degree of postirradiation grafting should not vary with the dose rate, as observed experimentally.

TABLE I
Effect of Dose Rate on the Degree of Grafting

Beam current, mA	Calculated dose rate, eV g^{-1} sec^{-1}	W/W_0
0.10	0.33	1.35
0.27	0.89	1.45
0.56	1.8	1.42
0.83	2.7	1.47

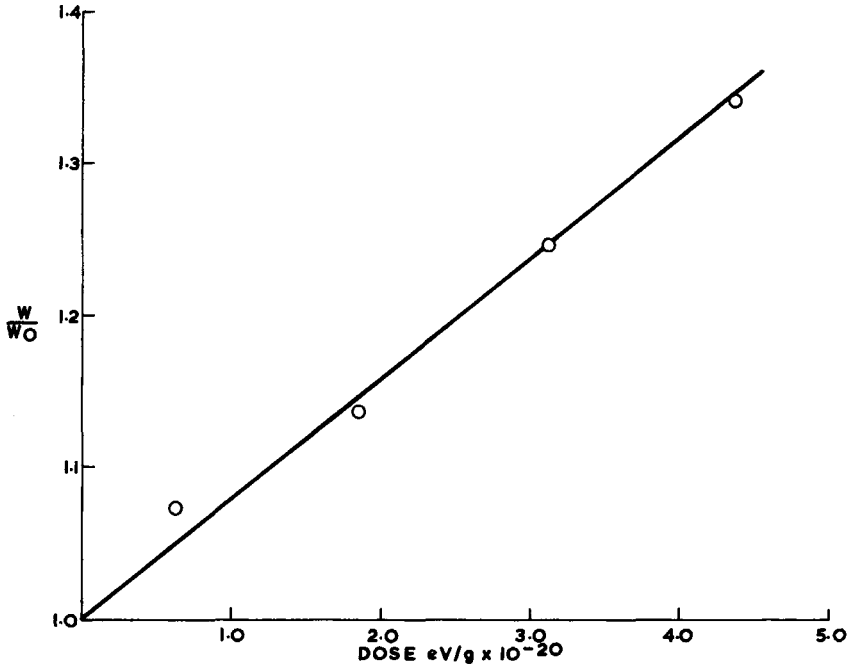

Fig. 3. Variation of degree of grafting with radiation dose.

Influence of Moisture Content of the Paper

The rate of moisture regain by dried paper was measured at a relative humidity of 63% at 20°C (see Fig. 8). Samples of paper with known moisture contents were then prepared by exposing dried paper for measured periods at this humidity and sealing them in polyethylene bags which had been equilibrated in the hygrostat. After irradiating to a dose of 3.1×10^{20} eV/g, the papers were grafted using a 2.81 mole/l. aqueous acrylamide solution at 20°C. The degree of grafting was found to decrease linearly with the moisture content (Fig. 4), indicating the production of lower trapped radical concentrations with increase in the water content of the paper before irradiation. This effect has previously been reported for the long-lived radicals in γ-irradiated paper[2] and cotton.[1]

