Grafting of Chloromethylstyrene to Polypropylene Fibers by the Use of Ionizing Radiation

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INTRODUCTION

Today, there is a sizeable body of evidence which indicates quite strongly that polypropylene and polyolefins in general are polymers interesting not only to the scientist but also to the marketplace. When one considers the possibilities of making polypropylene fibers commercially acceptable to the textile industry, he finds that the material possesses numerous drawbacks which detract considerably from its main advantages of cheapness, low density, and excellent mechanical properties.

These detracting features are:

(*1*) The fiber is not dyeable to deep shades by conventional techniques; many regular procedures impart no color at all, others create pale pastel shades. Thus, the fibers cannot be mixed with other fiber materials, woven into cloth, and then dyed.

(*2*) The fiber is so hydrophobic that it has extremely poor water retention, feels greasy, and develops static charge easily.

(*3*) The fiber has a low melting point (165°C.) which limits its general usefulness. Also, its "sticking" temperature (140°C.) is too low and enhances the possibility that it would adhere to a hot iron in many normal pressing procedures.

(*4*) The material is sensitive to oxidation and to ultraviolet light and requires certain additives to impart stability.

(*5*) The structure of the fibers is smooth and is essentially without voids, pores, or channels. Thus, materials put on the finished fibers are often removed rather quickly through abrasion, washing, etc.

The problem of improving polypropylene is a very interesting one to the radiation chemist. To him, it seems quite likely that a possible solution to the difficulties can be achieved by using the technique of radiation grafting. Today, it is probably safe to say that practically any vinyl monomer can be grafted to any polymeric substrate by using ionizing radiation providing the correct conditions are developed for a given monomer-polymer pair.

In the case of polypropylene, a great deal of research effort has gone into

attempts at making it dyeable. Two synopses of efforts along these lines are to be found in *Chemical Week*[1] and in a newspaper article.[2] These accounts cover brief references to melt dyeing, vat dyeing, addition of polar, dye-receptive substances to the melt, and radiation grafting to fibers or fabrics. The monomer mentioned in the last case was methacrylic acid. A more recent note[3] provides some information on radiation grafting of 4-vinyl pyridine to I.C.I.'s Terylene fabric as well as to polyacrylonitrile and polypropylene fibers. These latest results employed a two-step grafting procedure involving the formation of peroxide intermediates. Using a dose of 1 Mrad, a pick-up of greater than 100% was achieved with polypropylene. Dyeability was greatly increased with respect to acid dyes, but microscopic investigation revealed that the fibers were ring dyed. Two recent patents[4,5] disclose compositions consisting of hydrophilic polymers added or grafted to polypropylene to confer dyeability.

In this paper we present an account of our approach which consists of grafting chloromethylstyrene monomer to pre-formed polypropylene fibers by ionizing radiation. Chloromethylstyrene was chosen for three reasons:

(a) It possesses the ability to swell polyolefins thereby permitting good penetration.

(b) The chloromethyl group is reactive and can function as a dye-site in a non-aqueous dye bath, or can be reacted with a nucleophilic reagent so as to make the polyolefin dyeable in conventional aqueous dye baths.

(c) Potentially, it is a cheap monomer.

In what follows, it will be shown that all the above-cited detracting features save number (4) have been overcome by this technique.

EXPERIMENTAL

Materials

The polypropylene fiber used was Reevan 3 denier tow obtained from Reeves Brothers. Chloromethylstyrene monomer (hereafter designated by CMS) was supplied by these Laboratories, and was prepared by methods described in a patent.[6] It was washed free of inhibitor successively with 3% aqueous sodium hydroxide and water. The monomer was then dried over $MgSO_4$ and vacuum distilled from CaH_2. The distillate was chromatographed over a column of activated alumina. The pyridine used was of reagent-grade quality from J. T. Baker Chemical Company. All the dyes used (see Table I) were manufactured by the American Cyanamid Company.

Procedures

A sample of polypropylene tow was weighed and placed in a 3-liter Büchner funnel having a coarse fritted disk up through which a vigorous stream of nitrogen was maintained. After half an hour the fiber was transferred under nitrogen to a wide-mouthed bottle which was then filled

with CMS previously purged with nitrogen. A piece of Mylar film was drawn over the bottle top and the lid screwed on tightly. The bottle was put in a water bath (60°C.) for 30 min. and then irradiated at ambient temperature (~25°C.). Either of two *sources of radiation* was employed. One was a General Electric Maxitron 250 x-ray unit producing 250 kvep x-rays. The other was a High Voltage Engineering Model KS (3 Mev/3 kw) Van de Graaff accelerator equipped with a gold target to give x-rays having energies extending from 0.3 to 3.0 Mev, an average energy of 1.0 Mev, and a yield vs. energy curve with a maximum at about 0.5 Mev.[7]

TABLE I
Identification of Dyes Used in This Investigation

Dye	Color index number	Dyes employed in	
		DMF bath	Aqueous bath
Calcodur Turquoise GL	Direct Blue 86	—	×
Calcomine Fast Orange 2R	Direct Orange 26	×	×
Calcomine Red FC	Direct Red 1	×	—
Calcomine Violet N Conc.	Direct Violet 1	×	×
Calcocid Alizarin Blue SAPG	Acid Blue 45	×	×
Calcocid Alizarin Green CGN	Acid Green 25	×	—
Calcocid Green B Conc.	Acid Green 1	—	×
Calcocid Phloxine 2G	Acid Red 1	—	×
Calcocid Brilliant Scarlet 3RN	Acid Red 18	×	×
Calcocid Fast Red A	Acid Red 88	×	×
Calcocid Yellow MCG	Acid Yellow 23	×	×

When the irradiated bottle was opened, the excess monomer was decanted and the fiber rinsed several times in benzene. The fiber was then placed in a Soxhlet extractor and extracted with benzene until benzene washings squeezed from the fiber produced no turbidity in methanol. About 2 hr. was usually required for complete extraction. The sample was then rinsed in methanol, blotted on paper, dried at 100°C. for 1 hr., and weighed.

Non-aqueous dyeing was accomplished by immersing a fiber sample in a DMF dye bath held at some constant temperature between 115 and 130°C. for 1 hr. Dye baths were made up according to the proportions 1 g fiber: 0.1 g. dye: 500 ml. DMF. The dyed fiber was rinsed with water and finally boiled in water for 1 hr.

Quaternization of the chloromethyl groups was achieved by immersing a weighed sample of grafted fiber in a volume of pyridine sufficient to cover it completely. The fiber-pyridine mixture was held at a constant temperature between 50 and 60°C. for 1 hr. The fiber was then removed from the pyridine, allowed to drain, washed with methanol, blotted, and extracted with benzene in a Soxhlet extractor for about 2 hr. to remove all excess pyridine. Finally, the sample was air dried and weighed.

The procedure for *dyeing* pyridine-treated samples in an aqueous medium utilized the following proportions of reagents: 1 g. fiber: 0.1 g. dye: 2 g. Na_2SO_4: 0.43 g. conc. H_2SO_4: 500 ml. H_2O. The samples were sometimes immersed in boiling dye for 1 hr., rinsed with water, boiled in water for another hour and dried. With samples containing more than about 10% CMS this technique gave too quick a dye strike. All the dye was taken up up on the outside of the fiber, i.e., ring dyeing occurred. Complete dye penetration in such samples was achieved by immersing them in a dye bath at about 50°C. and subsequently bringing them to a boil over a period of 30 min. followed by another 30 min. at full boil.

Microscopical Investigations

The *swelling* of polypropylene tow by CMS and acrylonitrile was determined microscopically by noting the increase in filament diameter as a function of time at 40, 60, and 90°C. The filaments to be measured were immersed in CMS in a closed cell. The diameters were measured at room temperature, and then the cell was placed on a Kofler hot stage which was heated to the prescribed temperature. The diameters were measured after 5, 10, 15, 20, 25, 30, and 60 min. Finally, the cell and its contents were allowed to cool to 25°C. and the diameters measured again. The diameters of ten filaments were measured at each temperature. (The microscope objective had a focal length of 4.2 mm. and a numerical aperture of 0.65. A 10 × Leitz filar micrometric eyepiece was used.)

The changes produced in the *birefringence* of polypropylene fibers (tow) immersed in various media were measured at 60 and 90°C. as a function of time. The procedure was similar to that for the determination of swelling with the additional measurement of the optical retardations in the fiber centers employing a Leitz Berek Compensator useable through 3 to 4 orders of interference colors. Birefringence was calculated by the relation, Birefringence = Retardation/Thickness. Monochromatic illumination was provided by a sodium vapor lamp.

Fibers whose cross-sections were to be examined microscopically were first potted in polymethyl methacrylate. Then, by the use of a microtome, cross-sections were cut 10 μ thick for light microscopy and 500–1000 A. thick for electron microscopy. Grafted but undyed sections were examined visually by a Zeiss ultraviolet microscope equipped with quartz optics using a Bausch and Lomb UV Photomicroscope Attachment equipped with an R.C.A. Ultrascope Tube (Image Converter) and a 7× viewing magnifier. Ultraviolet light was obtained from a B. and L. grating monochromator (grating blazed at 3000 A., efficiency = 38% at 3100 A.) illuminated by a Hanovia No. 5353 (108 watts) quartz burner. A spectral slit width of about 30 mμ (geometrical slit width 4.5 mm.) was used. For taking UV photomicrographs, the image converter was bypassed, and Ansco Hy Scan film was used. An R.C.A. type EMU-3C electron microscope was employed for obtaining electron micrographs. In the visible region, photo-

micrographs of thin sections of grafted and dyed films were obtained using both bright- and dark-field illumination and Kodacolor film.

