

Radiation-Induced Graft Copolymerization of Mixtures of Styrene and Acrylamide onto Cellulose Acetate. IV. Studies on Some Physical Properties and Structural Characterization by Means of Scanning Electron Microscopy

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Synopsis

Binary mixtures of monomers, e.g., styrene and acrylamide in 1:1 methanol:water solution, were grafted onto cellulose acetate film by taking recourse to preirradiation grafting procedure. The surface modification of the films due to grafting was examined by means of scanning electron microscopy. The mechanical properties, e.g., tensile strength elongation at break, and elasticity as well as water vapor permeability of the grafted films, were investigated. In the case of ungrafted films or when acrylamide was grafted to a low extent, the film surfaces were smooth and hence were not modified to any significant extent. But when acrylamide was grafted appreciably, or when styrene was grafted singly or in binary mixture with acrylamide, the surfaces were found to be covered with fibrils. The pattern of the surface modification also changes with the increase of the extent of grafting. The observed properties of the grafted films were explained on the basis of the electron microscopic results.

INTRODUCTION

The improvement in properties of the grafted copolymers depends on the nature, amount, and chain length of the grafted branch as well as on the type of distribution of the monomers in the base polymers. The properties which might be incorporated into the base polymer are determined by the evaluation of various parameters,¹⁻⁶ e.g., elongation, elasticity, permeability, etc. To set up a correlation between the physical properties and structural changes, a knowledge of the model of distribution of the monomers in the trunk polymer is essential. Moreover, the structural changes are also dependent on the nature of the base polymer as well as the monomer,⁷⁻⁹ the method of graft copolymerization,¹⁰⁻¹⁴ medium in which reaction occurs,^{7,15} and lastly the extent of graft copolymerization.^{7-9,16} As we have chosen two monomers, e.g., styrene and acrylamide of different polarities in a 1:1 methanol:water solvent system, it will be interesting to examine how they are accommodated in cellulose acetate which is taken as the base polymer in the present investigation. Electron microscopy is a powerful tool for the measurement of the distribution of the monomers in the trunk polymer matrix. We have examined such changes by taking recourse to scanning electron microscopy and also measured various physical properties, e.g., tensile strength, elongation, elasticity, water vapor permeability of the grafted co-

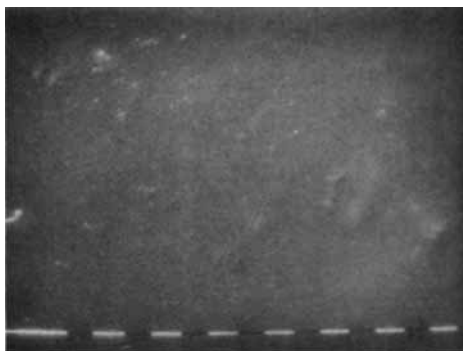


Fig. 1. Scanning electron micrograph of unmodified cellulose acetate film. Magnification 800 \times ; scale bar = 10 μm .

polymer, and correlated the observed physical properties with structural changes induced in the base polymer due to grafting.

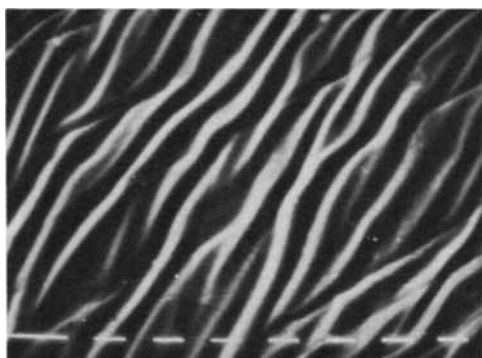
EXPERIMENTAL

Materials: The cellulose acetate films of thickness ~ 0.005 cm were prepared¹⁷ from purified cellulose acetate powder (acetic acid content, 53.5–54%). The monomers, styrene and acrylamide, were purified in the usual way.¹⁷ Other reagents used were all of reagent grade.

