The Modification of Wool and Cellulose Fibers by Grafting

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INTRODUCTION

Grafting to fibers has been studied extensively since the early 1950s as a technique for modifying their properties. Extensive reviews are available on this general subject [1-4]. Although the main emphasis has been with textile fibers, considerable work has also been carried out with paper-making fibers and on paper itself [1, 5].

Grafting by most of the known methods only adds a small number of side chains per backbone; there is little pertubation, therefore, of the properties of the polymer molecule itself. Furthermore, with direct grafting to the fibers themselves, there is an important additional factor. Monomer cannot diffuse into the ordered regions such as the crystallites, but only into the amorphous or disordered regions. Since the mechanical behavior of the fibers is largely determined by the ordered structure, grafting does not bring about any drastic changes in these properties. On the other hand, it can add certain properties of the grafted side chains such as hygroscopicity and flame retardancy to the fibers. In other words, grafting provides a method of adding

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certain properties to a fiber without greatly disturbing the strength
and other mechanical behavior features.

Recently, it has been found that if the crystallinity of the base fiber
is partially or fully dissolved by treatment with a suitable solvent,
which is later removed, the properties of the side chain become more
developed. Similar treatments can be worked out with wool; for
example, by treatment with reagents such as thioglycollic acid, which
serves to remove the disulfide cross-links. In this way, grafted
fibers with quite different properties such as high elasticity and high
sorbency can be prepared.

In summary, grafting to fibers can be used to lend additional prop-
erties or to bring about quite new properties, according to the grafting
techniques which are used. Some examples of these two types of
modification will be presented in this paper. In the same vein, by
varying the methods and conditions, the grafted side chains can be
located at the surface, throughout, or in the core of the fiber.

Many desirable properties of textile fibers only need surface
modification. These include the following areas of improvement:

1. Static electricity buildup and dissipation
2. Oily stain adsorption and release in detergent solutions.
3. Soil deposition, release, and redeposition in detergent solutions.
4. Wettability and adhesion.
5. Wettability and dispersion, e.g., for wetlaid nonwovens.
6. Abrasion resistance.

It is easy to envisage as a textile finishing operation the chemical
or radiation grafting of a monomer within the surface regions of a
fiber microstructure, resulting in a great change in the fiber surface
properties. There should be good washfastness of such a finish due to
the possibility of chemical bonding to the substrate. Indeed, there is
extensive literature on grafting treatments of textiles to alter their
surface properties.

Most of the important phenomena listed above are related to the
relatively low surface energy or hydrophobic nature of the surfaces
of most synthetic textiles. In addition, the surfaces of some resin-
treated natural textile materials which are originally hydrophilic in
nature may also become more hydrophobic during resin finishing, and
therefore will exhibit surface behavior similar to the synthetic fibers.

Grafting hydrophilic monomers to low energy fiber surfaces should
increase the surface moisture content and thus (1) the rate of static
dissipation, (2) the rate of release of oily stains in detergent solutions,
and (3) wettability, adhesion, and dyeing to and within the fabric.
Dyeing will be enhanced throughout the fiber cross section if the graft
penetrates across this area. In the special cases where ionized vinyl
monomers are grafted, the fiber will be very sensitive to the charge
on molecules (e.g., dyes, stains) or particles (e.g., soil) to which the
surface is exposed, and this may turn out to be an advantage or a

disadvantage. On the other hand, grafting hydrophobic monomers to higher energy or more hydrophilic fiber surfaces will result in a reduced wetting by all liquids, including oil stains.

Grafting of hydrophobic monomers such as styrene has also been shown to greatly improve the drip-dry characteristics of wool. This is presumably due to changing the surface characteristics since the overall sorption of water was found to be only modestly affected.

Properties which may be modified by grafting techniques but which are probably mainly due to "bulk" grafting include:

1. Crease resistance and permanent press.
2. Thermal and thermomechanical properties.
3. Modest changes in mechanical behavior.
4. Rot and mildew resistance.
5. Flame resistance.
6. Water sorption.

Similar considerations apply to grafting to paper-making fibers. Since the strength of paper is influenced to a considerable degree by the strength of the fiber-fiber bonds, surface grafting could become highly significant. In fact, grafting to increase the hydrogen bonding capacity of pulps with high lignin (high yield pulps) and increasing their fiber to fiber bonding capacity per se has been studied in these laboratories [6-8].