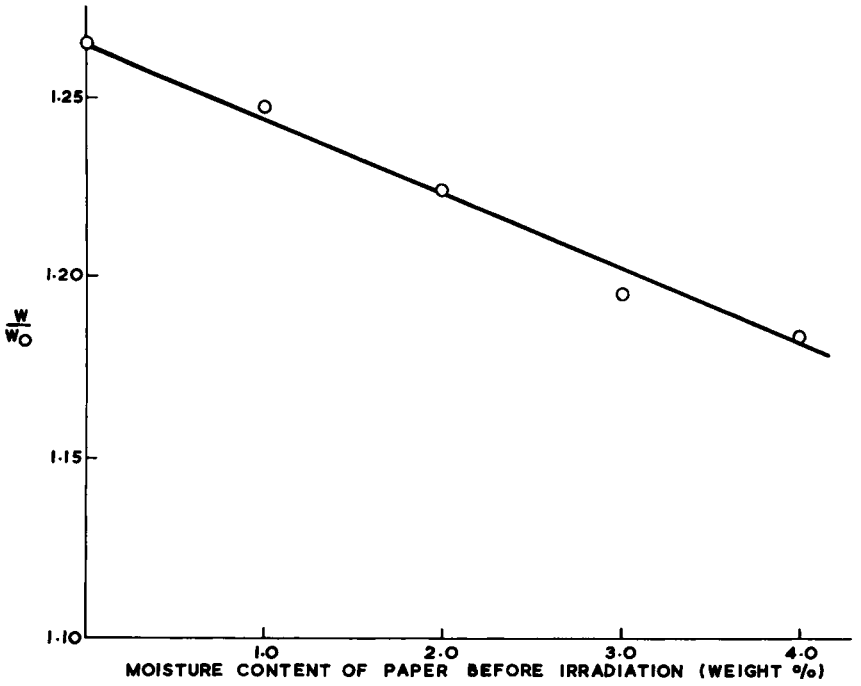

Fig. 4. Influence of moisture content of paper on degree of grafting.

Stability of the Trapped Radicals

After irradiation to a dose of 3.1×10^{20} eV/g, paper samples were left in the polyethylene bags for measured periods of time at 20°C before immersion in the grafting solution at the same temperature. The degree of grafting decreases slowly with the period the samples have been kept before grafting (Fig. 5). This must be due to decay of the trapped radicals, and since the grafting is proportional to the trapped radical concentration, then this must fall by 32% in 5 hr at 20°C. This is eightfold faster than the decay of radicals in Whatman No. 41 chromotography paper after irradiation with ^{60}Co γ-rays to a dose of 6.2×10^{20} eV/g (Dilli et al.[2]). However, the paper used had a different water content from that in the present work, and this is known to influence the radical concentration produced and their rate of decay.[2] The extent of grafting of ethyl acrylate to cotton has also been observed[10] to decrease on storage of the dry γ-irradiated material before carrying out the copolymerization reaction.

Effect of Temperature

Paper samples were irradiated to a dose of 3.1×10^{20} eV/g and then immersed in acrylamide solutions (2.81 mole/l.) for 2 hr at various temperatures. From Figure 6 it is seen that the degree of grafting decreases linearly with increase in the temperature; a plot of log $(W - W_0)$ against

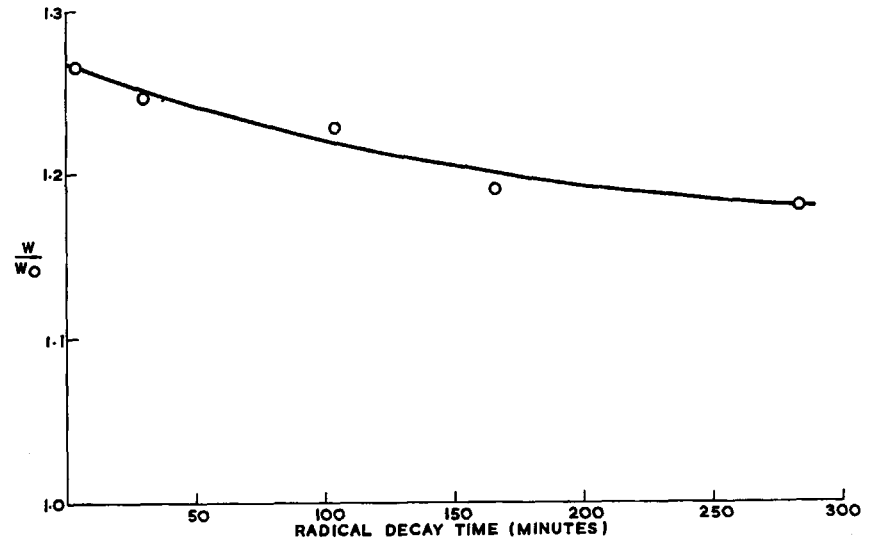

Fig. 5. Effect of radical decay on degree of grafting.