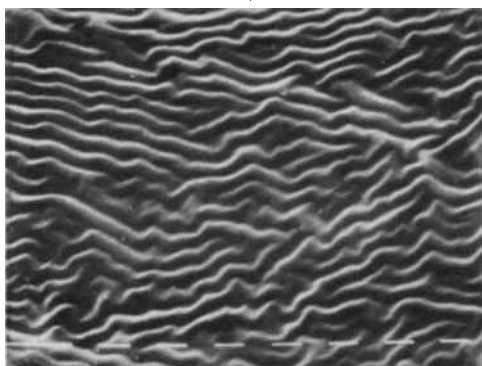
Methods: Cellulose acetate films were irradiated with cobalt-60 gamma rays at room temperature in presence of air to a total dose of 4.2 Mrad. The irradiated films were treated with monomers solutions in a 1:1 methanol:water mixture. The detailed procedure for the preparation of graft copolymer has been reported earlier.¹⁷

For scanning electron microscopic examination the unirradiated, irradiated, and grafted films just after washing were immersed successively in graded ethanol, i.e., 70%, 80%, 90%, 95%, for 1 h and then kept in absolute alcohol overnight to fix the film surface. The films were later air dried. The dried samples were mounted with double-faced adhesive tape on specimen holder and then coated under vacuum with a thin layer of gold to a depth of 100 \AA . The films so treated were later scanned by oscilloscope viewing and TV monitoring before being photographically recorded in a Philips SEM-500 Unit.

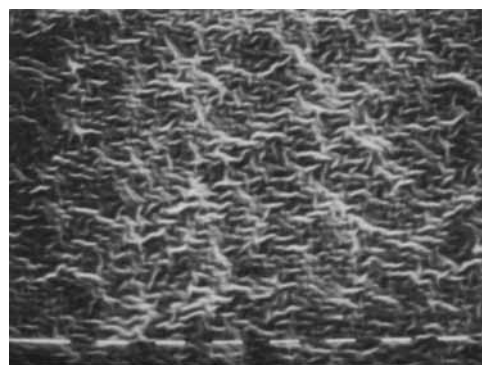
The mechanical properties, e.g., tensile strength, elongation at break, and extension cycling of the original film, irradiated film, and the film with grafted copolymers, were measured from the stress-strain curves obtained on a Instron tensile strength testing machine (Model 142). An average of five to seven samples was always examined to ascertain the data for a particular property. For each test the samples were subjected to a constant rate of elongation and the gauge length, crosshead speed, and chart speed were maintained at 4 cm, 0.5 cm/min, and 20 cm/min, respectively. Full scale load was always used as 5 kg for simple tensile strength and elongation at break measurements. The immediate and delayed recovery percentages were calculated for the first and the 10th cycles of the extension cycling measurement using 2 kg as full load and fixed extension point varying from 0% to 1%.



(a)



(b)



(c)

Fig. 2. Scanning electron micrographs of styrene grafted cellulose acetate film. Magnification 800 \times ; scale bar = 10 μ m. Styrene grafted (%): (a) 4.8; (b) 19.8; (c) 41.7.

The water vapor permeability was measured by using the conventional cup method. The test film was fastened over the mouth of the cup which contained silica gel, and the whole system was weighed and placed in a desiccated atmosphere. The desiccator was maintained at constant humidity of 18%, 52%, 90%, and 95% at room temperature. In this way a humidity gradient was maintained, and the cup was reweighed at different intervals. The specific permeability, e.g., weight of water vapor transmitted per unit time for unit area and unit thickness, was calculated from the observed weight increase of silica gel at different time intervals.

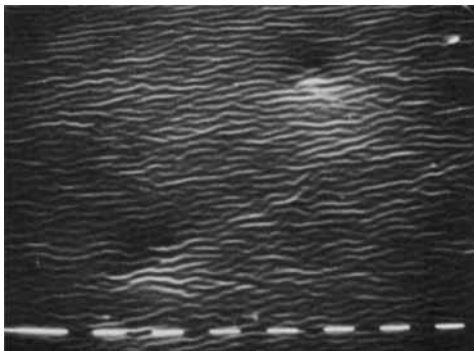


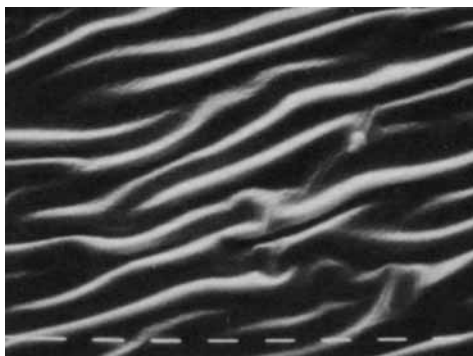
Fig. 3. Scanning electron micrograph of acrylamide grafted (26.2%) cellulose acetate film. Magnification 800 \times ; scale bar = 10 μ m.