It is clear that controlling the location of the grafted side chains would add greatly to the usefulness of the process. Very few of these unique features have been successfully developed and almost none of them utilized on a commercial scale. The authors are confident that the future will bring successful commercial exploitation of this technology.

RECENT WORK ON GRAFTING TO TEXTILE FIBERS

Many methods of grafting are available (see, for example, Refs. 1-4); however, in recent years radiation grafting has been almost exclusively used in these laboratories. It is clean, controllable, and adaptable to virtually any monomer-polymer system. The general philosophy has been that if a useful grafting system was developed, alternative methods could always be explored at that time.

In general, two techniques have been used. These have usually been designated as the mutual method and the pre-irradiation method. In the former the fibers are directly irradiated in the presence of the monomer and possibly a suitable swelling agent for the fiber. This method is particularly suitable when the monomer or the monomer-swelling agent mixture is not sensitive to radiation. The grafting is

not therefore accompanied by excessive homopolymer formation. The
pre-irradiation method involves irradiating the fibers separately and
then adding the monomer system. Since the grafting is initiated mainly
by the trapped macroradicals, very little homopolymer is produced.
The pre-irradiation method is well adapted to electron beam process-
ing technology, although both methods can be successfully used with
electron beams.

Two examples of recent work with the mutual and the pre-irradia-
tion techniques will be described. Both are concerned with monomers
leading to elastomeric polymers. The dienes are insensitive to radi-
ation and therefore ideally suited to the mutual method whereas ethyl
acrylate polymerizes rapidly with radiation and is therefore best
grafted using the pre-irradiation method.

The Mutual Radiation Grafting of Dienes [9]

This work was initially undertaken to see if the faster drying
qualities of styrene-grafted wool [10-12] could be achieved without
the poor hand which developed with the hard polystyrene grafts. It
will be seen later that this was not successful. Later the studies were
extended to cotton and to the bromination of the grafted diene side
chains. Good flame retardant properties were imparted in this manner.

Experimental

The wool used for all the experiments to be described consisted of
fabric (J. P. Stevens Style No. 31200-1); the individual fibers had an
average diameter of 22 μm. The cotton fabric used was an S-423 twill,
7.5 oz/yd^2 obtained from Test Fabrics, Inc., New York, New York.
Before use, these were extracted 8 hr each with diethyl ether, ethanol,
dioxane, and benzene, washed with distilled water and dried at room
temperature under a moderate vacuum. The monomer and solvents
used were all freshly distilled prior to use.

The mutual irradiation grafting experiments were carried out in
glass ampules. A weighed strip 2 × 0.5 in. (about 0.17 g) was placed
in the tube and the monomer-solvent solution added. The monomer
content was maintained at 3.06 M in dioxane and the methanol content
was varied as shown in the actual data. The tubes were then degassed
by three freeze-thaw cycles at below 10^{-4} Torr and sealed under
vacuum. The samples were then irradiated for the desired dose in
a ^{60}Co gamma source. Following irradiation, the samples were opened
and extracted in a suitable solvent for the homopolymer, usually
benzene, overnight. The samples were then dried and weighed and the
increase in dry weight × 100 was recorded as the percent grafting.

Fabric strips 1/2 in. were used for the flammability studies. Following grafting, the samples were brominated by exposing to bromine vapor in a closed container at 25°C for the desired period of time. The percent bromine was taken as the weight increase on a dry basis.

Flammability tests were carried out using the match test angle method as described by Walsh, Bittencourt, and Rutherford [13]. Basically, the test measures the maximum angle at which the sample fails to burn, i.e., higher burning angles indicate better degrees of fireproofing.

Results and Discussion

Typical grafting versus dose curves for butadiene, isoprene, and chloroprene to wool are presented in Figs. 1-3 and for isoprene to cotton in Fig. 4. The curves were all linear from the origin but began to curve towards the dose axis in most cases. The reason for this is not clear, but it is believed to be related to the reduced swelling of the grafted fiber leading to reduced diffusion of monomer to the active centers. A similar phenomenon was observed in the mutual radiation grafting of styrene to cellulose acetate membranes and was investigated in some detail [14].