Mechanical and Physical Testing

Tensile strength and *elongation* were measured with an Instron Tensile Tester using a 100%/min. rate of elongation and a 1-in. gage length. *Denier* was determined with a Manra Vibrascope. *Creep* was measured according to ASTM procedure D-1774-60T. AATCC wash test No. 3 (45 min. at 160°F. in aqueous 0.5% soap, 0.2% Na_2CO_3) was used to judge wash fastness. *Moisture regain* was calculated to be the per cent increase in weight of a bone-dry sample after an interval of 48 hr. at 25°C. and 50% relative humidity.

To measure *sticking temperature*, samples of grafted tow were teased by hand into specimens of yarn about 1 ft. long. A sample of this yarn was lightly stretched along the underside of a flat glass bar and snubbed at each end of the bar. It was then pressed onto the polished top surface of a hot copper bar 10 in. in length along which a temperature gradient existed. This bar is a part of the Parr Melting Point Apparatus, Series 3821. The temperature prevailing at that point along the bar's temperature gradient at which the fiber became tacky and adhered to the bar when the glass bar and the yarn were lifted was reported as the sticking temperature.

Antistatic behavior was evaluated in a test in which tufts of fibers were withdrawn with a metal gripping device from a pad of fiber packed in a bank of metal combs. The tendency of the withdrawn fibers to spread apart and curl back on the grip was rated on a 1 to 5 scale with 1 being the case where the fiber shows no motion and 5 the case where the tuft balloons out as the free ends leave the combs after which the fibers fly back and attach themselves to the grip.

Spectral reflectance curves were run between 400 and 700 mμ on a modified General Electric Hardy Spectrophotometer for samples of ungrafted polypropylene, grafted polypropylene, and pyridine-treated grafted material dyed with Calcocid Alizarin Blue SAPG and Calcocid Yellow MCG after exposures of 0, 20, 40, and 80 hr. in a Carbon Arc Fadeometer. The stability of the dyed samples was compared with that of wool cloth which had been dyed with the same dyes and similarly treated in the fadeometer. Reflectance curves were also run on the grafted material and on untreated polypropylene after 30 min. in an oven at 114°C. to determine the degree of yellowing produced by heat.

RESULTS AND CONCLUSIONS

Swelling and De-Swelling Results

Figure 1 shows the increase in diameter of polypropylene filaments as a function of time upon swelling at several temperatures in acrylonitrile and in CMS. The average initial diameter of a filament was 23.10 μ. Neither

monomer caused detectable swelling at 25°C.   However, when the swollen filaments were permitted to cool to 25°C., it was found that they returned to a fixed size somewhat larger in diameter than that which they had prior to swelling.   Volume increases, shown in the right-hand scale of the figure, were calculated assuming that the per cent of dimensional change was the same in all directions.
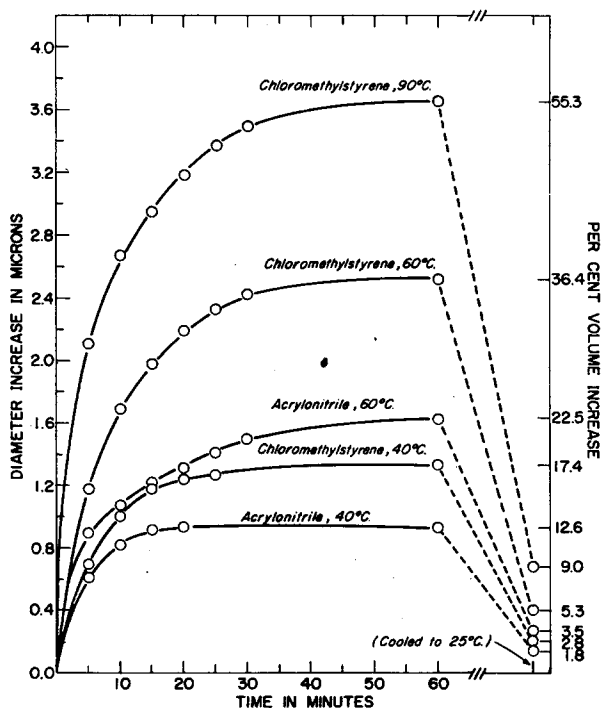

Fig. 1. Swelling of polypropylene fibers by chloromethylstyrene and acrylonitrile at several elevated temperatures.   Values of per cent volume increase, shown at right, obtained after equilibrium had been reached at the elevated temperatures and after de-swelling had occurred at 25°C.

Graft vs. Dose

The relation of the amount of CMS grafted on polypropylene to the total dose of radiation administered at 25°C. with 16 hours' post-irradiation time is shown in Figure 2.   Points were obtained at dose rates of 0.4 and 0.03 Mrad/hr.   The fact that these points all fall on one curve indicates a lack of dose-rate dependence for the amount of monomer grafted provided the post-irradiation time is long compared to the duration of the actual irradiation.   It is probable that the dose rate may exert a marked effect on the relative number of the grafted side chains and on their relative lengths. However, experimental data bearing directly on this point were not obtained in this investigation.
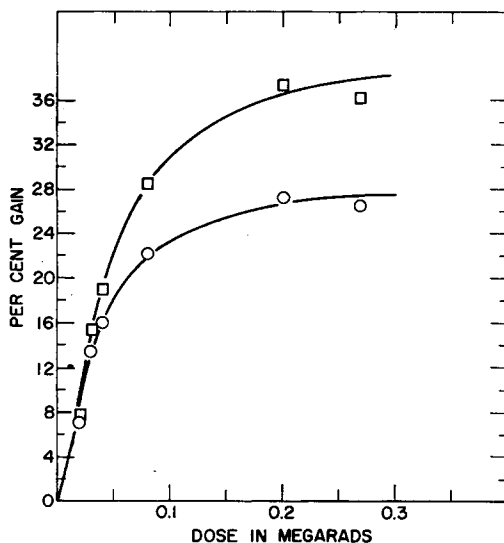
Fig. 2. Per cent pickup and per cent graft as functions of total dose at 25°C. with 16 hr. of post-irradiation time: (○) per cent graft (based on final weight); (□) per cent pickup (based on initial weight).

Post-Irradiation Grafting

The linear relationship between the log per cent pickup and the log post-irradiation time depicted in Figure 3 is what one would expect from such a grafting reaction.[8] At 60°C. the initial pickup is higher than that at 25°C. because of a higher rate of propagation. However, it is seen that the in-
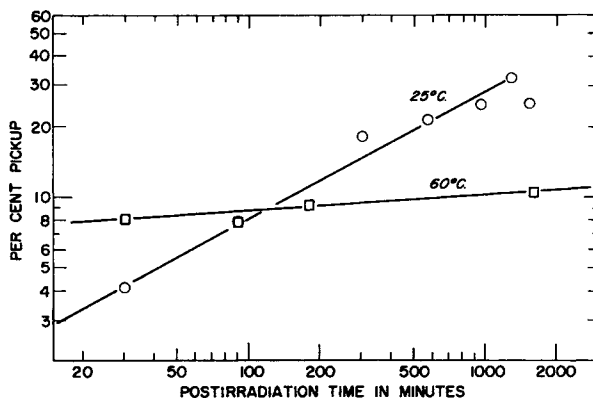
Fig. 3. Log per cent pickup versus log post-irradiation time at 25 and 60°C.
Doses were 0.06 Mrad at 0.4 Mrad/hr.

crease in pickup with time is less at the elevated temperature. This latter effect, in all probability, is attributable to an increase rate of radical termination.

Mechanical Properties of Grafted Fibers

Figure 4 shows straight and loop tenacities and denier as functions of the per cent of CMS grafted to polypropylene. The nonbrittle nature of the grafted fiber is demonstrated by the fact that both straight and loop tenacities have essentially the same values. The increase in denier with per cent graft is represented by the same curve as the one which depicts the decrease in tenacity with per cent graft. This brings out the interesting point that the *tensile strength* of a given filament is constant regardless of the amount of graft.

Per cent elongation is plotted as a function of per cent graft in Figure 5.
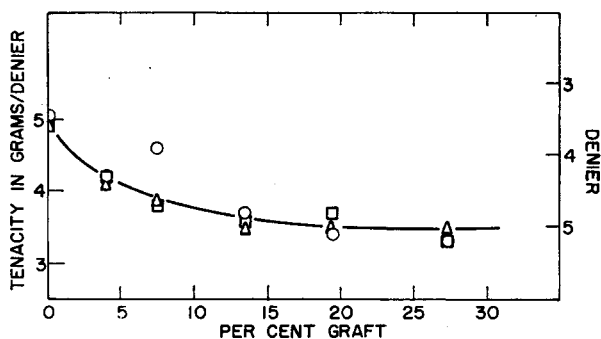
Fig. 4. Tenacity and denier (grams per 9000 meters) versus per cent graft: (O) denier; (□) straight tenacity; (△) loop tenacity.
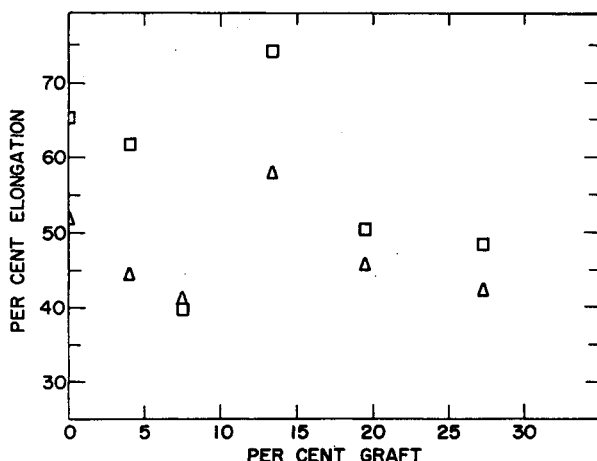

Fig. 5. Per cent elongation versus per cent graft: (□) straight; (△) loop. The points are badly scattered, and no attempt has been made to show trends.