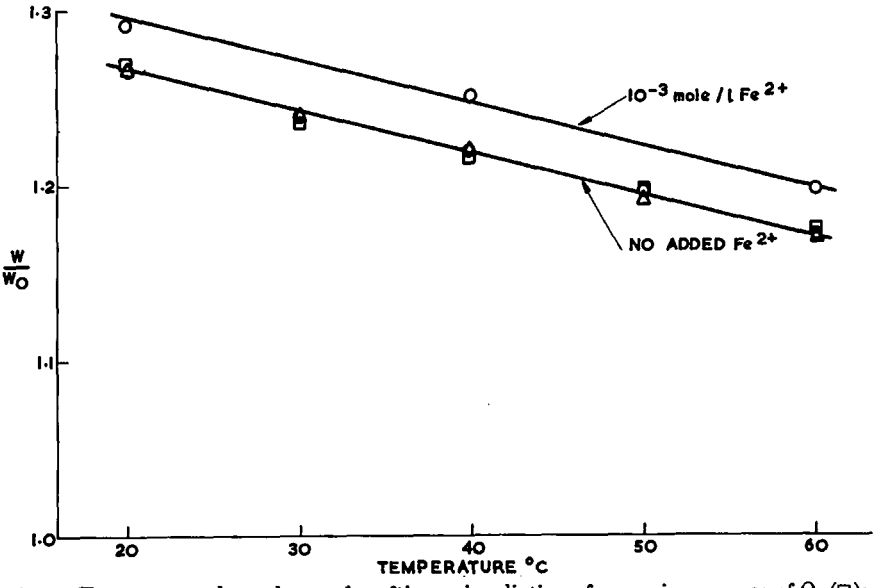

Fig. 6. Temperature dependence of grafting: irradiation of paper in presence of O_2 (□); N_2 (△); air (○).

the reciprocal temperature led to a temperature coefficient of −2.2 kcal/-mole.

For a homogeneous addition polymerization in which the initiation rate is independent of temperature, the molecular weight increases with the temperature, the temperature coefficient for the change being about 5 kcal/mole.[11] A similar behavior might be expected for the heterogeneous

grafting to cellulose since the propagation reaction will be controlled by the diffusion of monomer which will have an activation energy similar to this value. The increased molecular weight would lead to a higher grafting yield for a given initial radical concentration. However, increase in temperature rapidly increases the rate of radical decay in irradiated paper over the range 20° to 70°C.[2] This will decrease the number of radicals available to initiate polymerization and thus reduce the degree of grafting. If this decay results from the interaction of radical sites which have migrated along the cellulose chains by a process of successive H atom abstractions,[12] it would be expected to have a higher activation energy than that for the increase of molecular weight. Thus, the overall effect of increasing the temperature should be to decrease the degree of grafting, and the low negative temperature coefficient for the present system is consistent with the above mechanism.

It has recently been reported that the graft copolymerization of ethyl acrylate onto cotton shows a similar diminution in degree of grafting over the temperature range of 25° to 60°C.[10] It is expected that this would be the effect of temperature on most grafting systems employing preirradiated substrates.

Irradiation in the Presence of O_2 and N_2

Polyethylene bags containing dried paper samples were flushed with dry oxygen or nitrogen prior to sealing and irradiation to a dose of 3.1×10^{20} eV/g. The O_2 present in the bags is sufficient (7.6×10^{-3} mole) to react with all of the radicals produced at this dose. The papers were immersed in acrylamide solution (2.81 mole/l.) at temperatures from 20° to 60°C for a period of 20 min. Over the whole temperature range, the results for both gases (Fig. 6) were identical to the values of W/W_0 previouslv obtained for samples irradiated in the presence of air. Thus, under the conditions used in this work, thermal decomposition of cellulose peroxides or hydroperoxides does not contribute to polymerization initiation, which must therefore arise entirely from trapped radicals. Nakamura et al.[10] concluded from similar experiments that neither peroxides nor hydroperoxides of cellulose play a significant role in the grafting of ethyl acrylate to preirradiated cotton.

