Grafting onto Polyformaldehyde Fibers

H. T. LOKHANDE and A. S. SALVI, *Department of Chemical Technology, University of Bombay, Matunga, Bombay-400019, India*

Synopsis

Acrylic acid (AA), acrylonitrile (AN), and acrylamide (AM) were grafted onto polyformaldehyde (PF) fibers employing γ-ray irradiation as well as benzoyl peroxide initiation. The nature of the graft copolymer obtained from a given monomer was dependent on the type of method used for the grafting reactions. This was reflected in the various characteristics of the grafted PF fibers such as moisture regain and dyeability to disperse, direct, basic, and acid dyes. The extent of grafting was dependent on time, concentration of the initiator, concentration of monomer, and irradiation dose. The grafting reaction with all the three monomers and both methods of grafting studied followed first-order kinetics. The rate constant values for grafting with AA, AN, and AM were 0.493, 0.576, and 0.420 hr^{-1}, respectively for the irradiation method and 0.385, 0.385, and 0.346 hr^{-1}, respectively, for the benzoyl peroxide initiation technique. The increase in the moisture regain was directly proportional to the amount of graft in the fiber. Acrylic acid grafted PF fibers were rendered hydrophilic to the highest extent (7.9% M.R. for 42% graft), while AM-grafted fibers were rendered so to the lowest extent (7.23% M.R. for 76.5% graft). Considerable improvement in dyeability of PF fibers was observed as a result of grafting. In general, dyeability was proportional to the amount of graft introduced in the fibers. The AA-grafted PF fibers gave a six- to sevenfold increase in disperse dye content when the irradiation method was followed and a four- to fivefold improvement when the chemical method was used during the grafting reaction. The AA-grafted and AM-grafted PF fibers show considerable affinity toward direct cotton dyes. The two substrates could also be dyed with fiber-reactive dyes in deep fast shades, the AM-grafted PF fibers giving deeper shades as a result of higher reactivity imparted to the substrate by the NH_2 group of the graft copolymer. The AA- and AN-grafted PF fibers could be dyed in intense deep shades with cationic dyes. Similarly, AM-grafted substrates gave bright deep shades with acid dyes. Infrared studies, used to analyze the grafted PF fibers, indicated the presence of —COOH, —CN, and —NH_2 groups introduced in the fiber structure as a result of grafting with AA, AN, and AM.

INTRODUCTION

Sakurada and coworkers[1,2] carried out graft copolymerization of styrene onto poly(oxymethylene) fibers (Delrin and Celon) using irradiation and observed that the extent of grafting was higher at higher dose rates but could not obtain improvement in thermal stability or resistance to strong alkalis or mineral acids. Eguchi and Okaya,[3] however, claimed good thermal stability of the graft copolymer when the poly(oxymethylene) copolymers were grafted with vinyl compounds using the irradiation technique. The grafted copolymers when spun into filaments had improved bulkiness, crimp stability, and dyeability. Although the Japanese workers have carried out grafting on polyformaldehyde [poly(oxymethylene)] fiber, there is no work so far reporting the grafting on these fibers using the chemical initiation method, and hence no comparison of the two techniques could be drawn.

An earlier communication from our laboratories reported systematic investigation of electrokinetic properties of PF fibers.[4] The aim of the present

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communication is to report results on grafting of acrylic acid (AA), acrylonitrile (AN), and acrylamide (AM) onto PF fibers using both irradiation as well as chemical initiation techniques with a view to improve certain important properties such as hydrophilicity and dyeability with various classes of dyes.

EXPERIMENTAL

Polyformaldehyde Fibers

This fiber was kindly supplied by the Kiev Technological Institute of Light Industries, Kiev, U.S.S.R. It was prepared from the copolymer of formaldehyde and m-dioxane and was spun in the form of filaments on the laboratory spinning unit of the Institute.

Important characteristics of the polyformaldehyde fibers were as follows: (a) Characteristic viscosity in dimethylformamide (DMF) determined at 150°C = 0.5; (b) ratio of comonomers: formaldehyde and dioxolan = 98:2; (c) draw ratio = 8; (d) molecular weight (number average) = 50,000.

Chemicals and Dyes

The following monomers were used in the present investigation:

Acrylic Acid (AA). Laboratory reagent, Vio Soyuzchimexport (Moscow), kindly supplied by Colour Chem. Ltd. Bombay, was vacuum distilled to remove inhibitors. It was then stored as 50% solution at low temperature in polyethylene bottles.

Acrylonitrile (AN). C.P. grade, distilled to remove inhibitors. The fraction boiling in the range of 76–78°C was collected and used for grafting.

Acrylamide (AM). A solid powder of chemically pure grade was used.

All other reagents used in the present investigation were of chemically pure grade.

The following dyes were used in the present investigation:

Disperse Dyes. (1) Duranol Red 2R (C.I. Disperse Red 15); (2) Duranol Violet R (C.I. Disperse Violet 1).

Cationic Dyes. (1) Astrazon Orange G (C.I. Basic Orange 21); (2) Astrazon Orange R (C.I. Basic Orange 22).

Direct Dyes. (1) Congo Red (C.I. Direct Red 28); (2) Chlorazol Sky Blue FF (C.I. Direct Blue 1).

Acid Dyes. (1) Polar Red 2B (C.I. Acid Red 172); (2) Polar Red 10B (C.I. Acid Red 54).

Reactive Dyes. (1) Procion Brilliant Red H-7B (C.I. Reactive Red 4); (2) Procion Black H-G (C.I. Reactive Black 1); (3) Remazol Brilliant Blue BR (C.I. Reactive Blue 5).

Purification of Polyformaldehyde Fibers

The PF fibers used in the present investigation were purified by extraction with carbon tetrachloride for 16 hr.

Gamma Ray-Induced Graft Copolymerization

The PF fibers were swollen in 50% acrylic acid at 70°C for 18 hr. Graft copolymerization was accomplished by γ-irradiation from a ^{60}Co source. Different amounts of graft copolymers of acrylic acid were introduced by varying the time of irradiation. The homopolymer was removed by boiling water treatment.