RESULTS AND DISCUSSION

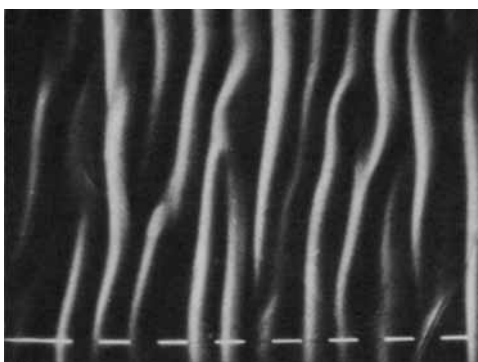
The scanning electron microscope (SEM) monitors the superficial changes of the polymer matrix. When the control cellulose acetate film was viewed through SEM, the surface was seen to be smooth (Fig. 1). This smoothness is, however, altered when styrene is grafted [Figs. 2(a), 2(b), 2(c)]. Even when grafting is pretty low [Fig. 2(a)], the surface of the film appears to be covered with parallel fibrils. These fibrils are, of course, not spread all over the film surface, but are only localized on the various parts of the surface. However, as the percent of graft increases, the portion of the surface that is covered with fibrils increases. Moreover, the fibrils appear to be curled ones [Figs. 2(b), 2(c)]. Their diameter also decreases, and they are thickly populated.

In contrast, if the grafting of acrylamide is not appreciable, the surface of the film appears to remain unaltered as shown in Figure 1. When grafting of acrylamide increases, the surface appears to get covered with parallel localized fibrils (Fig. 3) and resembles the surface when the grafting of styrene is not appreciable. When grafting is carried out from a binary system of monomers, e.g., styrene and acrylamide [Figs. 4(a), 4(b), 4(c), 4(d), and 4(e)], the structure of the surface in general resembles that obtained in case of grafting of styrene alone.

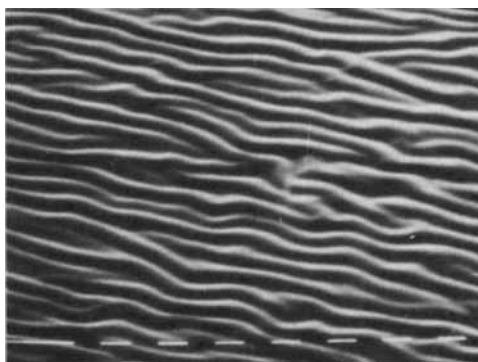
From the above observations one can presume that styrene is mainly responsible for the observed surface modification, whether it is present individually or in the binary monomer mixture with acrylamide. But acrylamide affects the surface only when its grafting is considerably large. This is indicative of the fact that styrene is grafted mostly on the surface whereas acrylamide is probably grafted throughout the film uniformly. This fact can be explained on the basis that cellulose acetate and acrylamide are both polar molecules whereas styrene is nonpolar. Hence in the grafting medium of 1:1 methanol:water, acrylamide rather than styrene will have easy access to the interior of the trunk polymer due to the formation of hydrogen bonding. In fact, swelling of acrylamide¹⁸ in such a solvent is found to be much larger than that of styrene. Thus acrylamide being highly soluble in the solvent accompanies the solvent in penetrating into the interior of the swollen trunk polymer. But styrene lags behind acrylamide in this respect. Hence acrylamide may be thought of being uniformly distributed in the interior of the base polymer, whereas styrene will be left principally on



(a)

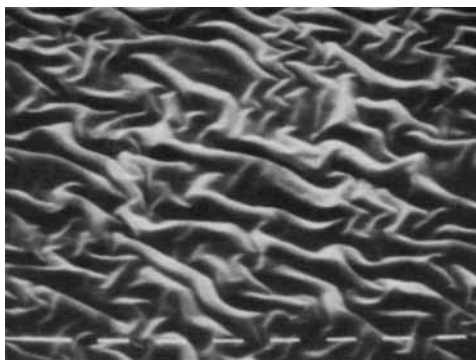


(b)