The initial rates of grafting can be obtained from the linear parts of the curve and are summarized for the three dienes and for styrene in Table 1. The rates vary with the monomer used and are in order of the propagation rate constants. The kinetics of the grafting process in this highly diffusion controlled reaction is complex although attempts have been made to describe the kinetics quantitatively [15].

The mechanical properties of a number of the grafted wool samples are presented in Tables 2 and 3. It can be seen that there are only minor changes in the fiber properties with grafting, and such changes seem to be independent of the nature of the grafted polymer. This is typical of the grafting process; the reasons have been presented in the Introduction and in Ref. 4.

Finally, a number of diene-grafted samples of both wool and cotton fabric were brominated in the manner described in the experimental section. All the samples brominated smoothly to close to the theoretical maximum in less than 24 hr. Samples containing 20 to 64% bromine were subjected to the match test angle flammability index. All failed to burn at the maximum angle of 180°C. No change in hand was observed, and the method appears to have some promise for flame retardancy. A somewhat similar approach of reacting double bonds imparted to cotton by reaction with N-methylol acrylamide to impart flame retardancy has been reported by Walsh et al. [13].
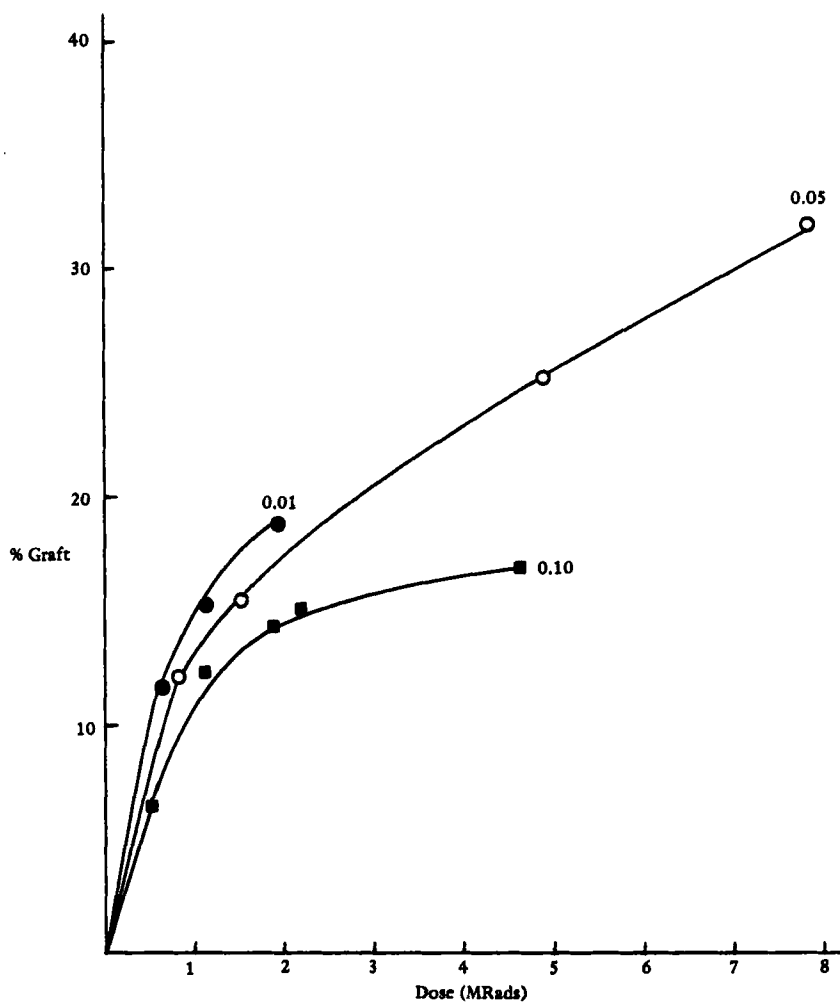
FIG. 1. Mutual grafting of butadiene to wool (3.06 M butadiene in dioxane and 18% methanol) at 25°C. Numbers refer to dose rates in Mrads/hour.
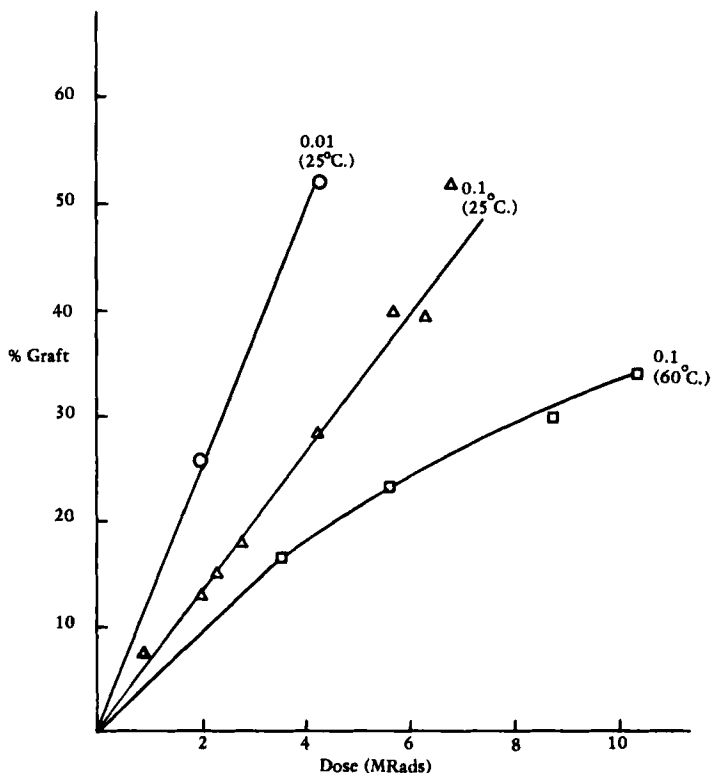
FIG. 2. Mutual grafting of isoprene to wool (3.06 $\underline{M}$ isoprene in dioxane and 18% methanol). Numbers refer to dose rates in Mrads/hour.