For the grafting of acrylamide and acrylonitrile, the PF fibers were preswollen in DMF (50% aqueous solution) at 30°C overnight. The swelling agent was then removed by boiling water followed by drying at room temperature. About 1–1.5 g of the swollen sample was soaked with 30 parts acrylamide and 20 parts DMF, or 40 parts acrylonitrile, and 60 parts DMF along with $M/50$ scavanger to inhibit homopolymerization. These mixtures were kept in sealed tubes for 18 hr at 75°C and were then irradiated as such with γ-rays from the ^{60}Co source. After the irradiation, the samples were tested for the presence of homopolymer by adding them to water. If a film formed, it indicated the presence of homopolymer. When film formation occurred, the grafted sample was washed with methanol several times, boiled, and dried to constant weight. Different amounts of graft copolymer on PF from acrylonitrile and acrylamide were obtained by varying the time of irradiation.

Benzoyl Peroxide Initiation

The PF fiber was swollen in a solvent–nonsolvent system consisting of DMF/water (30/70, v/v) at 70°C for 2 hr. DMF was removed completely from the fiber by treatment with boiling water. This swollen fiber was then used for grafting.

For graft copolymerization with acrylic acid, benzoyl peroxide (0.125 g) was dissolved in acetone (5–10 ml) and the solution was poured into distilled water (95–90 ml). About 5 ml acrylic acid was added to the mixture. To this was added about 1 g of the swollen fiber. The temperature of graft copolymerization selected was 80°C. Time of the grafting reaction was 1–6 hr. After the graft copolymerization, the fibers were treated with boiling water. In order to remove homopolymers, the graft copolymers were treated with solvents. The homopolymer of acrylic acid was removed by treatment with boiling water for 2 hr.

The same procedure was followed for graft copolymerization with acrylamide and acrylonitrile monomers, where 1 g acrylamide or 5 ml acrylonitrile along with 10 ml DMF was added to 1 g swollen PF fibers. The homopolymer of acrylonitrile was removed by treatment with DMF at about 70°C for several hours followed by treatment in boiling water for 1 hr.

The grafted samples were dried at 105°C for 2 hr and kept in a desiccator over P_2O_5, and the amount of graft on the PF fibers was determined on a weight basis. If W_1 = weight of the original PF fiber taken and W_2 = weight of the grafted PF fiber, then the amount of graft G (%) on the PF fibers is calculated as follows:
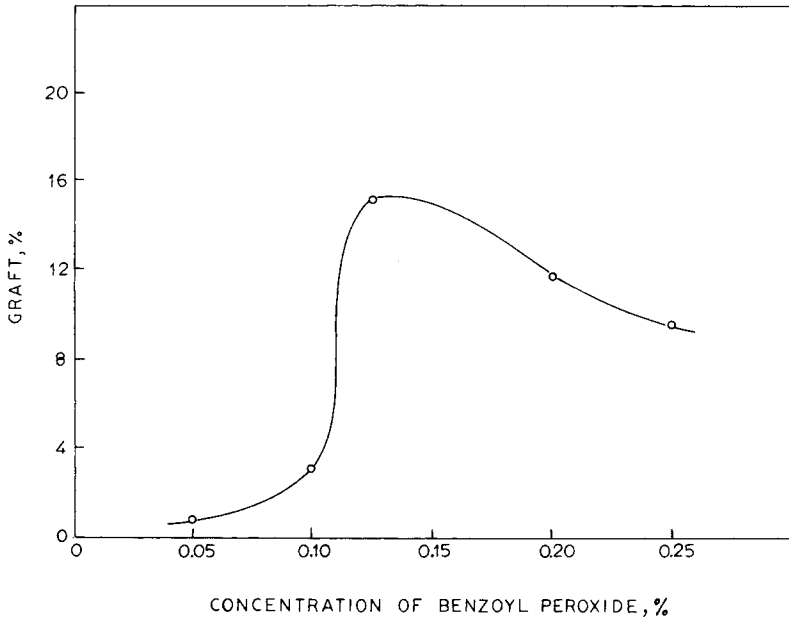
$$G = \frac{W_2 - W_1}{W_1} \times 100$$

Fig. 1. Percent graft of AA on PF fibers vs concentration of benzoyl peroxide.

Determination of Moisture Regain

The samples were conditioned for 72 hr over 75% R.H. at 30°C and then bone dried in an oven at 105°C for 2 hr. From the loss in weight of the samples before and after drying, the moisture regain values of the fibers were determined and expressed in terms of per cent moisture.
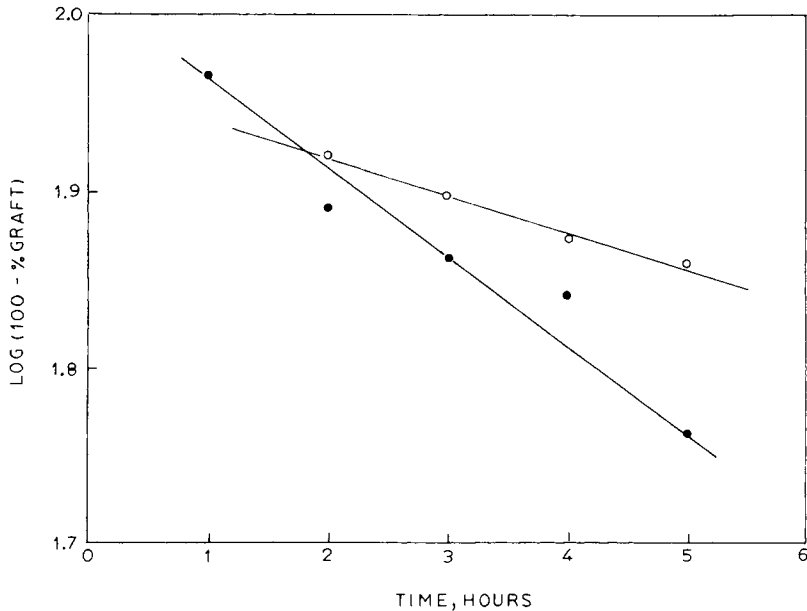

Fig. 2. Log (100 − % AA graft) on PF fibers vs time of treatment: (O) benzoyl peroxide method; (●) irradiation method.