Each point represents the average value of ten individual measurements on ten individual fibers. These same fibers provided the tenacity and denier data shown in Figure 4 which plot up very nicely. We are unable to explain

the poor reliability of the data on per cent elongation. It cannot be attributed to nonuniform grafting since this would lead to poor reproducibility in the tenacity data as well.

Dyeability and Related Tests

The deep and intense shades to which CMS-grafted polypropylene can be dyed may be seen in Figure 6. This depicts swatches of fiber with a 9% graft which were treated with pyridine and subsequently dyed in conventional aqueous dye baths with either acid or direct dyes.

A visual comparison of pyridine-treated, grafted polypropylene tow and wool fabric, dyed simultaneously in identical aqueous baths, indicates no difference in color between the two materials.

In comparing the dyeability of CMS-grafted fibers in a non-aqueous dye bath (such as DMF) with that of CMS-grafted, pyridine-treated fiber in an aqueous dye bath, it has been noted consistently that for a given dye, a given depth of shade can be achieved at a much lower level of graft when the grafted fibers are treated with the nucleophile. If the nucleophile is pyridine, the per cent of CMS graft can be in the range of 5–10%.

The ability of grafted fiber dyed in DMF to withstand several hours of boiling in a 1% soap solution without losing any dye is remarkable. While fiber with a lower graft which has been pyridine treated and dyed cannot (just like most other fibers) withstand such rigorous test of wash fastness, it will easily pass a conventional wash test (AATCC No. III) without changing color and without imparting any color to the soap solution.

Yellowness

The spectral reflectance curves show that the CMS-grafted material is whiter than the original Reevan polypropylene tow and that it gets even whiter after a treatment at 114°C. for 30 min. The original material actually becomes less white during this oven test. This may be attributable to the presence of small amounts of various protective agents which would have been removed through solvent action during the grafting procedure employed in our research-scale experiments. If CMS-grafted material is treated with pyridine, the yellowness increases, and it increases still further after the heat treatment. However, to the eye, the material still looks colorless at this stage. When treated in the carbon-arc fadeometer, the original Reevan tow is actually bleached to a slight extent while the CMS-grafted material remains colorless after 40 hr. but is yellow to the eye after 80 hours' exposure. The yellowness index ratings produced by these various treatments are to be found in Table II.

Light Stability of Dyed Samples

Samples of 3 denier polypropylene tow were grafted with CMS, treated with pyridine, dyed, and exposed in the carbon-arc fadeometer. Spectral reflectance curves were obtained after 0, 20, 40, and 80 hours' exposure.

TABLE II
Yellowness Index Ratings[a]

			Treatments			
				C Arc Fadeometer,[b] hr.		
No.	Sample	None	30 min., 114°C.	20	40	80
1	Reevan 3 denier Pp tow	6.94	10.81	6.06	5.33	5.43
2	(1) with 7% CMS graft, pyridine treated	9.1	12.7	—	—	—
3	(1) with 23.6% graft of (CMS + styrene + DVB)	4.39	4.07	8.65	12.2	23.4

[a] June 1961, test assigned to ASTM Standards Committee on Calorimetry for final review prior to adoption. Yellowness Index $= 100(1.28X - 1.06Z)/Y$, where X, Y, and Z are tristimulus values.

[b] FDA-R (C Arc) Fadeometer (120°F., Black Panel).

In the cases of samples of wool fabric dyed to equivalent deep shades with the same dyes, 80 hours' exposure was required to produce a change apparent to the eye. With the CMS-grafted (7%), pyridine-treated samples of polypropylene tow, a somewhat greater degree of change (but still not a really marked change) was produced after 40 hours' exposure. When dyed samples having a higher level of graft (23.6 % mixed CMS + styrene + DVB) were treated in the same way, noticeable (but not marked) changes occurred after only 20 hours' exposure. Quantitative data on the *color differences* produced by exposure to light are to be found in Table III.

Microscopical Investigations

In addition to the studies of swelling and de-swelling, the questions of uniformity of graft throughout a filament and of radial depth of penetration of dye into the filament were answered by microscopical examinations.

Uniformity of Grafting

Fiber specimens which had been grafted to the extent of 27.3% with chloromethylstyrene (CMS) were "potted" and sliced by a microtome as described in the Experimental section. Figure 7 portrays the transmission of a cross section at two wavelengths in the ultraviolet. Note that at λ 3650 A. both the polypropylene and poly CMS are essentially transparent, while at λ 2654 A. the polypropylene still transmits and presents a marked contrast to the poly CMS which absorbs quite strongly. (The original, as-spun, polypropylene fibers exhibit virtually no absorption at any wavelengths corresponding to mercury lines in the interval 2654–3650 A.) Thus, these UV photomicrographs show that in most of the fibers, the CMS graft extends all the way to the center. Another important difference noted in comparing UV photomicrographs of grafted and nongrafted fibers is the appearance of definite optical discontinuities in the grafted samples versus

TABLE III
Color Differences Produced in Dyed Samples by Exposure in FDA-R (C Arc) Fadeometer (120°F., Black Panel)

Hours	Sample	Red[c]			Yellow[d]			Blue[e]		
		A-N[f]	MacA[f]	H-S[f]	A-N	MacA	H-S	A-N	MacA	H-S
20	Wool fabric	6.5	8.7	4.4	2.0	1.6	0.5	3.0	5.3	3.1
	Pp tow[a]	—	—	—	14.0	16.0	2.9	9.2	10.0	6.1
	Pp tow[b]	12.5	13.0	5.6	22.0	28.0	6.2	14.0	13.0	10.0
40	Wool fabric	9.8	13.7	6.3	3.7	4.0	1.3	5.6	8.4	4.8
	Pp tow[a]	—	—	—	22.0	29.0	5.3	15.0	24.0	9.5
	Pp tow[b]	22.0	47.0	14.0	38.0	49.0	9.7	24.0	34.0	16.0
80	Wool fabric	13.0	21.0	8.3	7.6	9.1	2.0	8.4	12.0	7.2
	Pp tow[a]	—	—	—	31.0	40.0	7.6	24.0	39.0	15.0
	Pp tow[b]	37.0	94.0	27.0	53.0	72.0	15.0	36.0	66.0	27.0

[a] Reevan polypropylene tow (3 denier), 7% graft of CMS, pyridine treated.
[b] Reevan, polypropylene tow (3 denier), 23.6% graft of mixed (CMS + styrene + DVB), pyridine treated.
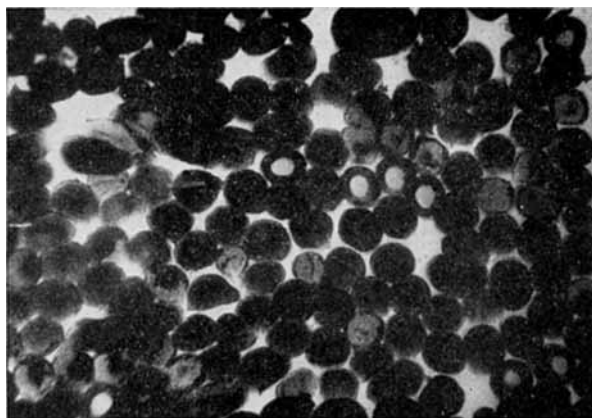[c] Calcocid Phloxine 2G.
[d] Calcocid Yellow MCG.
[e] Calcocid Alizarin Blue SAPG.
[f] Color difference evaluations by equations attributable to Adams-Nickerson, MacAdam, and Hunter-Scofield; see Deane B. Judd, Color in Business, Science, and Industry, Part II, Wiley, New York, 1952.
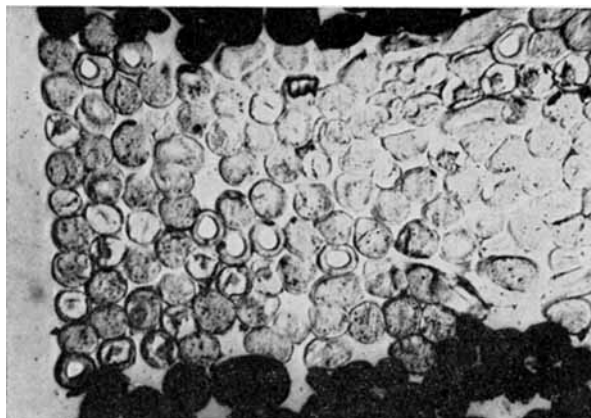
(a)

(b)

Fig. 7. Photomicrographs obtained in UV microscope with monochromatic illumination showing the degree of uniformity of grafting. Cross sections (~10 μ thick) of 3 denier polypropylene fibers radiation-grafted with CMS (27.3%). (a) Hg λ 3650 A., both polypropylene and poly CMS are nearly transparent. (b) Hg λ 2654 A., polypropylene transmits while poly CMS absorbs strongly. (The original as-spun, fibers do not absorb in the wavelength interval employed here.) The opaque fibers at top and bottom of both (a) and (b) are wool fibers employed for mechanical support in preparing samples for examination.

a comparatively smooth, homogeneous texture possessed by the ungrafted material.