The Pre-irradiation Grafting of Ethyl Acrylate

This work was initiated for similar reasons as the diene grafting work. Since ethyl acrylate polymerizes rapidly with radiation, the pre-irradiation method was selected. The first experiments were conducted using the monomer in a dioxane-water solution which was highly successful in the mutual grafting of styrene and other monomers to various fibers and films. However, only limited degrees of grafting could be obtained as illustrated in Fig. 5. Similar results were obtained with other mixtures of water and organic solvents such as acetone. It was thought that this was due to the rapid diffusion of
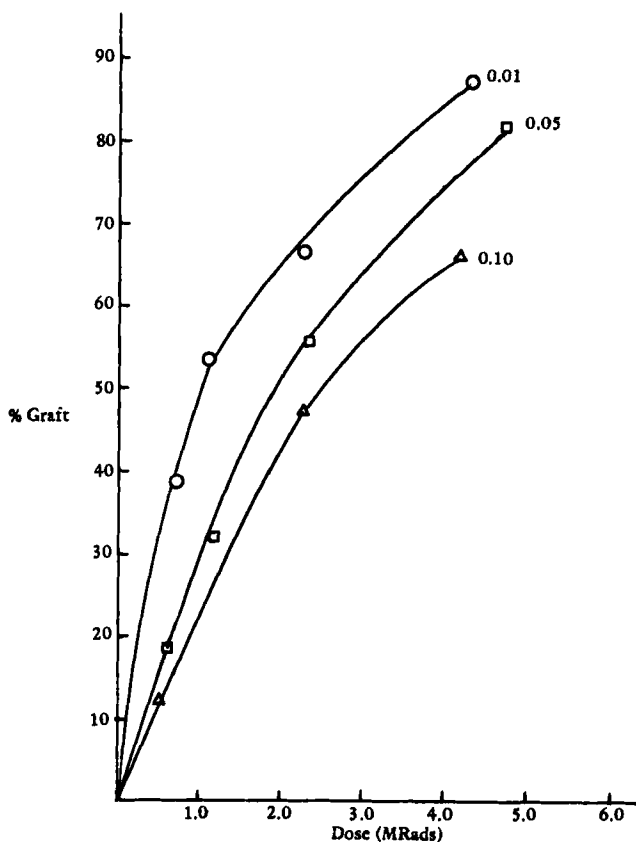
FIG. 3.   Mutual grafting of chloroprene to wool (3.06 $\underline{M}$ chloro-prene in dioxane and 18% methanol) at 25°C.   Numbers refer to dose rates in Mrads/hour.

water into the fiber causing plasticization, and consequently the rapid termination of both trapped radicals and the growing chains. Slower diffusing swelling agents such as isopropanol were therefore investigated but without success.