TABLE I
Effect of Variation in Time on Amount of Graft on Polyformaldehyde Fibers

Monomer	Irradiation method		Benzoyl peroxide method	
	Time of irradiation, hr	Graft, %	Time of Treatment, hr	Graft, %
Acrylic acid	1	7.00	1	4.00
	2	22.05	2	15.20
	3	26.60	3	20.70
	4	30.10	4	39.10
	5	42.00	6	56.40
Acrylonitrile	1.5	4.20	1	3.8
	3.0	14.86	2	7.0
	5.0	24.93	3	11.2
	—	—	5	18.3
	—	—	6	24.8
Acrylamide	1	15.2	2	6.1
	2	39.6	4	13.5
	5	76.5	6	21.5

TABLE II
Rate Constants for Different Monomers

Monomer	Rate constant k, hr^{-1}	
	Irradiation method	Benzoyl peroxide method
Acrylic acid	0.493	0.385
Acrylonitrile	0.576	0.385
Acrylamide	0.420	0.346

Infrared Studies

Infrared spectra of the PF fibers and grafted PF fibers were recorded using the KBr disc technique.[5]

Purification of Direct and Acid Dyes

Direct and acid dyes were purified according to the method recommended by Robinson and Mills.[6] The detailed procedure for the purification has been given in the previous communication.[4]

Purification of Cationic Dyes

Purification of cationic dyes was carried out according to the method suggested by Balmforth et al.[7] The dye was extracted with 10 volumes boiling absolute alcohol. Easily filterable crystals were recovered after chilling the solution overnight. This procedure was repeated thrice to ensure purity of the dye.

Purification of Disperse Dyes

Duranol Violet R (C.I. Disperse Violet 1). The commercial product was crystallized three times from acetone and finally dried at 50°C. The purity of the dye was checked by determining the optical density of a standard solution in acetone. After the second crystallization, the optical density of the standard

solution did not show any change.   The melting point of the purified product
was 261°C.

Duranol Red 2R (C.I. Disperse Red 15).   The commercial dye was dispersed
in hot distilled water.   To this dispersion was added benzene, which extracted
the dye on vigorous shaking from the aqueous phase.   Similar extractions were
repeated about seven to eight times.   Finally, the dye was crystallized three times
from benzene and dried at 60°C.   The melting point of the purified dye was
210°C.

Purification of Reactive Dyes

Purification of reactive dyes was carried out by the method suggested by Mehta
et al.[9] and Mehta and Shah.[10]   A commercial sample of the dye was dissolved
in cold DMF and filtered through a sintered glass crucible (G-3).   Addition of
acetone to the filtrate precipitated the dye, which was washed with acetone and
petroleum ether and dried at 30°C.   This procedure was repeated until the op-
tical density of the solution of a given concentration of purified dye remained
constant.   All the dyes were preserved in a desiccator over P_2O_5 under vacuum
at 30°C.

Dyeing Procedures

Dyeing with Disperse Dyes.   Fine suspensions were prepared by grinding
the dyestuffs with distilled water for 48 hr in a rod mill to a state of dispersion
which could be easily suspended in water.   Dyeings in 4% shade were carried out
at 100°C for 1 hr by keeping the liquor ratio at 100.

Dyeing with Cationic Dyes.   The PF fibers and the grafted PF fibers were
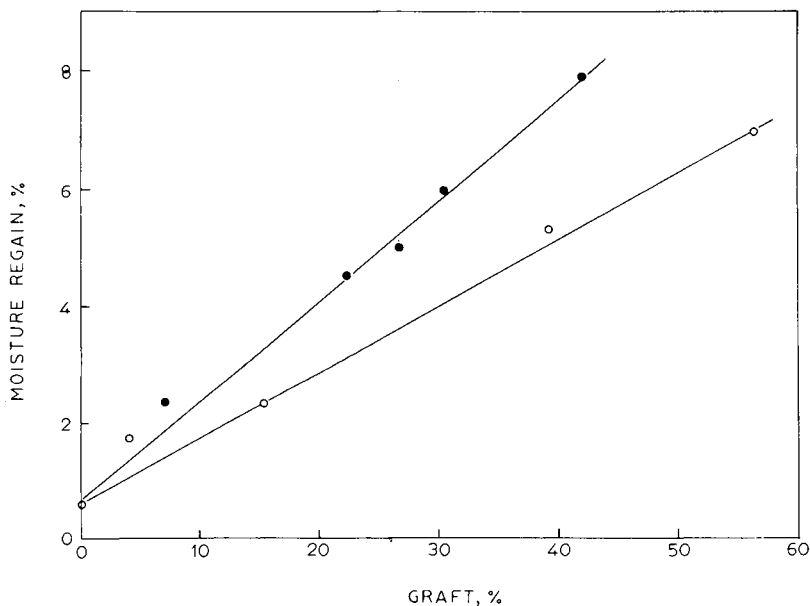

Fig. 3. Moisture regain of AA-grafted PF fibers vs % AA grafts: (O) benzoyl peroxide method;
(●) irradiation method.

dyed with cationic dyes at 100°C for 2 hr. The pH of the dye liquor was maintained at 4–5, and the liquor ratio, at 100 (4% shade).

Dyeing with Acid Dyes. The AM-grafted PF samples were dyed with acid dyes at 100°C at pH 4–5. The fibers were introduced at 60°C, and the temperature was then raised to the boil in 45 min and dyed for 1 hr at the boil. The liquor ratio maintained was 100 (2% shade).

Dyeing with Direct Dyes. AA-Grafted and AM-grafted PF fibers were introduced in a dyebath containing dye liquor set at 60°C. The temperature of the dyebath was then raised to the boil and the dyeing continued for 45 min. Sodium chloride (10 g/l. of dye liquor) was added to ensure better exhaustion of dye from the dyebath. The liquor ratio was maintained at 100 (2% shade).

Dyeing with Reactive Dyes. AA-Grafted and AM-grafted PF fibers were introduced into the dye liquor which was kept at pH 5.5. The temperature of the dyebath was raised to the boil and dyeing was continued for 45 min. Fixation of the dye on AA-grafted fiber was effected by increasing the pH from 5.5 to 10.5 by the addition of sodium carbonate. Dyeing was continued further for 40 min at the boil. Dye fixation on AM-grafted fiber, however, was effected by lowering the pH to 4.

Determination of Dye Content

To find the dye content of the fibers, calibration curves (plots of concentration of dye in g/l. vs optical density of the solutions) in appropriate solvents were constructed using a Hilger Pattern Biochem Absorptiometer No. C.100/71426 at an appropriate wavelength.