Radial Penetration of Dyes

We have already pointed out that if the grafted sample is treated with a nucleophile such as pyridine, a lower level of graft is required to confer dyeability on a sample dyed in an aqueous dye bath than is the case when CMS grafting alone is used and dyeing is conducted in a DMF bath. It is interesting to compare the degree of penetration of various dyes achieved
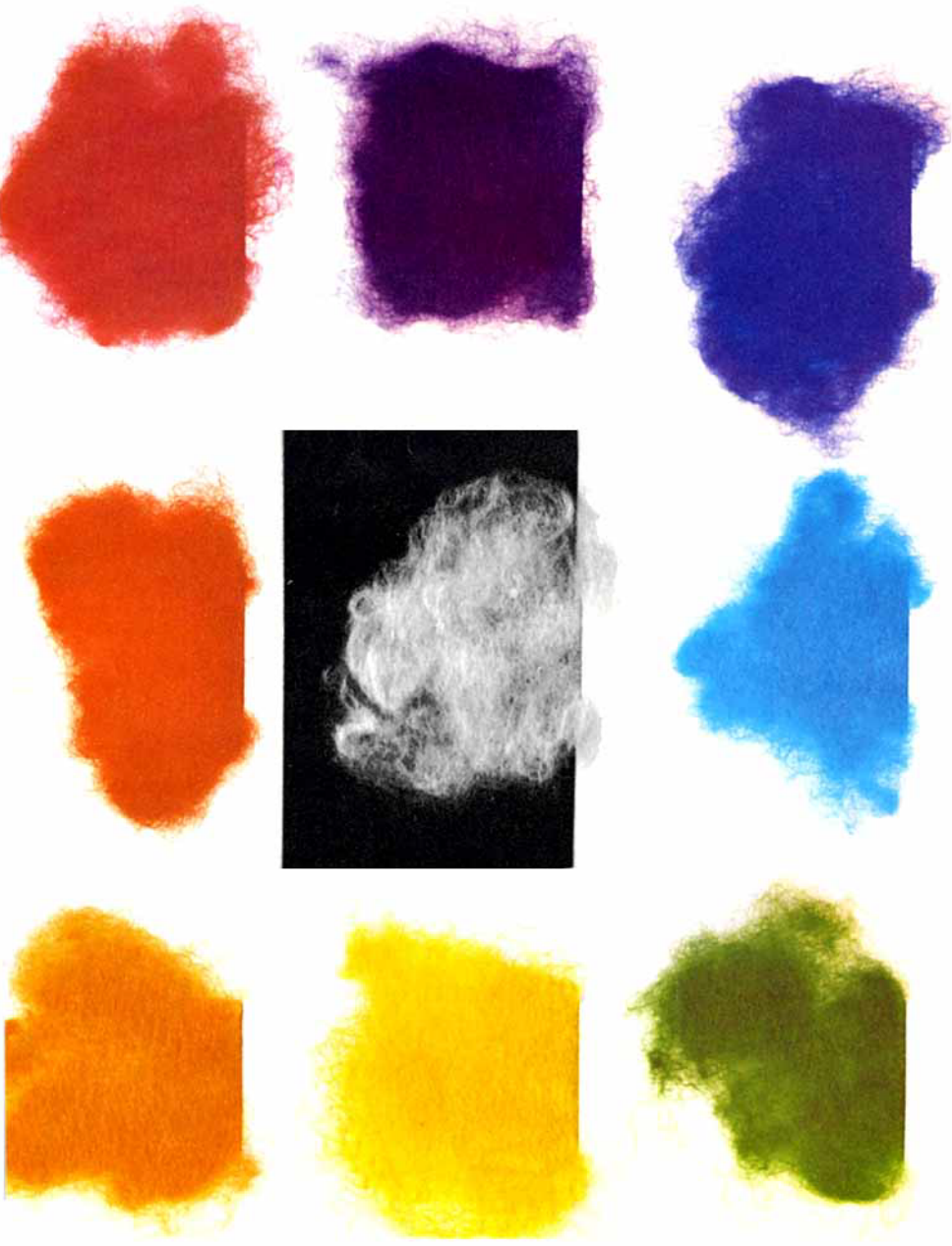
Fig. 6. Three-denier polypropylene tow radiation-grafted (9%) with chloromethylstyrene; treated with pyridine at 70°C.; dyed in aqueous baths for 1 hr. dye baths exhausted. Samples: (top left) Calcomine Fast Orange 2R, (top center) Calcocid Brilliant Scarlet, (top right) Calcocid Phloxine 2G, (middle left) Calcocid Yellow MCG, (middle center) Undyed, heated at 110°C. for 1 hr., (middle right) Calcomine Violet N concd., (bottom left) Calcocid Green B. concd., (bottom center) Calcodur Turquoise GL, (bottom right) Calcocid Alizarin Blue SAPG. See Table I for Colour Index Numbers of dyes.
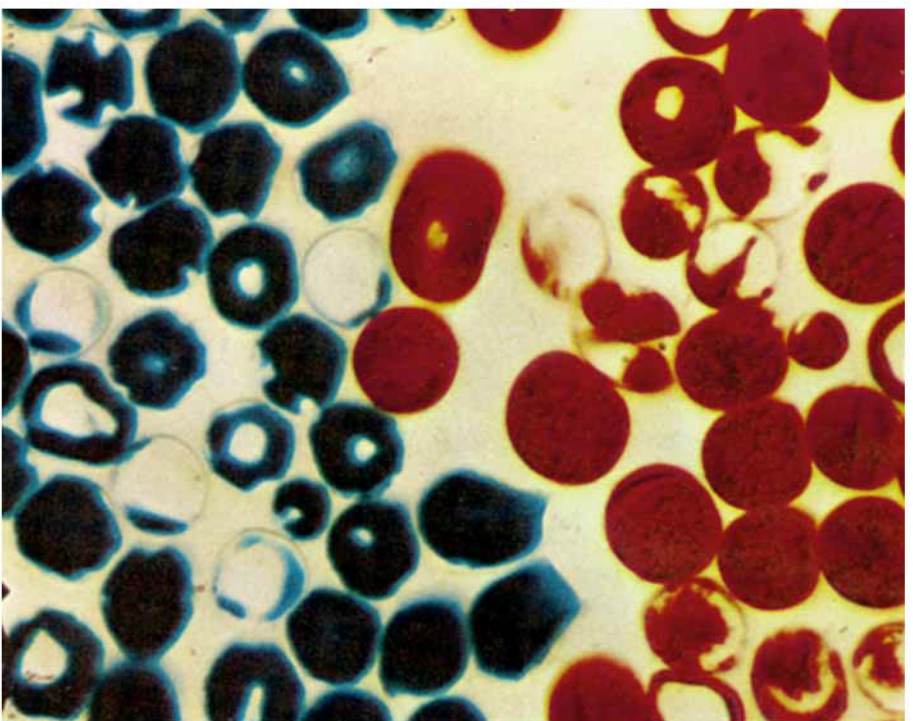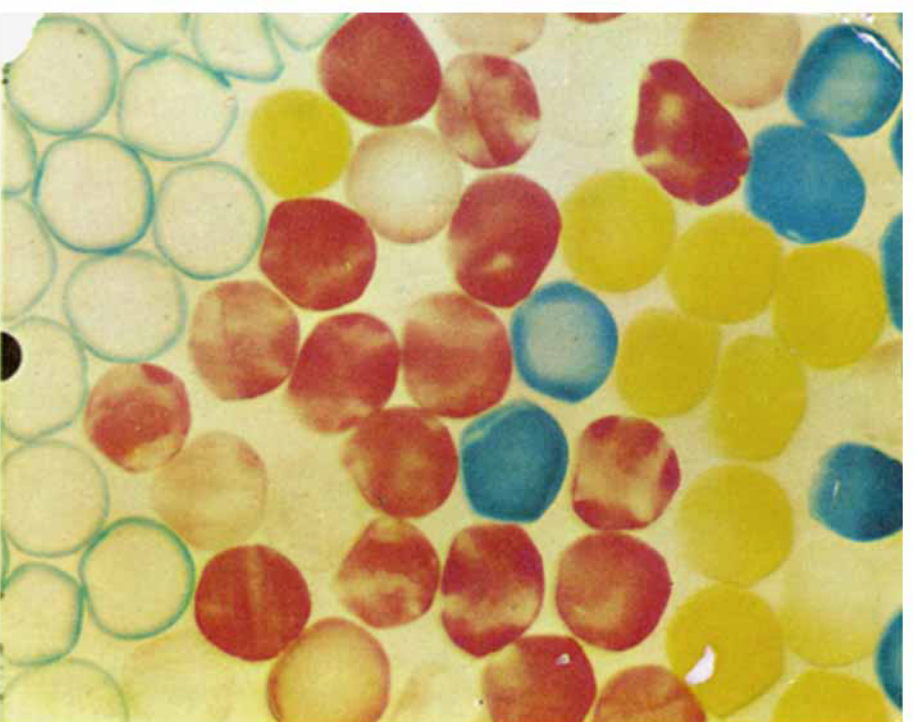
Fig. 9. Photomicrographs taken on color film showing the degree of radial penetration of dyes achieved by various treatments. (a, right) 9.9% CMS graft, pyridine treated, dyed in aq. baths for 1 hr. at 60°C.; dye baths exhausted 3 times. Calcocide Alizarin Blue SAPG and Calcocid Fast Red A.