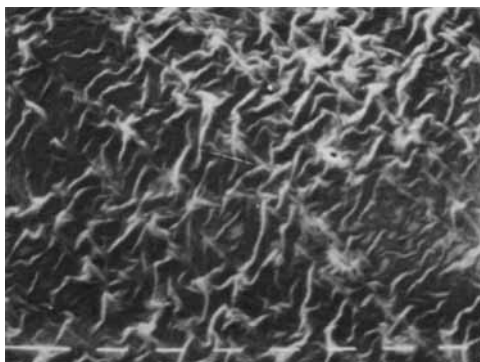


(c)

Fig. 4. Scanning electron micrographs of cellulose acetate films grafted with a mixture of acrylamide (A) and styrene (S). Magnification 800 \times ; scale bar = 10 μ m. Initial A:S, total graft (%): (a) 4:1, 2.4; (b) 1:4, 4.8; (c) 1:8, 10.3; (d) 4:1, 35.8; (e) 1:1, 58.4.



(d)



(e)

Fig. 4 (Continued from the previous page.)

the surface. Moreover, since the molecular reactivity¹⁷ of styrene-to-cellulose-type free radical is more than the corresponding affinity of acrylamide, styrene that lags behind in its penetration to the interior of the trunk polymer gets itself readily entrapped by the cellulose acetate matrix.

Mechanical properties of the original cellulose acetate film as well as those of the irradiated base polymer and the grafted film were examined by an Instron tester. Due to irradiation, both tensile strength and elongation of the cellulose acetate film decrease (Figs. 5 and 6). With the increase of the extent of styrene grafting, the tensile strength recovers to its original level initially and then decreases sharply (Fig. 5). In the case of acrylamide grafting, the tensile strength increases slowly with the increase of grafting yield. But in the case of mixed graft the tensile strength reduces considerably with the increase of extent of grafting (Table I). In the latter case tensile strength neither follows the sequence of styrene content nor the acrylamide content in the mixed graft.

Similar to tensile strength, elongation of the styrene grafted films increases initially and then decreases considerably (Fig. 6) with the increase of grafting yield. In the case of acrylamide grafting, however, elongation decreases initially very slowly with the increase of grafting yield and then remains almost constant. When both acrylamide and styrene are grafted (Table I), elongation is not affected considerably; rather it resembles that which follows from the acrylamide content in the binary mixture.

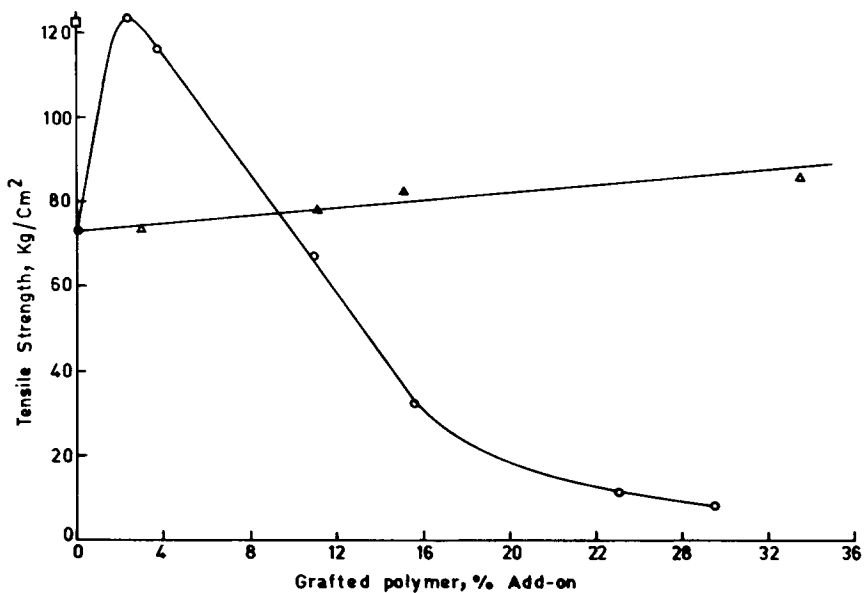


Fig. 5. Effect of the extent of graft copolymerization of acrylamide and styrene on the tensile strength of cellulose acetate films: (□) unirradiated; (○) styrene-grafted; (Δ) acrylamide-grafted.