Direct and Acid Dye Content. Accurately weighed 20 mg dyed fiber was extracted in 10 ml 25% aqueous pyridine or DMF solution, and the optical density
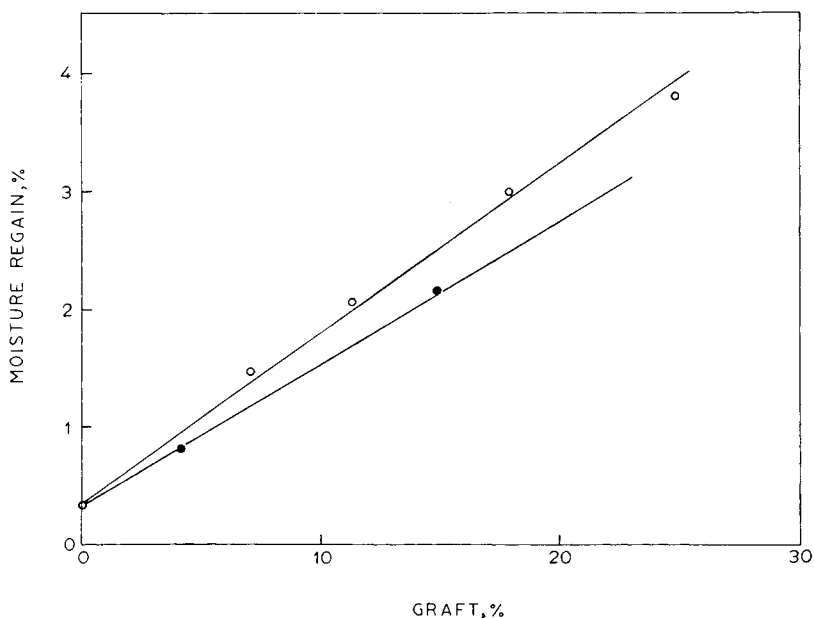

Fig. 4. Moisture regain of AN-grafted PF fibers vs % AN graft: (O) benzoyl peroxide method; (●) irradiation method.

was determined. Using the calibration curve, the dye content of the fiber was determined.

Disperse Dye Content. Samples dyed with disperse dyes (20 mg) were extracted in chlorobenzene to give a final volume of 25 ml. Optical density of the solution was determined and the dye content calculated.

Cationic Dye Content. Accurately weighed (5 mg) dyed samples were extracted in aqueous acetic acid (50%) solution to a final volume of 50 ml. The optical density of the extract was determined and the dye content was calculated.

Reactive Dye Content. Quantitative estimation of reactive dye content in the AA-grafted and AM-grafted PF fibers could not be carried out since no solvent could either extract the dye from the fiber or dissolve the dyed substrate at room temperature. It was, however, possible to dissolve the dye in DMF but only at 150°C.

RESULTS AND DISCUSSION

In order to determine the optical concentration of benzoyl peroxide that could give the maximum amount of graft on PF fiber, grafting of AA was carried out on PF fibers using varying concentrations of benzoyl peroxide. Figure 1 shows the plot of per cent graft versus concentration of benzoyl peroxide. It can be seen that with increase in benzoyl peroxide concentration there is a sharp increase in the amount of AA graft on the PF fibers up to a concentration of 0.125% (w/w) of the initiator. An increased amount of benzoyl peroxide may be producing a higher number of free radicals on the backbone of the poly(oxymethylene) chain leading to the increased amount of graft. Beyond a concentration of 0.125% (w/w) of the initiator, however, a decrease in the amount of graft content of PF fibers is observed. Under these conditions it is likely that the rate of homopolymer formation has increased to a considerable extent leading to the lower grafting yield. Thus, the optimal concentration of benzoyl peroxide seems to be 0.125% (w/w), which gives the maximum amount of AA graft, namely, 15.2%, when the grafting reaction is carried out for 2 hr. This optimal benzoyl peroxide concentration was used in all the grafting experiments by the chemical initiation method.

Table I shows the dependence of the extent of graft (graft yield) on time of irradiation as well as time of benzoyl peroxide initiation. At a given temperature, the penetration of the monomer in the fiber structure is a continuous process, which seems to be strongly time dependent; hence, with increase in contact time, increased grafting yield is obtained.

Figure 2 is a plot of log (100 − % graft) versus time of grafting both by irradiation and by the chemical initiation method. The first-order behavior shows that rate of grafting is proportional to the concentration of monomer used. The rates of grafting with the two methods, however, are unequal. The rate constant for grafting by irradiation is $0.393 \ hr^{-1}$, while for the chemical initiation method it is $0.385 \ hr^{-1}$.

In case of the two other monomers studied, viz., AN and AM, the grafting reactions both by irradiation method and the chemical initiation method also follow first-order kinetics, although the rates vary with the nature of monomer and method of grafting. The values of the rate constants are given in Table II.
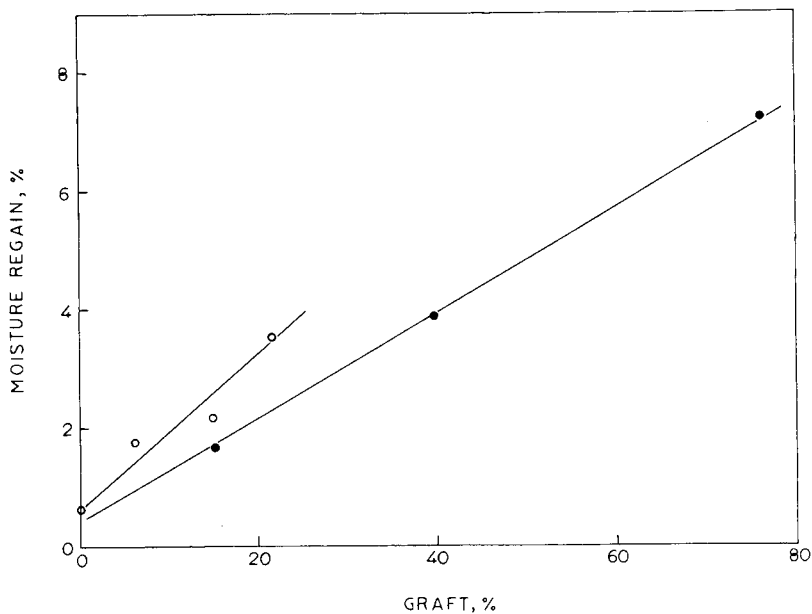
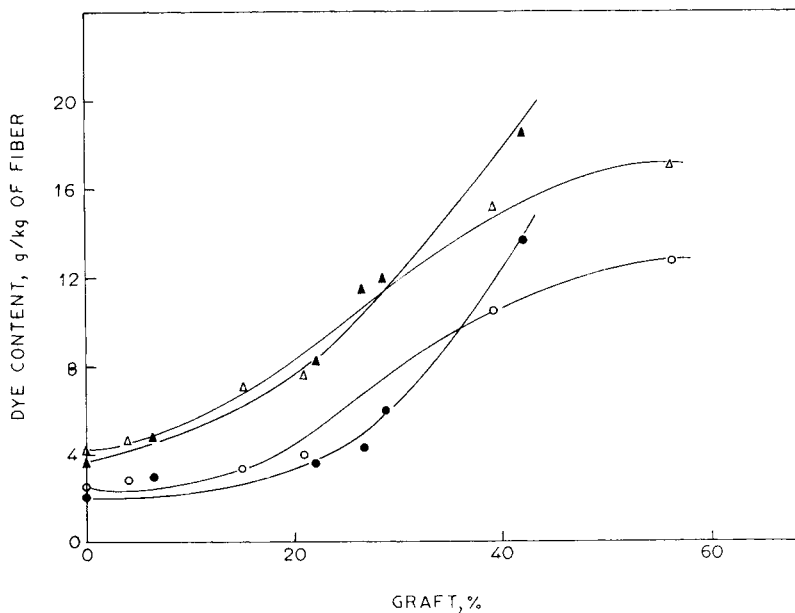Fig. 5. Moisture regain of AM-grafted PF fibers vs % AM graft: (O) benzoyl peroxide method; (●) irradiation method.