(b, left) 23.6% graft, mixed monomers (CMS, Styrene, DVB), pyridine treated, blue, yellow, and red samples heated slowly to 100°C. in aq. dye baths, green sample put directly into aq. dye baths at 100°C.; dye baths exhausted once. Calcocid-Phloxine 2G (Red), Yellow MCG, Milling Fast Green CR9, and Alizarin Blue SAPG.

with these different treatments. An evaluation of some of these results appears in Table IV. The data from this table show that although the nonaqueous dyeing technique requires a greater concentration of CMS, the degree of penetration achieved is somewhat better probably because of a combination of both chemical and physical factors which have not been investigated sufficiently to permit giving a detailed explanation at this time. However, for the pyridine-treated samples, with CMS grafts at levels less than 10% by weight, the degree of penetration is still quite good, particularly if the fibers are heated slowly to boiling in the dye bath. Contrariwise, if the grafted and pyridine-treated fibers are put directly into the
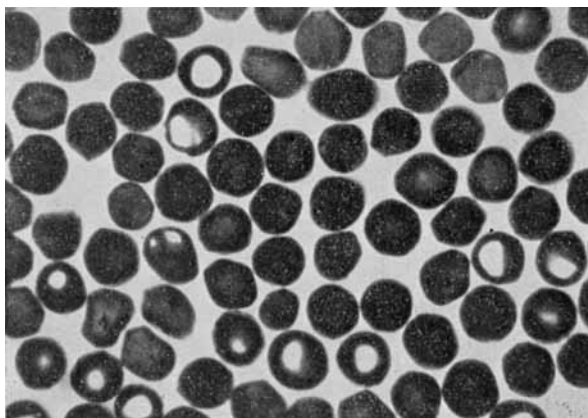

Fig. 8. Photomicrograph showing extent of dye penetration into polypropylene fibers containing 27.3% graft of chloromethylstyrene dyed with Calcocid Alizarin Blue SAPG in dimethylformamide at 120°C. Bright-field illumination, 350×.

boiling dye bath, a quick strike often occurs, and ring dyeing may result. The colored plates (Figs. 9a and 9b) which demonstrate the different degrees of dye penetration achieved under various conditions are referred to in Table IV; the dyes involved are listed in the captions accompanying those figures.

The Structure Created by Grafting

The microscopical investigation of these various fiber sections (~10 μ thick) disclosed the existence of certain types of optical discontinuities in the grafted fibers which were not present in the starting material. These discontinuities can be detected most easily when using dark-field illumination during a microscopical examination. They can also be seen in the bright-field UV photomicrographs (refer to Fig. 7). Here, as the wavelength is decreased, the discontinuities stand out more boldly. From the appearance of these heterogeneities, from the changes produced in appearance as the wavelength is altered, and from the fact that they do not appear in electron micrographs of sections of grafted fibers, we are inclined to attribute them to voids produced during grafting rather than to isolated

TABLE IV
Penetration of Direct and Acid Dyes into Treated Polypropylene Tow (3 Denier Fibers)

No.	Treatment	Dye bath	Penetration rating[a]	See Fig. No.
1	As received	DMF or aqueous	0	—
2	As received + pyridine	DMF or aqueous	0	—
3	16% CMS graft	DMF	75% (2), 25% (3–4)	—
4	27.3% CMS graft	DMF	10% (2–3), 90% (4)	8
5	9.9% CMS graft + pyridine	Aq., exhausted once	75% (1–2), 25% (4)	—
6	9.9% CMS graft + pyridine	Aq., exhausted twice	80% (2–3), 20% (4)	—
7	9.9% CMS graft + pyridine	Aq., exhausted thrice	40% (2–3), 60% (4)	9a
8	23.6% graft, mixed[b] + pyridine Treated fiber put directly into 100°C. dye bath	Aq., exhausted once	100% (1)	9b
9	23.6% graft, mixed[b] + pyridine Treated fiber heated slowly to 100°C. in dye bath	Aq., exhausted once	25% (2), 75% (4)	9b

[a] Ratings of 0, 1, 2, 3, and 4 correspond to penetrations of $^0/_0$, $^1/_4$, $^1/_2$, $^3/_4$, and $^4/_4$, respectively, of the filament radius by the dye.

[b] Mixed monomers (47.34% styrene, 47.34% CMS, 5.32% DVB) grafted to polypropylene tow. Ended up with 23.6% graft of which 36% (8.5% of total weight) was poly CMS.

pockets of heavily-grafted material. The specks seen in the starting material (Fig. 14a) appear to be solids rather than voids. However, oddly enough, no such optical discontinuities appeared in the samples of tow grafted with the mixed monomers (Nos. 8 and 9 in Table IV, Fig. 9b).

When much thinner sections (0.05–0.1 μ) were examined by direct transmission in an *electron microscope*, an entirely different type of structure became apparent. Here the most information was disclosed by electron micrographs of fibers which were not grafted all the way to the center. (For what follows below, refer to Figs. 10a–d.) The sample of tow which provided these electron micrographs had been swollen in CMS and irradiated (3 Mev x-rays, 0.2 Mrad at 0.4 Mrad/hr.) in the presence of excess CMS all the while being tied in a bundle. Thus, certain fiber-fiber contacts, which were inevitable, prevented free and equal access of the monomer to the entire surface areas of all the fibers. Therefore, it is our belief that the inhomogeneities in grafting observed are attributable to this factor, to the use of too short a swelling time or too low a swelling temperature. At a magnification of 5000×, the cross sections of the as-spun fibers show a smooth, continuous structure containing an occasional speck of (probable) impurity (Fig. 10a). As grafting proceeds, at the same magnification, what appears to be a three-dimensional network commences at the periphery of the fiber and works its way (either directly or deviously) into the center of the fiber. If the monomer has not penetrated to the core of the fiber, incomplete grafting occurs (Figs. 10b and 10c). The type of structure resulting from complete penetration can be seen in Figure 10d. Here, at 5000×, a very spongy structure seems to exist throughout the entire cross section; this provides a marked contrast when compared with Figure 10a. Since the heavy chlorine atoms would absorb the electrons more strongly than carbon and hydrogen, the dark areas in the positive prints belong to the regions rich in grafted CMS. In addition, in all probability, the only regions grafted at the temperatures employed (ambient) were those occupied by the amorphous polypropylene. If this hypothesis is valid, then the streamers and ripples seen in the lightly-grafted fibers whose cross sections are shown in Figures 10b and 10c, give a good indication of the orientation of the network of crystalline polypropylene which exists in the fibers and which is buried in a mass of amorphous polypropylene. At higher levels of graft, the CMS goes into the more inaccessible amorphous regions lying closest to the crystallites, nearly obliterates the ripples, and gives the more random structure seen in Figure 10d.

Birefringence

The polypropylene fibers used in these experiments contained about 60–65% isotactic material, the remainder being amorphous. It is well-known that the high mechanical strength of the fiber is attributable to the crystalline polypropylene. During the course of this investigation, it was assumed that grafting carried out at temperatures in the range of 25–60°C. probably would occur only in the amorphous regions and that the crystal-
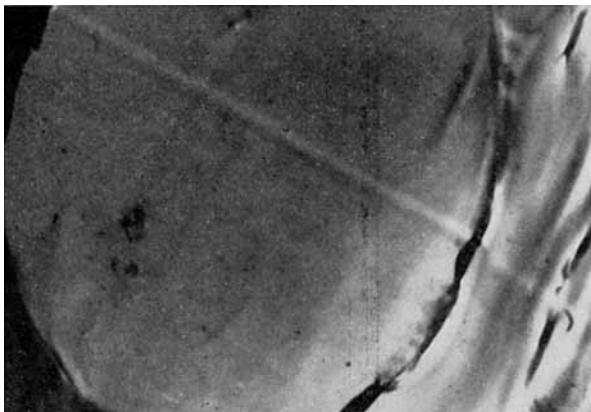
(a)
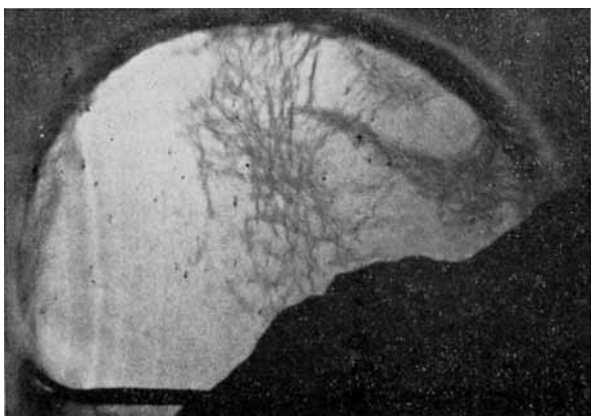
(b)

Fig. 10. Electron micrographs of thin sections (500–1000 A. thick) of polypropylene fibers (containing radiation-grafted poly CMS) showing details of structural changes effected during various stages of grafting. (a) As-spun fibers. The surface irregularities are believed to be foreign material. The structure appears to be smooth and continuous. (b) Very slightly-grafted fiber which, in the case of this section, shows that a small degree of grafting can proceed along preferred channels all the way to the center without necessarily grafting the entire periphery first. (c) Cross section of a fiber with a moderately-

lites, remaining virtually unchanged, would retain their melting point of 165°C. In addition, it was considered possible that a relatively low degree of grafting to the crystalline portions might raise the melting point without seriously impairing the mechanical strength. Therefore, it was decided to study the birefringence of the fibers immersed in various liquid media at elevated temperatures in order to judge whether or not the crystalline regions were being penetrated by a given liquid medium.