Finally, the ethyl acrylate monomer was added as a simple slurry in water, or as an emulsion, to the irradiated fibers. The change in the grafting versus time curves was remarkable; a typical curve is included in Fig. 5.

A number of interesting features of this type of grafting kinetics were found and investigated in some detail and have been reported

FIG. 4. Mutual irradiation grafting of isoprene to cotton fabric at 0.1 Mrads/hr and 25°C in a solution of 55.6% dioxane, 31.1% isoprene, and 13.3% methanol.

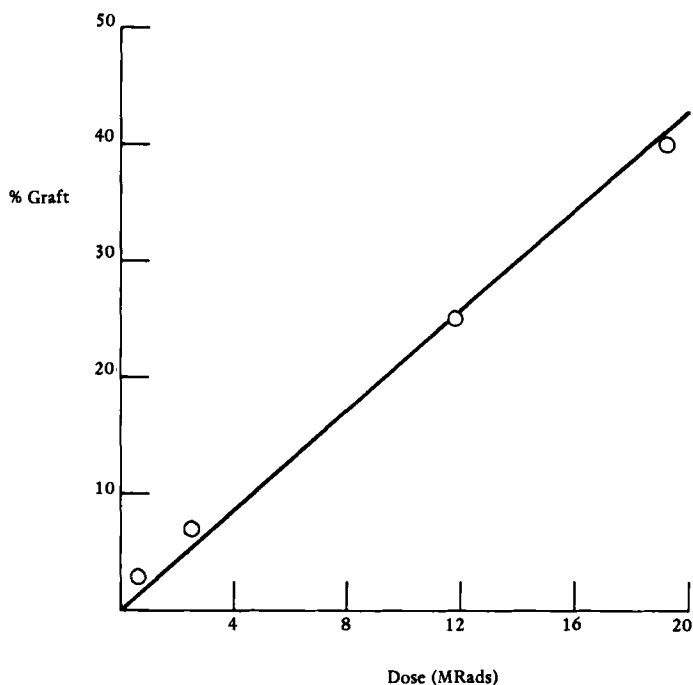elsewhere [16-19]. One of the most important of these findings was that the fibers, grafted to more than about 700%, became highly elastic but retained their integrity. Later it was found that the grafted poly-ethyl acrylate held the fiber intact while the crystalline structure was dissolved by the use of a suitable solvent. These experiments were mainly with cellulose where solvents such as zinc chloride or cup-prammonium hydroxide solutions could be used. When the solvent was removed, by washing for example, the cellulose recrystallized to very low values due to the presence of the grafted side chains. The high elasticity then developed at much lower degrees of grafting. This effect is illustrated in Table 4. It can be seen that the tenacity was decreased by the treatment. Both chemical and radiation grafts showed this effect, but the radiation method gave far higher elasticities at lower levels of grafting. This is believed to be due to the lower radical concentrations at the core of the fiber with chemical initiation due to the slow or limited penetration of the bulky hydrated metal ions such

TABLE 1. Initial Grafting Rates for Diene Monomers to Wool at 25°C at Different Dose Rates[a]

	Grafting rates (%/hr)		
Dose rate (Mrads/hr)	0.1	0.05	0.01
Butadiene	1.10	0.7	0.17
Isoprene	0.70	-	0.12
Chloroprene	2.10	1.4	0.50
Styrene	3.00	1.75	0.70

[a]Grafting solution was 3.06 $\underline{M}$ monomer in 18% methanol-82% dioxane solution.

as ferrous or ceric which were used. No doubt, with a correct choice of reagents and conditions, chemical grafting could be used success-fully. Large degrees of grafting brought about by chemical initiation do indeed lead to high elasticity, without the decrystallization process, as shown by Negishi, Nakamura, Arthur, and others [20-22].