After the grafting reaction had been carried out at 60°C, the solution was cooled to 20°C and an equal volume of dioxan was added. This had previously been shown to precipitate polyacrylamide from such solutions, but caused only a very slight turbidity in the present case. Thus, there is no significant production of homopolymer under these conditions, confirming that the decomposition of hydroperoxides of cellulose makes a negligible contribution to the initiation of grafting.

Effect of Fe^{2+} Ions on the Grafting Reaction

Dried paper samples were irradiated to a dose of 3.1×10^{20} eV/g and then grafted at 20°, 40°, and 60°C with 2.81 mole/l. aqueous acrylamide

solution containing 1.0×10^{-3} mole/l. ferrous ammonium sulfate for a period of 2 hr. At each temperature the presence of Fe^{2+} ions in the reaction medium increases the degree of grafting (Fig. 6). This indicates that the irradiation of paper in the presence of air produces hydroperoxides which are decomposed by the reaction

$$ROOH + Fe^{2+} \rightarrow RO^{\cdot} + OH^{-} + Fe^{3+}$$

to yield radicals capable of initiating graft copolymerization. The species $RO^{\cdot}$ must therefore be a cellulose alkoxy radical. The difference between the lines in Figure 6 indicates that at 20°C the initiation of grafting resulting from the above reaction is 11% of that due to trapped radicals, but that when grafting is carried out at 60°C, the contribution of the above reaction is 17% of that arising from trapped radicals, since at the higher temperature some of the latter decay before being able to initiate polymerization. The parallel nature of the curves in Figure 6 indicates that the contribution of radicals produced by the above reaction is independent of the temperature. Figure 6 also confirms that thermal decomposition of hydroperoxides makes no significant contribution to the initiation reaction up to 60°C and substantiates the conclusion that in the absence of Fe^{2+} ions all grafting is initiated by trapped radicals.

Addition of Methanol to the Grafting Solution

After irradiation to a dose of 3.1×10^{20} eV/g, the paper samples were immersed in grafting solutions of acrylamide (2.81 mole/l.) prepared in mixed water + methanol solvents of various compositions at 20°C. The variation of grafting yield with methanol concentration is shown in Figure 7.

The sorption of methanol by cellulose (cotton) is about 93% of that of water.[13] It is therefore unlikely that the progressive decrease in grafting as the methanol content of the reaction medium is increased is due to differences in the behavior of these liquids as selling agents.

The trapped radical sites on the cellulose chains, particularly the alkoxy radicals,[2] would be expected to abstract H atoms from methanol with the formation of $^{\cdot}CH_2OH$ radicals. The subsequent polymerization initiated by these radicals will form a homopolymer. Thus, the presence of methanol will decrease the formation of grafted polymer. There will be a competition between acrylamide and methanol for the trapped radicals; and since the cellulose radicals are immobile, a progressive decrease in the degree of grafting with the mole fraction of the methanol is expected.

Confirmation of Grafting

The value of the degree of grafting obtained in this work by measuring the increased weight of the paper after extraction of homopolymer depends