Fig. 6. Disperse dye content of AA-grafted PF fibers vs % AA graft: (△) Duranol Violet R (benzoyl peroxide method); (O) Duranol Red 2R (benzoyl peroxide method); (▲) Duranol Violet R (irradiation method); (●) Duranol Red 2R (irradiation method).

Evaluation of Properties of the Grafted Samples

Polyformaldehyde fiber is highly hydrophobic in nature, and moisture regain at normal temperature and humidity is less than 0.4%. Figure 3 shows the plots of moisture regain versus AA graft introduced in the PF fiber by irradiation as well as benzoyl peroxide initiation. The moisture regain increases from about 0.6% for the control (swollen fiber) to about 8% for fibers containing 42% AA graft induced by the irradiation technique. Grafting with AA not only brought about opening up of fiber structure, albeit to a limited extent, but also increased the hydrophilicity of the fibers as a result of the introduction of polar groups, i.e., —COOH groups, in the backbone of the poly(oxymethylene) chains. The increase in the hydrophilicity is, therefore, responsible for the increased amount of moisture absorption by the fiber.

A similar dependence of moisture regain on the amount of AA graft in PF fibers is also observed for the benzoyl peroxide method. The two methods of grafting, however, give two separate linear plots suggesting that the amount of graft introduced by the two techniques is of different nature. Apparently the amount of graft is distributed over a greater number of sites of attachment at the backbone of the PF fibers during irradiation as compared to a comparatively fewer number of sites of attachment produced by benzoyl peroxide initiation. It is likely that the powerful penetrating power of the γ-rays produces graft copolymers of PF fibers that have a larger hydrophilicity than the ones produced by the chemical initiation method.

Introduction of AN and AM grafts also brings about opening up of the PF fiber structure to a certain extent and increases the hydrophilicity of fibers as a result of introduction of polar amino groups in the AM-grafted PF fibers. Also in case of these two reagents, two separate linear plots are obtained for the two grafting techniques (Figs. 4 and 5).
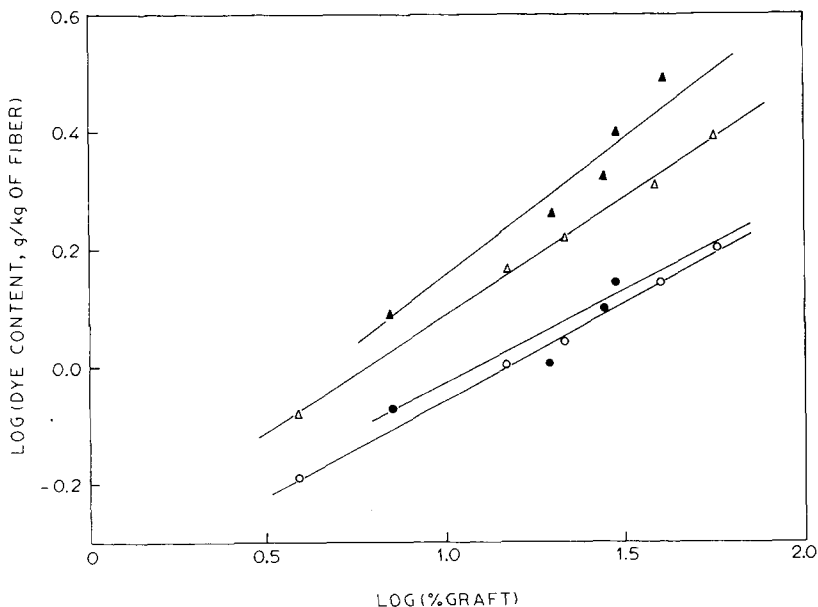

Fig. 7. Log (direct dye content of AA-grafted PF fibers) vs log % AA graft: (△) Congo Red (benzoyl peroxide method); (○) Chlorazol Sky Blue FF (benzoyl peroxide method); (▲) Congo Red (irradiation method); (●) Chlorazol Sky Blue FF (irradiation method).

Among the three graft copolymers of PF fibers studied in the present investigation, AA imparts a higher amount of hydrophilicity, while AN improves the hydrophilic character of PF fibers to the least extent.

Dyeing Characteristics of Grafted PF Fibers

The dyeability of the AA-grafted PF fibers, in general, increased with the amount of graft introduced (Figs. 6–8). Figure 6 gives the plot of disperse dye content versus AA graft in the PF fibers. The dye uptake increases with increase in the amount of graft introduced in the fiber, the increase being significant at the higher amount of graft. In general, the introduction of AA graft in the PF fibers lowers the glass transition temperature (T_g), perhaps to a significant extent at the higher amounts of graft introduced in the fibers; therefore the dyeability of the AA-grafted PF fibers with disperse dyes seems to have been increased to an appreciable extent. Figure 7 gives results on dyeability with direct dyes.

The normal PF fiber cannot be dyed with direct dyes, but on grafting with AA, the dyes are absorbed by the grafted fibers to an appreciable extent, the absorption being proportional to the amount of graft present in the PF fibers. A straight line is obtained when the log–log relationship is plotted between amount of graft and direct dye content of the fibers. This could be attributed to the hydrophilicity imparted to the PF fibers as a result of grafting of acrylic acid. Figure 8 gives the results on dyeability of grafted PF fibers with basic dyes, which form a salt linkage with —COOH group in the grafted PF fibers; therefore the amount of dye taken up by the grafted fiber increases with increase in the amount of graft present in the fiber. The basic dye content and the amount of AA graft give a linear relationship when the two are plotted on the log–log scale.