Heating the fibers in a nonswelling medium such as silicone oil produces a slight permanent increase in birefringence possibly attributable to the
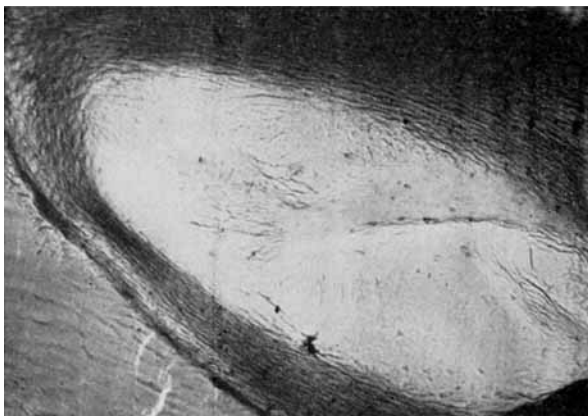
(c)

(d)

heavy graft extending radially inwards for about ¹/₂ the radius but only lightly grafted in the center. This probably occurred because after swelling and de-swelling, the central portion contained only a small amount of monomer. The fiber was in contact with xs liquid monomer during grafting, hence, the radial gradient. (d) Fully- and evenly-grafted fiber at a level of about 27.3% poly CMS. This portrays that which we designate as the spongy structure resulting from the grafting operation.

annealing or "heat setting" of the polymer. The diameters of the fibers are not increased by contact with the silicone oil at a temperature as high as 90°C. and exposures as long as 1 hr. Acrylonitrile, CMS, and toluene swell the fibers appreciably at elevated temperatures (see Fig. 1) and produce nonpermanent decreases in birefringence. After de-swelling occurs, and the fibers are again at 25°C., most of the original birefringence returns. Consequently, it seems probable that the crystalline regions are not disturbed, but rather that the solvent molecules penetrate between (and force apart) the weakly intermolecularly bound macromolecules comprising the amorphous regions, thereby disturbing the axial orientation of the polymer

chains in these regions. The slight loss of the original birefringence of the
fibers when cooled to 25°C. probably can be assigned to the effects of re-
tained solvent and parallels the slight increases in diameters of the fila-
ments over those possessed before heating. Figure 11 gives the changes in
birefringence over and above those observed in silicone oil under similar
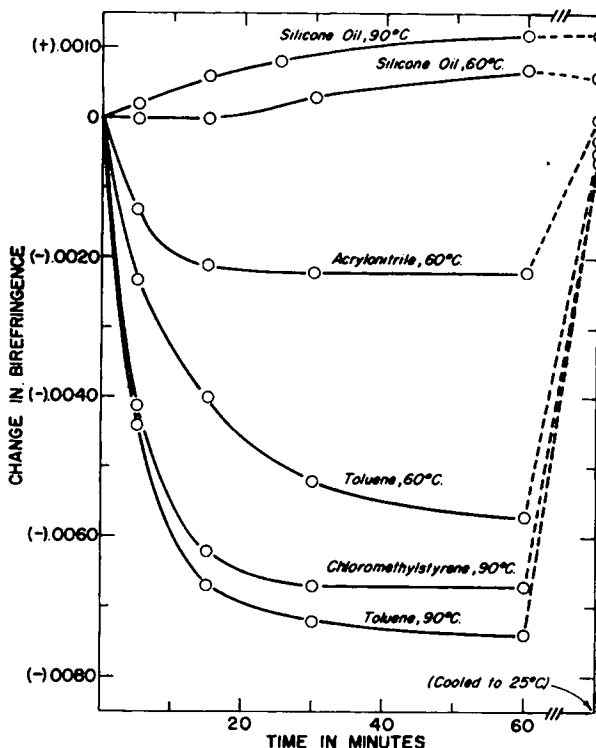conditions of time and temperature.

Fig. 11. Change in birefringence of 3 denier polypropylene fibers produced by swelling
and by thermal means. Results with nonswelling silicone oil considered to be thermal
alone. Ordinate values for other liquids corrected for thermal effects; thus, values shown
are attributable to swelling alone for acrylonitrile, CMS, and toluene.

The idea that the liquids discussed do not penetrate the crystalline re-
gions is supported by the results of the following experiments. A film, 30 μ
thick, was formed by melting some of the fibers and then cooling to 121°C.
at which temperature many large spherulites 100–500 μ in diameter were
grown. Some of the larger of these highly-crystalline spherulites were ex-
amined while being heated in CMS and in toluene. The maximum change
observed in the birefringence of any spherulite was a decrease of only 8%
when heated in toluene at 90°C. for 1 hr. No dimensional changes in the
spherulites were observed, and the birefringence reverted to the original
value after cooling to 25°C. Next, in order to remove the most-easily-dis-
solved amorphous material, these same films were extracted in toluene,

heated to 100°C. in fresh toluene, removed from the solvent, and then heated and annealed at 130°C. to enhance the degree of crystallinity of the spherulites. The birefringences of these spherulites were then measured again as before while immersed in CMS or in toluene. In comparison with the values observed at room temperature, no changes in birefringence and no change in diameter were detected while noting the behavior of three spherulites in contact with each liquid at 90°C. for 1 hr. The conclusions drawn from these experiments are that the highly-crystalline polypropylene is not affected by these liquids at temperatures as high as 90°C. and contact times as long as 1 hr.; that the swelling of the fibers by these same liquids must be confined to the amorphous regions; and that loss of birefringence of the fibers is attributable to the disruption of fiber-axial orientation of the polymer chains in the regions actually penetrated by the liquids. This is in accordance with the known fact that isotactic polymers are insoluble in solvents which dissolve the amorphous polymers.

Microscopical Melting Point

The melting characteristics of untreated and treated polypropylene fibers were noted by measuring their birefringences at elevated temperatures achieved by means of a Kofler hot stage. For the untreated material, the melting point (disappearance of positive birefringence) occurred at 166–167°C.; the material also flowed at 167°. In the case of fibers containing a graft of 15.9% CMS, the birefringence disappeared slowly in the temperature range of 170–180°C. and they flowed only slightly at 190°C. For a sample containing 50% by weight of grafted CMS, obtained by carrying out the grafting step with the fibers and CMS vapor at 125°C., the positive birefringence disappeared in the range 165–175°C.; however, at 170–175°C., a low negative birefringence appeared in the filaments and persisted to a temperature well over 300°C. Slight flow was observed from 190–200°C., but the fibers retained their shapes throughout the time required to heat them to a temperature above 300°C.

Sticking Temperature

In the Parr Bar test, the untreated sample stuck at 140°C. and melted on the bar above 165°C. The treated fibers exhibited abnormal behavior in this test. They hardly ever stuck to the copper bar or to the underside of the flattened glass bar by means of which they were pressed onto the copper bar, even at the hot end which was at a temperature as high as 270°C. However, sometimes the crystalline polypropylene would melt, and the individual fibers would fuse together to form a flattened ribbon. Typical data appear in Table V.

The data show that the sticking temperature is increased to about 165°C. by grafting alone and to about 185°C. by grafting plus pyridine treatment when the levels of graft are in a practical range. Thus, a marked improvement (25°C.) has been achieved by grafting alone, and additional improvement (another 20°C.) by the pyridine treatment.

For some applications it is possible that a sticking temperature higher than 185°C. would be desirable. However, it was anticipated that difficulties would be experienced in achieving this. The difficulties stem from the following factors. Polypropylene must contain a high percentage of

TABLE V

Sticking Temperatures of Polypropylene Fibers Containing Radiation-Grafted Poly CMS

No.	Treatment	Softening temp., °C.	Sticking temp., °C.
1	Original material	140	140
2	8.3% CMS + pyridine	—	178–190
3	15.9% CMS	—	162–170
4	9.6% (S + CMS + DVB)	—	168
5	23.6% (S + CMS + DVB)	160–180	>270
6	(5) + pyridine	160–180	>270
7	45% (CMS + AN) + 15% pyridine	Glazed ~175	>270
8	50% CMS + pyridine	170–180	180–190

isotactic material to maintain its excellent mechanical strength. This crystalline material melts sharply at 165°C. In any ordinary method of grafting a vinyl monomer onto the polymer, the grafting does not encroach on the crystalline regions and occurs only in the amorphous regions. In order to change this state of affairs, it appeared possible that a crosslinking or grafting procedure might be successful if it were employed at a temperature high enough to induce enhanced molecular motion in the isotactic material. This requires a delicate touch because too much modification of the isotactic material will certainly lower the tensile strength, and even a slight modification may not be tolerated. Attempts to achieve such results have been made here by radiation-induced crosslinking and by radiation grafting of CMS from the vapor phase, both at elevated temperatures.

Crosslinking at Elevated Temperature

Lawton, in a patent,[10] has disclosed certain results on crosslinking obtained by electron beam (800 k.v.p.) irradiation. In the work reported in the present paper, doses of 1.7, 3.3, 6.7, and 13.3 Mrads (3 Mev electrons) were given to samples of tow contained in evacuated glass ampoules at room temperature after which they were placed in an oven (135°C.) for 30 min., to induce crosslinking and kill off all free radicals. Figure 12 gives the straight and loop tenacities as well as the percent elongation of the treated filaments as functions of dose. The decrease in strength which occurred with increasing dose indicated that this probably was not the best way to proceed, and the effort along these lines was not pursued further. It is conceivable that an improvement in mechanical properties might have been noted if the experiments had been continued to much higher dose levels. However, this was not done.
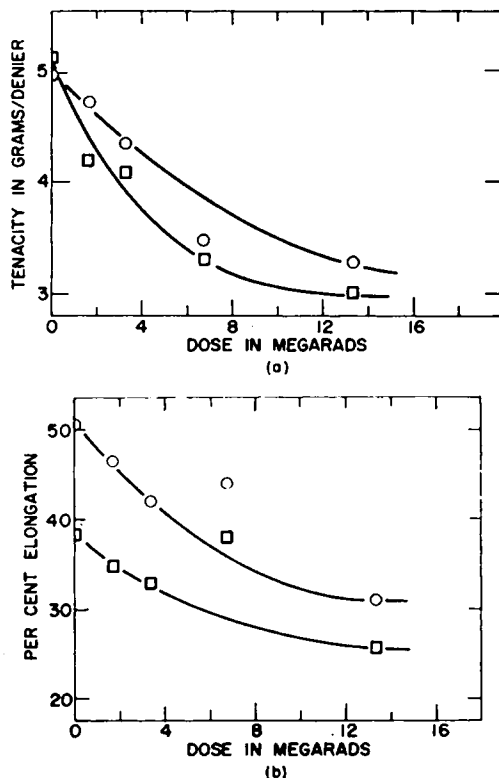
Fig. 12. Mechanical properties of 3 denier polypropylene fibers after irradiation with 3 Mev. electrons at 25°C. in vacuum followed by heating at 135°C. in vacuum for 30 min. (*a*): (○) Straight tenacity, (□) loop tenacity. (*b*): (○) Straight % elongation, (□) loop % elongation.