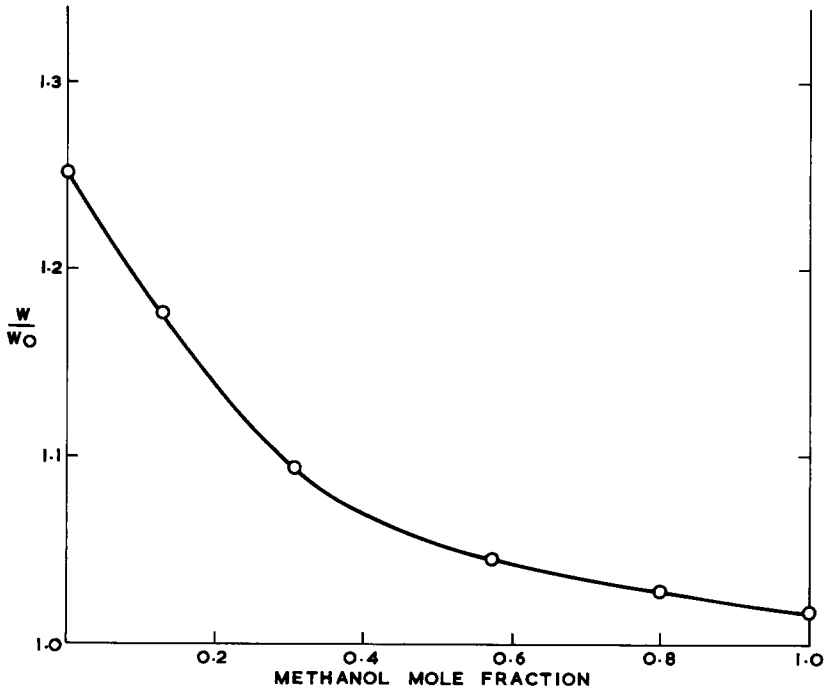

Fig. 7. Degree of grafting in solutions containing methanol.

on *all* of the polyacrylamide being dissolved. To establish whether this is occurring, grafted papers were analyzed by the cuprammonium method.[14,15] Cellulose, cellulose grafted with acrylamide, and polyacrylamide are soluble in cuprammonium hydroxide. On acidification, only the cellulose and graft copolymer are precipitated.

A sample of grafted paper (W/W_0 = 2.01; weight = 0.483 g after equilibration in 63% relative humidity at 20°C) was dissolved in cuprammonium hydroxide solution prepared according to the method of Gibson et al.[16]

The solution was carefully acidified with hydrochloric acid, keeping the temperature below 5°C to minimize hydrolysis of the cellulose. The precipitate was washed with more acid and then with distilled water, collected by centrifugation, and freeze dried. The product, after it was reequilibrated at the same humidity, weighed 0.477 g. Thus, 98.8% of the original material was cellulose and grafted cellulose.

The quantitative nature of the procedure was tested by repeating it with a physical mixture of 0.25 g cellulose and 0.25 g polyacrylamide. The latter remained in solution, and the weight of the precipitate was within 2% of the original amount of cellulose.

These results are a good indication that the acrylamide is chemically bonded to the cellulose and that it is not merely occluded in the cellulose

matrix. Moreover, they confirm the efficiency of the experimental method used to extract homopolymer.

Isolation of the Grafted Acrylamide

In order to isolate the grafted polyacrylamide, the cellulose was removed by the conventional hydrolytic technique using sulfuric acid. A sample of paper was grafted in 4.65 mole/l. aqueous acrylamide at 20°C after pre-irradiation to a dose of 3.1×10^{20} eV/g. After Soxhlet extraction with water, the resulting material ($W/W_0 = 2.01$; weight = 0.60 g) was dissolved in concentrated H_2SO_4 at 0°C: dissolution required 50 hr, and no charring was observed. The solution was diluted to 2 mole/l. H_2SO_4, the temperature being kept below 5°C until dilution was complete. It was then sealed under nitrogen in an ampoule and kept at 100°C for 96 hr. After neutralizing with 5 mole/l. NaOH, the solution was dialyzed for 24 hr and then freeze dried. The molecular weight of the white powder which was isolated was found to be 150,000 by gel permeation chromatography[17] on a Porasil D column, samples of glucose and dextran of known molecular weight being used to calibrate the column.

The molecular weight of the grafted acrylamide chains may be calculated from the weight increase on grafting with a given radiation dose if G-value for the production of trapped radicals which initiate polymerization in the paper is known. This has not been measured in the present work, but Dilli et al.[2] reported a value of 1.2 for γ-irradiated Whatman No. 41 filter paper. For the sample described above, this value would lead to a concentration of 3.72×10^{18} radicals/g, and the weight increase shows that 8.59×10^{21} molecules of acrylamide are grafted per g of paper. Thus, if every trapped radical initiates a polymerization chain and the termination reaction is an unimolecular process or is entirely by disproportionation of pairs of growing chains, then these values lead to a number-average molecular weight of 1.64×10^5 which is reasonably close to the molecular weight (between $\bar{M}_n$ and $\bar{M}_w$[17]) measured experimentally. If termination occurred entirely by combination of radical pairs and the actual yield for the present irradiation conditions was twice that for γ-irradiation, then the predicted molecular weight would again be 1.6×10^5. Thus, the present work does not permit any conclusions regarding the nature of the termination reaction of the polyacrylamide chains.