The extension cycling measurement was carried out to determine elasticity of the films. The tensile strength recovery of the first and the 10th cycle is listed in Table I. From the table it is evident that the elasticity of the film decreases due to irradiation of the film. With the increase of extent of grafting of either

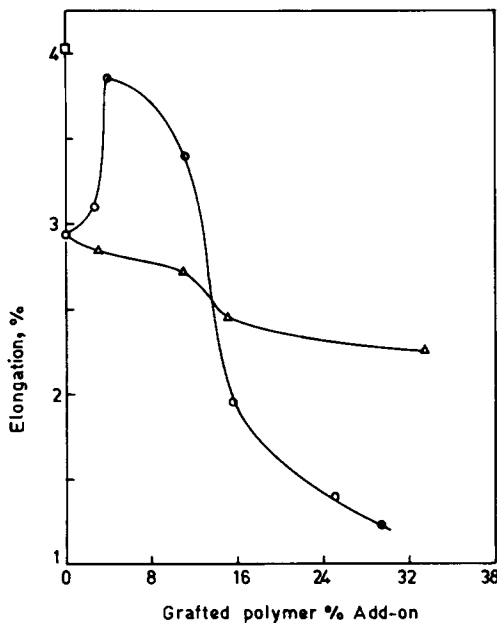


Fig. 6. Effect of the extent of grafting of acrylamide and styrene on the extensibility of cellulose acetate films: (□) unirradiated; (○) styrene-grafted; (Δ) acrylamide-grafted.

TABLE I
Mechanical Properties of Grafted Cellulose Acetate Films

Nature of the film	Grafting (%)	Tensile strength (kg cm ⁻²)	Elongation at break (%)	Tensile strength recovery (%)			
				Immediate		Delayed	
				1st cycle	10th cycle	1st cycle	10th cycle
Unirradiated		122.16	4.09	67.9	66.5	32.1	33.5
Irradiated		73.01	2.94	65.0	57.5	35.0	42.5
Acrylamide grafted	3.06	73.00	2.85	60.6	51.4	39.4	48.6
	15.15	82.05	2.46	53.2	49.4	46.8	50.6
Styrene grafted	3.70	116.23	3.86	50.0	45.0	50.0	55.0
	11.00	67.17	3.40	49.1	47.4	50.9	52.6
Acrylamide: styrene ratio in the graft copolymer							
1:2.0	2.80	91.4	2.57	48.7	44.8	51.3	55.2
1:3.9	19.04	30.25	2.88	55.0	52.5	45.0	47.5
1:3.8	20.88	25.55	2.81				
1:5.9	31.48	4.09	2.03				

styrene or acrylamide, elasticity decreases very slowly. In case of the acrylamide-grafted films, the elasticity is, however, relatively greater than that of styrene-grafted films. In the case of mixed graft, the elasticity is higher than what could be expected from the styrene content in the mixed graft; rather it is nearer to that which may arise from the acrylamide content.

Due to irradiation, some microvoids might be formed in the trunk polymer on account of the operation of the abstraction mechanism and the scission of the main chain to some extent. Therefore, the loosening of the cellulose structure might be responsible for leading to the decrease of tensile strength, elongation, and elasticity on irradiation of the cellulose acetate film. As we have discussed earlier, from the electron microscopic results that styrene is grafted mostly at the surface of the film, the structural irregularity at the surface may be thought of as being filled up partially even when styrene is grafted to a low extent; hence both the tensile strength and elongation increase of initially with the increase of styrene grafting. Then with further increase of the extent of styrene grafting, the surface is expected to be covered more with styrene [Figs. 2(b) and 2(c)]. However, since cellulose is polar but the styrene is not, the chemical bonds inside the cellulose structure are diluted, and this may be the reason why both the tensile strength and elongation decrease with the further increase of styrene grafting. Now, it has been discussed earlier that acrylamide is grafted uniformly, and so, as its extent of grafting increases, the microvoids are expected to be filled up. This uniformity in the structural makeup may determine the reason why tensile strength increases with the increase of acrylamide grafting. It is evident from Figure 6 that elongation decreases very slowly with the increase of acrylamide grafting. This indicates that, in spite of the polar character of both acrylamide and cellulose acetate, acrylamide does not chemically mix up uniformly in the cellulose structure. Moreover, it is worthful to note that both polyacrylamide and polystyrene are known to be rigid polymers; that is why elongation as well as elasticity are found to decrease with the increase of the extent of grafting of either monomer. In the case of mixed graft the tensile