Vapor-phase Grafting

A sample of tow was grafted to the extent of 50% poly CMS using 3 Mev x-rays and a total dose of 6 Mrads. This procedure was carried out at 125°C. and in a vacuum with the fibers in contact with CMS vapor but not in contact with the liquid monomer. Electron micrographs of cross sections of these fibers show cracks and channels in the structure (see Fig. 13) and bear no resemblance to the spongy structure depicted in Figure 10*d*. In addition, the results obtained (see above) by studying the birefringence of these fibers at elevated temperatures (up to 300°C.) indicated that grafting had occurred in the crystalline regions. Despite this, the fibers contained material that exhibited softening at 165–170°C.

Sauer et al.[11] by dynamic mechanical measurements have shown that crystalline polypropylene undergoes a marked "softening" above ~127°C. before reaching the melting point at 165°C.. Thus, both crosslinking and grafting should be able to affect the crystalline regions when carried out at the temperatures used here (135 and 125°C., respectively). However, by

the observations reported here as a result of the present investigation, neither of these approaches (crosslinking or vapor-phase grafting at elevated temperatures) appeared to give the desired results; it was not possible (by the means employed) to raise the melting point of the crystalline material without losing tensile strength.
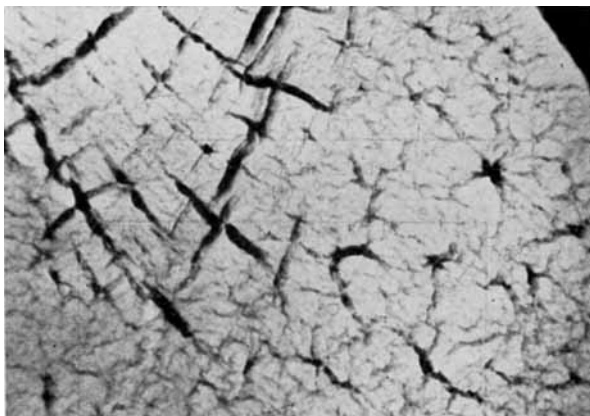

Fig. 13. Electron micrograph of heavily-grafted sample of polypropylene fiber (50% by weight of CMS graft) obtained by vapor-phase grafting at 125°C. Compare with Fig. 10d.

Moisture Retention

Untreated, unmodified fibers of polypropylene have a slippery, greasy, cold feeling. The ability of such fibers to retain moisture is practically nil. Consequently, fabrics made from such material rate very low in *antistatic behavior*, in *moisture regain* and in *hand*. By grafting CMS to the fibers and then treating with pyridine, marked improvements are made in all three of these properties. The improvements effected are great enough to make the fibers just as acceptable as other typical synthetics. For example, the modified polypropylene fibers have a pleasant, warm *hand* similar to

TABLE VI
Antistatic Ratings of CMS-Grafted Polypropylene Fibers

No.	Treatment	Antistatic rating 1–5 scale, 1 is best
1	Polypropylene with no modification and no additives	5
2	Reevan 3 denier tow, as received	2
3	(*2*) Treated with DMF at 120°C. for 1 hr.	3
4	(*2*) with 19.4% CMS graft, dyed in DMF, 120°C., 1 hr.	3–4
5	(*2*) with 8.3% CMS graft, pyridine treated	2
6	(*5*) Dyed in aq. bath, 100°C., 1 hr.	2
7	Typical acrylic fiber	~2
8	Typical wool (80's wool top)	1–2

lamb's wool; also, they have a moisture regain (16% CMS graft, pyridine treated) of 3.88% which is higher than the ratings[9] accorded to Dynel (0.3), Dacron polyester fiber (0.4), Orlon acrylic fiber (0.9), Acrilan acrylic fiber (1.7), and nylon (3.8) but lower than the ratings[9] for acetate (6), cotton (7–8.5), viscose rayon (13) and wool (16). Typical values for *antistatic behavior* are given in Table VI. It is to be remembered that the antistatic rating must be favorable not only to impart desirable properties to a fabric but also reduce the tendency to build up static charge during the processing steps of spinning, weaving, etc.; these modified fibers should be quite tractable during such manufacturing operations.

DISCUSSION

Advantages in Using Chloromethylstyrene

Thoroughness of Graft

In order to effect improvements in dyeability, moisture regain, antistatic behavior, and sticking temperature in a polyolefin fiber such as polypropylene by grafting something into or onto the fiber, we believe that a logical choice would be a monomer which has a reactive group as well as the ability to swell the polypropylene. It has been demonstrated here that the chloromethylstyrene penetrates the fiber easily and swells it (see Fig. 1) without dissolving it; thus, the grafting occurs all the way through the fiber as was demonstrated by the photomicrographs of the grafted and undyed fibers obtained with the UV microscope (see Fig. 7). However, incomplete penetration of some fibers did occur. This could be attributed to fiber-fiber contacts which prevented free access of monomer to certain fibers in the small-scale, static systems employed in the grafting experiments.

Length of Grafted Side Chains

Chloromethylstyrene is a good chain-transfer agent in free radical polymerization reactions. Thus, it is quite reasonable to expect that the side chains grafted onto the polypropylene backbone are numerous but short in length. Accordingly, it would follow that the dye sites should also be numerous and spaced fairly closely together and regularly along the backbone rather than being confined to long side chains fastened to the backbone at widely-spaced intervals. The reactive dye sites on such short, numerous side chains should be more readily accessible to dye molecules, and thus, a relatively low percentage of graft should be sufficient to achieve good dyeability. This has been found to be the case experimentally.

Structure of the Grafted Copolymer

The act of grafting this particular monomer to pre-formed polypropylene fibers loosens up the structure of the polypropylene and makes it more porous and more spongy. For example, Figures 14a and 14b, obtained
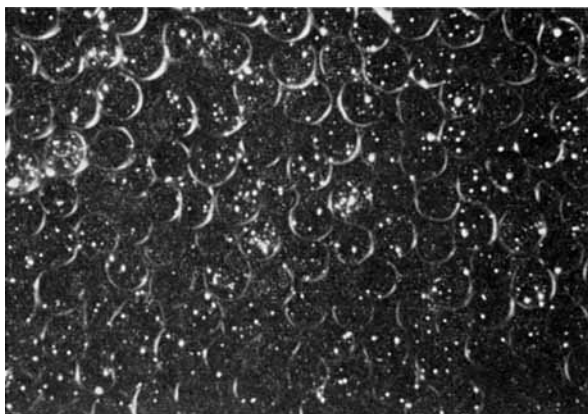
(a)
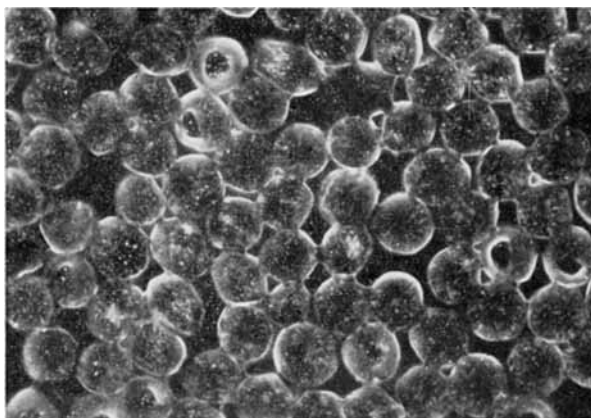
(b)

Fig. 14. Photomicrographs of cross sections of (a) ungrafted and of (b) grafted polypropylene fibers taken with dark field illumination. Note the marked increase of optical discontinuities in the grafted sample. These are believed to be voids.

microscopically by dark-field examination, show conclusively that many more discontinuities are present in the grafted sample than exist in the original polypropylene fibers. Evidence of the spongy structure developed is to be seen in the electron micrographs (Figs. 10a–d). Here, however, the structure seen by transmission of 100 kev. electrons through thin (500–1000A.) sections may be attributable to the fact that the transmissions of the grafted, chlorine-containing amorphous regions were much less than those of the nongrafted, hydrocarbon-like crystalline regions. This opening-up of the structure possibly expedites penetration of dye solutions and also enhances the moisture regain and the antistatic behavior.

Dyeing

It has been demonstrated experimentally that the modified fibers possess excellent dyeability, that true shades are obtained, that good dye penetra-

tion is achieved, and that the dyed fibers manifest excellent wash fastness and good light stability.