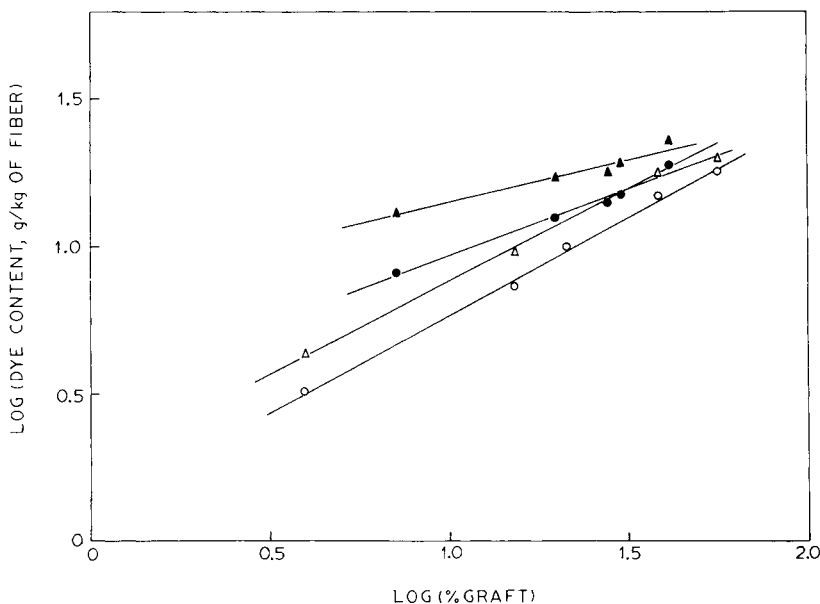For all the dyes studied, the irradiation method and the benzoyl peroxide

Fig. 8. Log (basic dye content of AA-grafted PF fibers) vs log % AA graft: (△) Astrazon Orange G (benzoyl peroxide method); (O) Astrazon Orange R (benzoyl peroxide method); (▲) Astrazon Orange G (irradiation method); (●) Astrazon Orange R (irradiation method).

initiation technique of grafting differ from each other and give separate linear plots, showing that the nature of the graft introduced in the fiber structure by these two techniques are different both in their physical state as well as in the chemical characteristics.

As regards the changes brought about in the dyeability of the AN-grafted and AM-grafted PF fibers, the experimental results revealed that there was only marginal increase in the disperse dye uptake. Similarly, in case of AN-grafted PF fibers containing as much as about 25% graft, dyeability with direct dyes could not be imparted. It seems that no affinity could be introduced to the fibers toward direct dyes as a result of grafting with AN. Figure 9 gives the results of dyeability of AN-grafted PF fibers with basic dyes. A log–log correlation exists between basic dye content and the amount of AN graft in the PF fibers, giving a linear plot. Dyeability with basic dyes can be improved considerably with progressive increase in the AN graft content in the PF fibers. The basic dye content of almost zero for the control was increased to about 4–5 g/kg of the fiber when an AN graft of about 25% was introduced in the PF fibers. It seems that the free CN group at the end of the poly(acrylic acid) side chain of the graft copolymer helps in the adsorption and retention of cationic dye molecules in the grafted substrate.

Figures 10 and 11 give the results on the dyeability of AM-grafted PF fibers with direct and acid dyes. Because of the considerable amount of hydrophilicity imparted to the PF fibers by the polyacrylamide graft, the grafted substrate has increased affinity for the direct dyes; in addition, the greater amount of opened structure makes dyeing with direct dyes possible. The direct dye content increases with increase in the amount of graft, giving a linear plot between direct dye content and the per cent AM graft in PF fibers (Fig. 10). As a result of introduction of amino groups in the PF fiber, dyeing with acid dyes was possible,
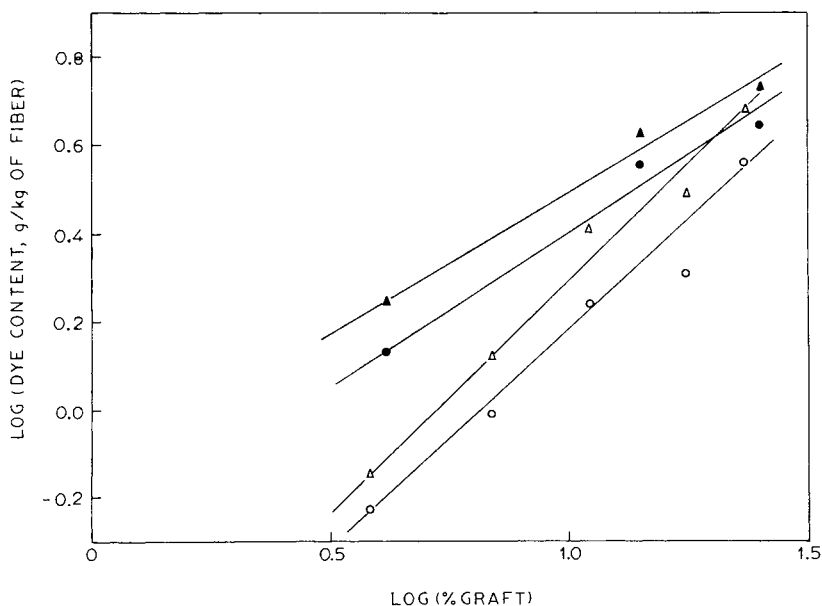

Fig. 9. Log (basic dye content of AN-grafted PF fibers) vs log % AN graft: (△) Astrazon Orange G (benzoyl peroxide method); (○) Astrazon Orange R (benzoyl peroxide method); (▲) Astrazon Orange G (irradiation method); (●) Astrazon Orange R (irradiation method).