The slope of the grafting-time curves accelerates sharply after an induction period (see Fig. 5, for example) instead of leveling off as the radicals terminate, as expected and as shown for solvent-water systems, also illustrated in Fig. 5. It is interesting that the addition of small amounts of methanol almost completely kill the reaction [17]. This is believed to be due to chain transfer to the methanol followed by diffusion of the $\cdot CH_2OH$ radicals out of the fiber. The long-lived growing chains are terminated in this way, preventing the grafting. (We are grateful to Professor Maurice Morton for this suggested mechanism.)

On the other hand, the addition of ethylene glycol dimethacrylate progressively increases the grafting yield as shown in Table 5. This is believed due to an enhancement of the gel effect, i.e., more trapped radicals continue to grow due to delayed termination. Finally, it was found that even without radiation after a very long induction period, grafting occurred, i.e., spontaneous grafting took place. This is believed to be due to radicals being formed by the swelling forces breaking bonds. A number of reasons led to this conclusion [19]. Thus the radiation gives an initial grafting which may be increased by the formation of extra radicals formed by the mechanical breaking of bonds. The effects of methanol and ethylene glycol dimethacrylate and direct ESR and molecular weight measurements all support this contention and have been discussed in detail [19].

TABLE 2. Tensile Properties of Grafted Wool Fibers at 70°F and 65% R.H.

Property measured	Control	16.7% Styrene	124% Styrene	24.4% Ethyl acrylate	30% Isoprene
Ultimate tenacity					
Grams/denier	1.06	0.93	0.65	1.10	0.82
CV, %	23.7	38.8	32.4	35.6	40.1
Ultimate elongation					
Percent	25.4	24.9	18.9	27.2	25.1
CV, %	-	52.2	57.8	-	49.2
Tenacity at various extensions, g/den					
1.0%	0.20	0.23	0.13	0.22	0.15
3.0%	0.60	0.58	0.36	0.63	0.41
5.0%	0.72	0.69	0.56	0.76	0.53
Stiffness, grams/denier/unit extension					
Average	4.17	3.72	3.44	4.04	3.27
Elastic	22.4	22.4	13.3	24.8	15.2
Modulus of resilience, g-cm/den-cm	0.0112	0.010	0.0102	0.01121	0.0085
Elastic limit					
Yield stress, g/den	0.71	0.66	0.52	0.74	0.51
Yield strain, %	3.17	2.95	3.92	2.98	3.35
Denier	7.48	8.39	16.24	8.00	9.46

TABLE 3. Wet Tensile Properties of Grafted Wool Fibers at 70° F

| Property measured	Control	16.7% Styrene	124% Styrene	24.4% Ethyl acrylate	30% Isoprene
Ultimate tenacity					
Grams/denier	1.09	1.02	0.54	0.97	0.81
CV, %	39.1	32.2	34.9	36.8	35.4
Ultimate elongation					
Percent	29.1	29.2	23.7	31.1	33.2
CV, %	-	26.2	47.7	-	7.89
Tenacity at various extensions, g/den					
1.0%	0.16	0.16	0.09	0.15	0.09
3.0%	0.48	0.46	0.25	0.42	0.25
5.0%	0.63	0.61	0.39	0.54	0.40
Stiffness, grams/denier/unit extension					
Average	3.75	3.49	2.28	3.12	2.44
Elastic	17.8	17.7	8.68	15.8	8.68
Modulus of resilience, g-cm/den-cm	0.0122	0.011	0.0078	0.0096	0.0083
Elastic limit					
Yield stress, g/den	0.66	0.62	0.37	0.55	0.38
Yield strain, %	3.71	3.5	4.26	3.49	4.38
Denier	7.95	-	16.24	8.00	9.46
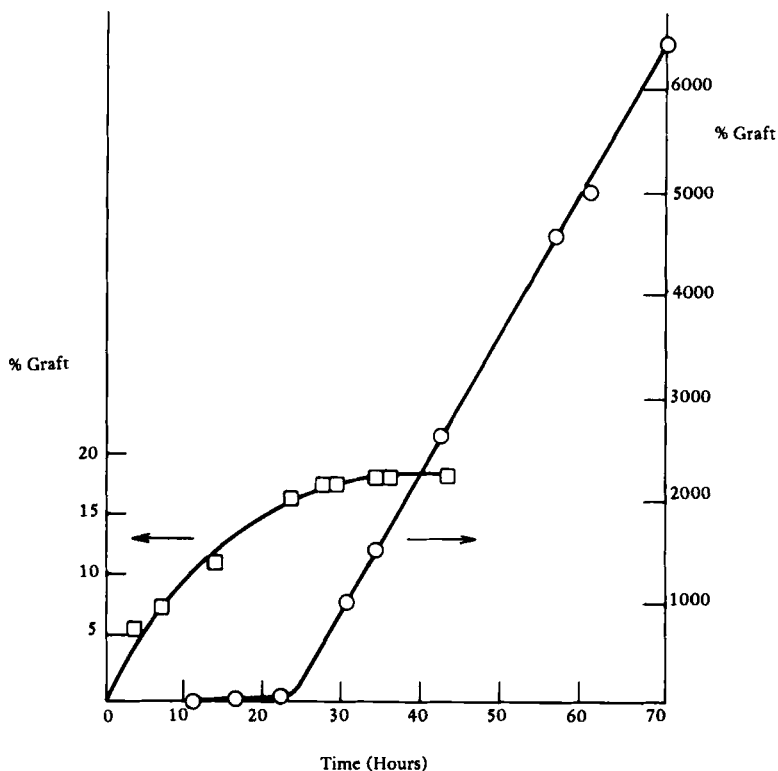
FIG. 5. Pre-irradiation grafting of styrene and ethyl acrylate
to wool. (□) Styrene in dioxane and 18% methanol (2 runs) dose,
2.25 Mrads at 0.01 Mrad/hr. (o) 40% Ethyl acrylate emulsified
with 3.2% aqueous Triton X-405 for 4.0 Mrads at 0.1 Mrad/hr.