The reactivity of the benzyl chloride groups makes it possible to dye the grafted fibers with a wide variety of commercially-available dyes. Dyes containing —SO₃Na groups and —NH₂ groups would be expected to react with the benzyl chloride units of the grafted side chains to form covalent (ester-type) bonds (—ArCH₂—O—SO₂—Dye) and secondary amines, (—ArCH₂NH—Dye). In the case of one dye, Calcocid Alizarin Blue SAPG, which possesses both of these groups (—SO₃Na and —NH₂), dyeing in hot (120°C.) DMF produced an extremely deep shade that could not be washed off by boiling vigorously for several hours in 1% soap solution. An examination of the infrared spectrum of the dyed fibers indicated the presence of a band which could be attributed to the sulfonate ester group.

In practice, non-aqueous dyeing would not be popular commercially. In addition, for a given dye, higher levels (2–3 fold) of graft are required to produce a given intensity of shade when comparing nonaqueous (DMF) dyeing of grafted fiber to aqueous dyeing of grafted fiber treated with a nucleophile such as pyridine. Nucleophilic agents other than pyridine which would be expected to be useful would include trimethylamine, β- or γ-picoline, iminodiacetic acid, and aminotriacetic acid.

Maintenance of Strength

Polypropylene is susceptible to degradation by the action of oxygen, heat, and light. The fibers employed as starting material contain certain additives to inhibit or prevent such degradation. The data presented here on mechanical properties show that the radiation-grafted fibers retain a goodly portion of their original strength. However, if the fiber is put through all the steps employed in grafting except the one involving radiation, the resulting fibers have virtually no strength at all. When an attempt is made to separate individual fibers in order to test their tensile strength (0.35 g./den. and 2.6% elongation at break, maximum values), the fibers literally fall apart. Thus, it would appear that in these batch-type, research-scale experiments, virtually all the protective agents are leached out of the fibers, and that it is the radiation step, resulting in grafting, which restores the original mechanical strength.

The Problem of Sticking Temperature

A marked improvement in sticking temperature (an increase from 140 to 185°C.) was achieved with a 9% graft followed by treatment with pyridine. Attempts to effect further improvements along these lines brought to light a fundamental difficulty involving the fixed melting point (165°C.) of the crystalline portion of the polypropylene. Experiments involving radiation-induced crosslinking and vapor-phase grafting (of CMS) conducted at elevated temperatures high enough to affect the crystalline

material, indicated that modification of the crystalline portions of the fibers by these means probably would lead to loss of tensile strength.

Possible Variations in Technique

One interesting variation was carried out with the swollen fibers irradiated (0.1 Mrad at 0.2 Mrad/hr.) under water. The grafted material (10% graft) had an extremely soft, silk-like hand and could be dyed in DMF or (after being treated with pyridine) in aqueous dye baths.

There are several ways of using a given monomer such as CMS to produce the changes in polyolefins necessary for achieving dyeability, printability, etc. We have shown results achieved by one-step and two-step grafting initiated by free radicals formed in the substrate by ionizing radiation. One could also use the well-known two-step grafting procedure involving the formation of peroxides or hydroperoxides.[12] In the latter case, complications involving loss of strength from oxidative degradation would probably occur with polypropylene. Another variation would involve grafting induced by photochemical means in which radicals would be generated in the swollen fibers by direct photochemical action on the CMS or on a photosensitizer. Since the pre-formed fibers can be swollen by CMS monomer, the possibility exists that the monomer could be polymerized inside the fibers by thermal energy alone and, because of entanglement, the resulting poly CMS could not be removed by ordinary means.

The possibility also exists that grafting (or entanglement) could be carried out before spinning after which melt spinning or solution spinning could be used to produce the fibers which would then be treated with an appropriate nucleophile. Several experiments in melt spinning already carried out along these lines suggest that some expendable solvent might be used in order to make it possible to spin at a temperature no higher than 250–260°C.

In conclusion, the authors wish to state that the radiation-induced grafting of chloromethylstyrene to polyolefins can be carried out easily and inexpensively and seems to be a practical solution to the general problem of conferring dyeability, printability, wetability, etc. to pre-formed articles (films, fibers, etc.) made from such materials. In addition, the possibility of modifying powders prior to molding or extrusion definitely exists.

Added in Proof. The bulk density of polypropylene is about 0.905 g./cc. The densities of three samples of fibers (original tow as received, 9.1% CMS graft, and 26.6% CMS graft) were measured in a density gradient column (EtOH + CCl₄, 3¹/₂ hr. residence time). The *apparent* densities of the *dry* fibers were also measured by determining the deniers (g./9 × 10⁵ cm.) on the Vibrascope and the diameters of the same fibers by means of a microscope. Assuming that any holes or channels in the fibers would be penetrated by the liquids, the first measurement should give the density of the solid material in the fibers while the apparent density would be that of solids plus voids. The data are shown in Table VII. For the grafted samples, the apparent densities are significantly less than those measured in the column. This lends credence to the claim that the optical discontinuities seen in the grafted fibers are voids and not specks of solid material.

TABLE VII
Densities (g./cc.) of Untreated and CMS-Grafted Fibers

	% Graft		
	0	9.1	26.6
Density gradient column	0.90	0.97	1.02
Apparent density	0.90	0.89	1.00

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Synopsis

Chloromethylstyrene monomer was grafted to 3 denier (preformed) polypropylene fibers by using ionizing radiation. At elevated temperatures, microscopical investigations of changes in diameter and in birefringence demonstrated that this monomer swells the fibers without dissolving them. Thus, it is comparatively simple to achieve grafting all the way to the center. Such grafted fibers can be dyed by direct or acid dyes in non-aqueous baths (e.g., dimethylformamide at 210°C.) using levels of graft of ~25% by weight. This leads to covalent bonding arising from reaction between the dye and the benzyl chloride group of the graft. Dyeing in standard aqueous baths can also be achieved at even lower levels of graft (less than 10% by weight) if the grafted material is treated with a nucleophilic reagent such as pyridine. Using thin cross sections of treated fibers, photomicrographs were taken with monochromatic UV radiation, and with visible light on color film. These, combined with electron micrographs of much thinner cross sections provide pictorial proof of the complete penetration of the graft and

of the dyes as well as showing the opening up of the structure effected by grafting. By the means employed, it was possible to achieve marked improvements in dyeability, sticking temperature, moisture regain, and antistatic behavior without diminishing the excellent mechanical properties of the polypropylene fibers.

Résumé

On a greffé du chlorométhylstyrène par radiation ionisante à des fibres de polypropylène (préformées) de 3 deniers. Si ce greffage a lieu à de températures élevées, les examens microscopiques des changements de diamètre et de biréfringence ont montré que ce monomère gonfle la fibre sans le dissoudre. Il est donc très simple d'effectuer le greffage progressivement jusqu'au centre. De telles fibres greffées peuvent être teintées par des colorants directs ou colorants acides dans des bains non-aqueux (par ex. diméthylformamide à 120°C) en utilisant de taux de greffage d'environ 25% en poids. Il se forme un lien covalent issu de la réaction entre le colorant et le groupe chlorure de benzyle du greffon. La teinture dans des bains aqueux standards peut être aussi effectuée à des taux de greffage plus faibles (moins de 10% en poids) si le matériel greffé est traité avec un réactif nucléophile tel que la pyridine. Sur la base de sections transversales fines des fibres treitées, on a pris des microphotographies au moyen de lumière monochromatique U.V., et en lumière visible sur film coloré. Ces micrographies, combinées avec des micrographies électroniques de sections transversales beaucoup plus minces, fournissent une représentation de a complète pénétration du greffon et des colorants de même que l'élargissement de la structure résultant du greffage. A l'aide de cette technique il a été possible d'apporter de notables améliorations dans la tinctoriabilité, la résistance à la température, l'absorption d'humidté et le comportement antistatique sans diminuer les excellentes propriétés mécaniques des fibres de polypropylène.

Zusammenfassung

Monomeres Chlormethylstyrol wurde mittels ionisierender Strahlung auf 3-Denier-(vorgebildete)-Polypropylenfasern aufgepfropft. Mikroskopische Untersuchung der Änderung des Durchmessers und der Doppelbrechung zeigte, dass die Fasern bei erhöhter Temperatur in diesem Monomeren quellen ohne sich zu lösen. Es ist daher verhältnismässig leicht eine Aufpfropfung bis zur Mitte zu erhalten. Solche aufgepfropfte Fasern können mit direkten oder sauren Farbstoffen in nichtwässrigem Medium (z.B. Dimethylformamid bei 120°C) bei einer Aufpfropfung von ~25 Gew. % gefärbt werden. Durch Reaktion zwischen dem Farbstoff und der Benzylchloridgruppe der Pfropfung werden kovalente Bindungen gebildet. In wässriger Standardflotte kann eine Färbung sogar bei niedrigerem Pfropfungsgrad (weniger als 10 Gew.%) erreicht werden, wenn das aufgepfropfte Material mit einem nucleophilen Reagens wie Pyridin behandelt wird. An dünnen Querschnitten behandelter Fasern wurden Mikrophotographien mit monochromatischer UV-Strahlung und mit sichtbarem Licht auf Farbfilm aufgenommen. Diese liefern zusammen mit elektronenmikroskopischen Aufnahmen an viel dünneren Querschnitten einen bildmässigen Beweis für die vollständige Durchdringung der Pfropfung und der Farbstoffe und zeigen die durch die Pfropfung bewirkte Aufschliessung der Struktur. Durch die verdendeten Mittel war eine merkliche Verbesserung der Färbbarkeit, der Klebetemperatur, des Feuchtigkeitsbeständigkeit und des antistatischen Verhaltens ohne Beeinträchtigung der ausgezeichneten mechanischen Eigenschaften der Polypropylenfasern möglich.