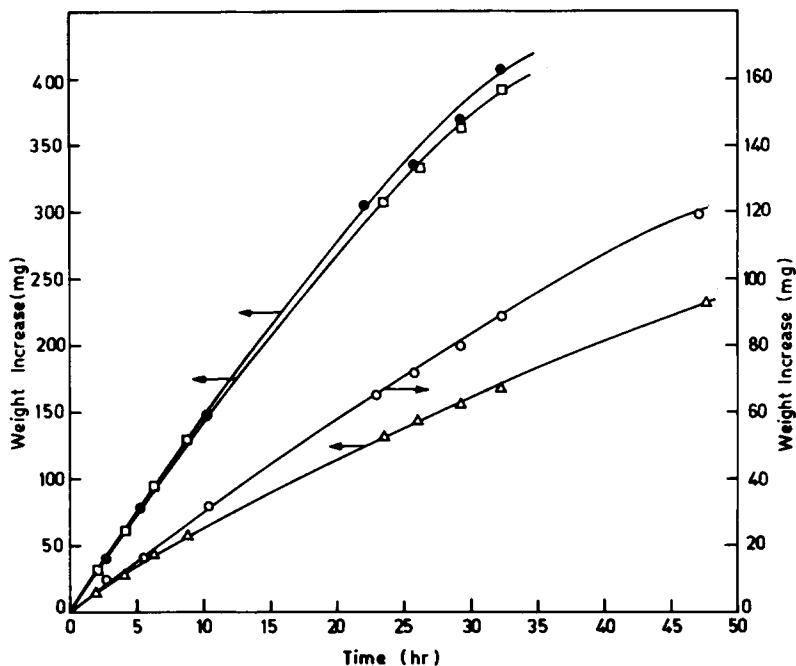


Fig. 7. A typical plot of the variation of the water vapor transmitted through the modified cellulose acetate films (styrene grafted 23.4%) with time at different humidities: (O) 18%; (Δ) 52%; (\square) 90%; (\bullet) 95%.

strength decreases with the increase of extent of grafting yield. But as observed in case of the grafting of styrene alone, the elongation does not decrease with the increase of styrene content in the mixed graft. This is indicative of the fact that in the mixed graft the component monomers do not exist as an individual identity, but rather form a copolymer of the two, thus leading to a new property.

TABLE II
Water Vapor Permeability of Grafted Cellulose Acetate Films at Various Relative Humidities

Nature of the film	Grafting (%)	Weight increase (mg) per unit time (s), per unit area (cm^2), per unit thickness (mm) at various relative humidities ($\times 10^3$)			
		18%	52%	90%	95%
Unirradiated		3.46	6.75	11.87	12.72
Irradiated		2.40	4.82	10.99	12.37
Acrylamide grafted	1.77	1.37	4.61	10.25	11.15
	3.75	3.49	6.56	10.81	15.40
	5.85	3.67	7.40	12.30	16.90
	14.76		9.21		
Styrene grafted	4.64	1.43	5.26	8.95	10.85
	17.08	1.28	3.26	6.89	8.19
	23.43	1.25	2.82	6.51	7.05
Acrylamide:					
styrene ratio in the					
graft copolymer					
1:2.2	1.70	1.95	3.73	8.10	9.11
1:4.8	7.41	1.20	3.50	6.48	7.48
1:4.3	16.09	1.57	4.34	8.24	8.68

The water vapor permeability at different relative humidities was measured and shown in Figure 7 and Table II. It is evident from the figure and the table that the permeability increases with the increase of humidity. In the case of acrylamide grafting, the permeability increases with the increase of grafting yield in all humidities. This may be due to the fact that acrylamide is polar and so can easily absorb water vapor, which is then transmitted to the silica gel kept to maintain humidity gradient. On styrene grafting, however, the permeability decreases because styrene is hydrophobic in nature and, moreover, styrene is grafted preferably on the surface. Permeability that is observed might result from water penetration through the surface that is not grafted with styrene. That the trunk polymer surface is not uniformly covered with styrene graft is already evident from electron microscopic study. In the case of mixed graft, the water permeability pattern, as is evident from Table II, resembles neither the behavior shown by acrylamide nor that shown by styrene taken separately. Rather the pattern pertains to that when both styrene and acrylamide have their effective roles to play.

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