and the acid dye content increased with increase in the amount of AM graft. The two parameters give a linear log–log relationship for both methods of grafting used in this investigation (Fig. 11). This is in contrast to the results on moisture
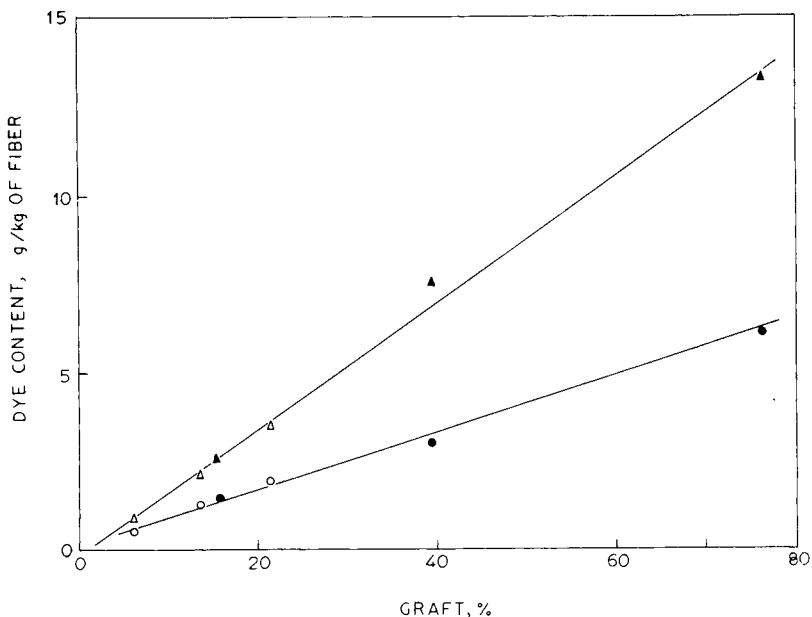

Fig. 10. Direct dye content of AM-grafted PF fibers vs % AM graft: (△) Congo Red (benzoyl peroxide method); (○) Chlorazol Sky Blue FF (benzoyl peroxide method); (▲) Congo Red (irradiation method); (●) Chlorazol Sky Blue FF (irradiation method).
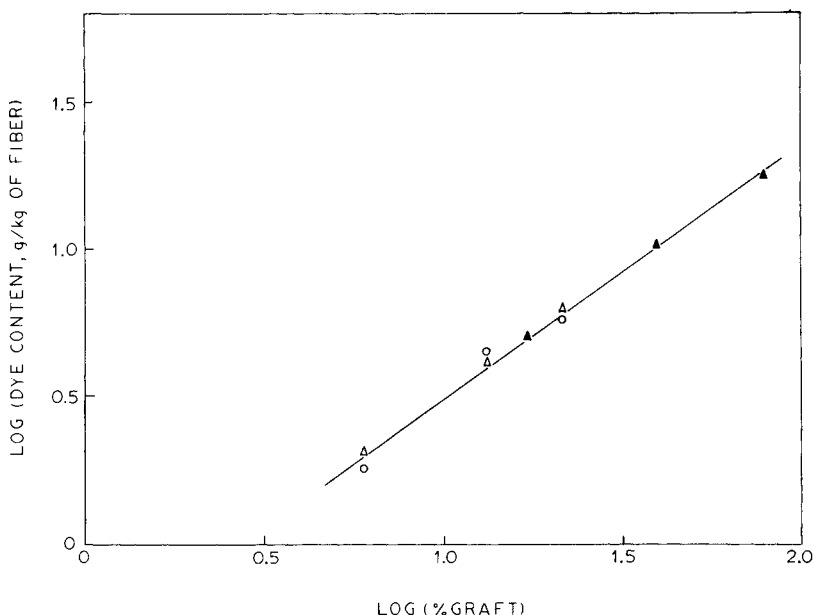