Since the molecular weight of the cellulose in the grafted paper was not measured, the average number of grafted acrylamide chains per cellulose molecule cannot be derived directly from the present work. However, if the degree of polymerization of the cellulose in the above sample is taken[3] to be about 250, it can be deduced that half of the cellulose molecules have a grafted acrylamide chain. This must represent an upper limit for the frequency of grafted chains since, although the cellulose used to produce the paper initially has a degree of polymerization of about 2000, this will be reduced during the manufacture of the paper (personal communication, W. & R. Balston Ltd.).

Properties of the Grafted Paper

Up to about 20% increase in weight on grafting, the appearance and handling properties of the dry paper were not significantly different from those of the untreated material. However, at high degrees of grafting, e.g., $W/W_0 = 3.0$, the paper was hard and brittle; it showed only a small decrease in its planar dimensions but was several fold thicker than the original paper.

To compare the moisture regain of papers with various amounts of grafted acrylamide, samples were dried in vacuum at 80°C for 24 hr. They were then placed in a hygrostat at 20°C and 63% relative humidity and weighed at increased intervals. The initial rate of water sorption (Fig. 8) into grafted samples was very similar to that of the unmodified

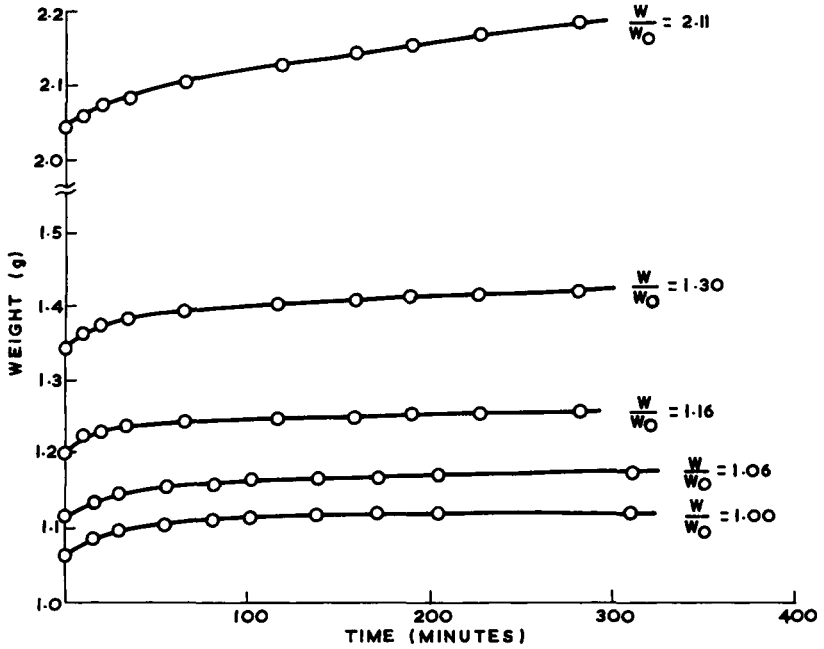

Fig. 8. Water regain of dry grafted cellulose.

paper ($W/W_0 = 1$), but the time required to reach equilibrium increases with the degree of grafting. Of the curves in Figure 8, only that for the ungrafted paper has reached equilibrium, and for this sample it can be deduced that $W_0'/W_0 = 1.06$ (i.e., the paper contains 6% moisture). Combining this value with the data in Figure 1 shows that the water regain at equilibrium progressively increases with the degree of grafting and for 100% graft ($W/W_0 = 2.0$) the product contains 9.6% moisture. Similar observations were reported by Schwab et al.[18] for paper grafted with acrylamide by the ceric ion method.

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