The molecular weights of the polyethyl acrylate side chains have
not been determined. Insoluble gels were always obtained after
destroying the wool or cellulosic substrate by sodium hypochlorite
or acid digestion. In the case of the styrene grafts, however, soluble
polystyrene was obtained after destruction of the fiber substrate and
the molecular weights could be measured. The results obtained are
highly interesting. The pre-irradiation grafted cellulose fibers, cotton
and viscose, all gave molecular weights in the 500,000 to 1,500,000
range whereas in the case of wool they were in the range 3800 to 4600,
both viscosity averages. This shows that the wool automatically yields
very short side chain grafts. Similar results were obtained previously
with the mutual radiation method [11]. It is clear that there is heavy

TABLE 4. Influence of Postdecrystallization on the Extensibility and Tenacity of Ethyl Acrylate Grafted Rayon (Pre-irradiation Technique) [18]

% Grafts[a]	Postdecrystallization	% Elongation	Tenacity (g/den)
70	-	25	0.65
70	+	490	0.08
352	-	26	0.27
352	+	798	0.07
419	-	25	0.20
419	+	595	0.05

[a]Dose = 3.9 Mrad at 0.1 Mrad/hr.
[b]Postdecrystallized in 70% ZnCl$_2$.

TABLE 5. The Effect of Ethylene Glycol Dimethacrylate (EGDM) on the Pre-irradiation Grafting of Ethyl Acrylate to Rayon (Semidull)[a]

% EGDM	Percent graft
0	480
1.6	675
3.1	3,900
6.0	4,310
8.8	20,900

[a]Dose 4.0 Mrad, dose rate 0.2 Mrad/hr.

chain transfer to the fiber itself, presumably to the sulfur-containing linkages. It must be predominately a back-biting type of transfer since the actual grafting yields per irradiation dose are just as large with wool as with cellulosic fibers. This points the way to making such grafts with cellulose by imparting, i.e., sulfhydryl groups and we are presently studying this approach.

In conclusion it can be said that new and interesting properties such as high elasticity can be imparted to fibers by a combination of grafting (to modest degrees) plus a postdecrystallization procedure. Alternatively, grafting to fibers in a partly decrystallized state should accomplish similar results. By the careful monitoring of the degree of grafting and the strength of the decrystallizing reagent, it has been found that excellent control of these properties can be obtained. Although this present work concentrates on highly elastic fibers, other properties such as sorbency can also be achieved in this way. Extensive work in all these areas is currently underway in these laboratories.

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