Fig. 11. Log (acid dye content of AM-grafted PF fibers) vs log % AM graft: (△) Polar Red 2B (benzoyl peroxide method); (○) Polar Red 10B (benzoyl peroxide method); (▲) Polar Red 2B (irradiation method).
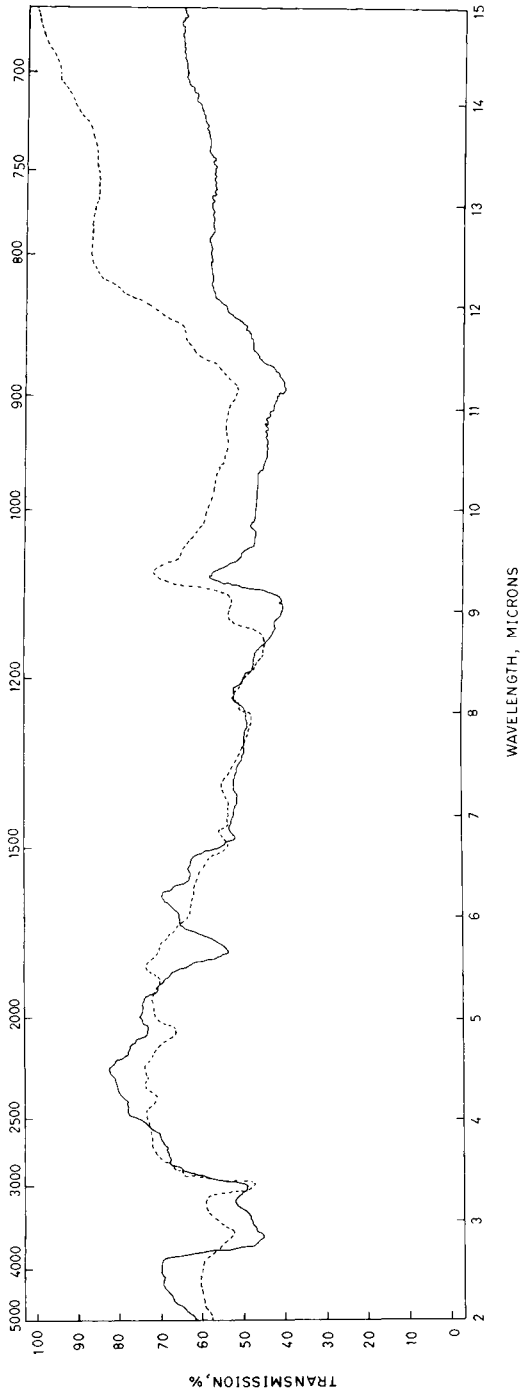
Fig. 12. Infrared spectra of PF fibers (- - -) and AA-grafted PF fibers (—).
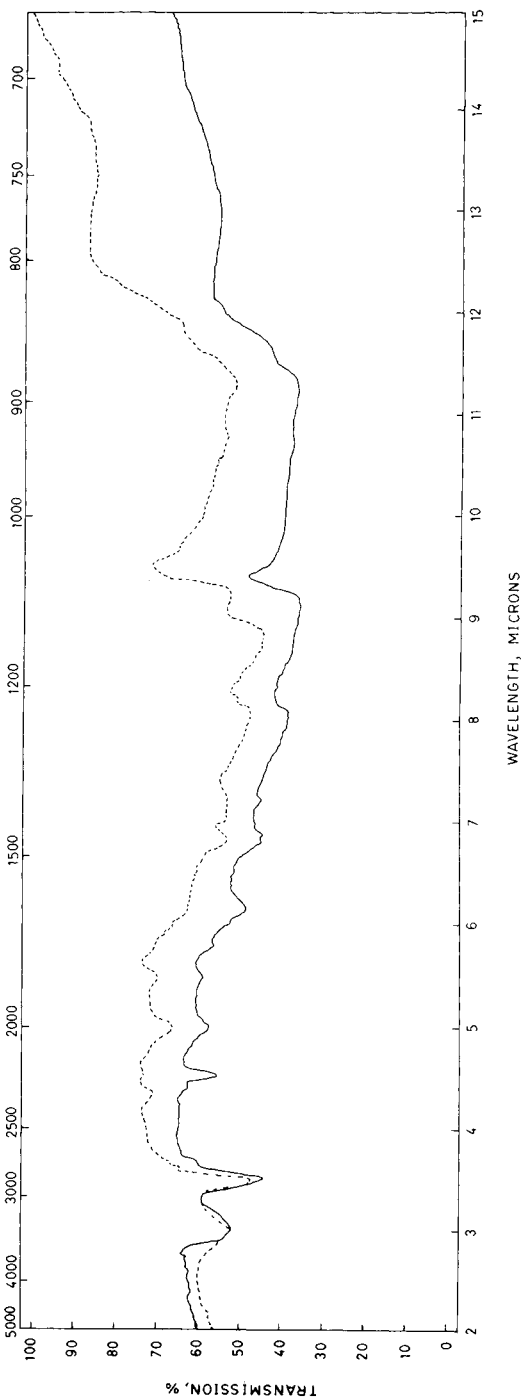
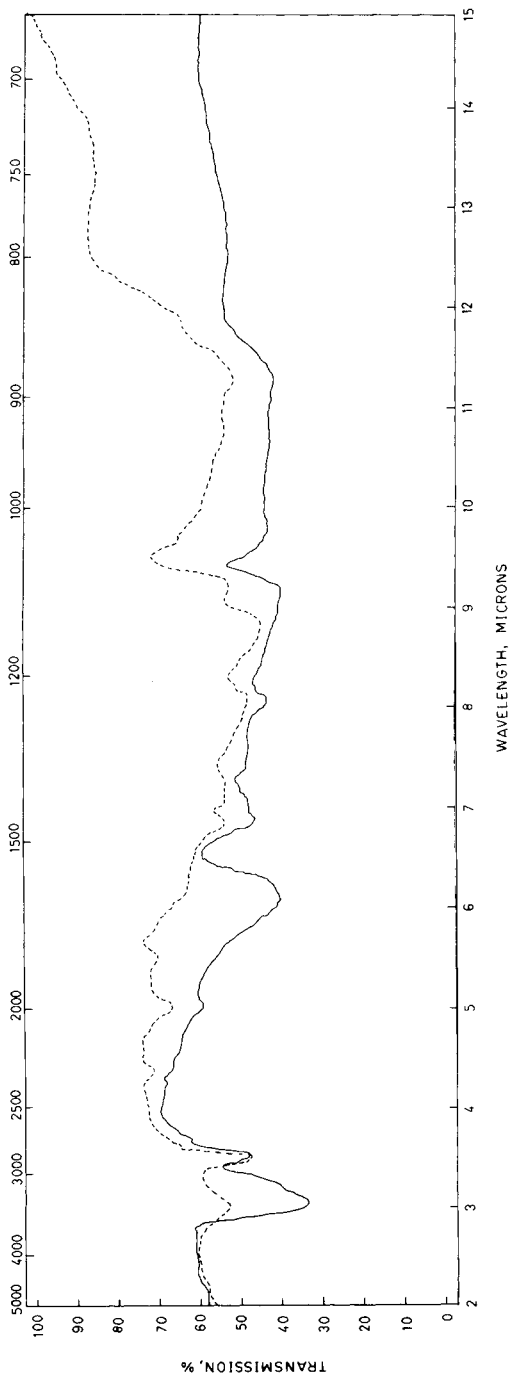Fig. 13. Infrared spectra of PF fibers (- -) and AN-grafted PF fibers (—).

Fig. 14. Infrared spectra of PF fibers (- - -) and AM-grafted PF fibers (—).

regain of the AM-grafted PF fibers (Fig. 5), where two straight lines were obtained for the two individual methods of grafting. It is likely that differences between the nature of graft obtained by the two methods may be too small to be differentiated during the dyeing with acid dyes.

Acrylic acid- and AM-grafted PF fibers could also be dyed with reactive dyes, the AM-grafted substrate giving much deeper shades than the AN- and AA-grafted substrates, presumably because of the higher reactivity of $-NH_2$ groups toward reactive dye molecules. Quantitative estimation of reactive dye on the fiber, however, was not possible because of nonavailability of proper solvents for PF fibers at room temperature.

Infrared Studies of Grafted PF Fibers

The infrared spectrum of PF fibers in the region of 2–15 μ shows only one strong absorption band around 3.2 μ showing the methylene linkage ($-CH_2-$). A weak band is also obtained in the 3-μ region arising out of a small proportion of end-OH groups present in the PF fibers in addition to the traces of absorbed moisture in potassium bromide. The infrared spectrum of PF fibers, therefore, reveals that the fiber is devoid of polar functional groups, hence the rigid hydrophobic character of the fiber, which is reflected in its nonsolubility in organic solvents even under severe conditions of treatment (Fig. 12).

Figures 12–14 give the infrared spectra of AA-grafted, AN-grafted, and AM-grafted PF fibers. An additional peak at 5.67 μ, which is assigned to COOH frequencies, appears in the AA-grafted PF fibers indicating the introduction of COOH groups in the internal structure of the fiber. Two additional peaks, at 4.46 and 6.29 μ, appear in the AN-grafted PF fibers, which are assigned to CN groups. The spectrum thus confirms the introduction of CN groups in the poly(oxymethylene) chain of the PF fiber. The intensity of the peak in the 3-μ region increased for the AM-grafted PF fibers as a result of the introduction of $-NH_2$ groups in the fiber structure.

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