Radiation-Initiated Graft Copolymerization of Binary Monomer Mixtures Containing Acrylonitrile with Cotton Cellulose*

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Synopsis

By the use of the cobalt 60 postirradiation grafting technique, purified cotton cellulose fibers were graft-copolymerized with binary mixtures of acrylonitrile and other monomers, including styrene, 1,3-butylene dimethacrylate, vinylpyrrolidone, vinylidene chloride, and methyl, butyl, lauryl, glycidyl, and allyl methacrylates. The irradiated cotton fibers were immersed in solutions of the monomers at 25°C to initiate graft copolymerization. Solvents were water, methanol, dimethyl sulfoxide, and methyl ethyl ketone, alone or in several combinations. The extent of graft copolymerization and the composition of the grafted copolymer depended on the composition of the binary mixtures of monomers and on the solvent or mixtures of solvents used. For example, addition of styrene, 1,3-butylene dimethacrylate, or vinylpyrrolidone to acrylonitrile increased the extent of graft copolymerization to a maximum value; addition of vinylidene chloride or allyl methacrylate to acrylonitrile did not greatly affect the extent of graft copolymerization; and addition of methyl or glycidyl methacrylate to acrylonitrile increased the extent of graft copolymerization without passing through a maximum value. The proportion of acrylonitrile in the grafted copolymer was generally less than that in the binary mixtures. As the reaction time was increased, the extent of graft copolymerization increased to a maximum value; however, the composition of the grafted copolymer did not change significantly. Generally, the addition of water to the solutions increased the extent of graft copolymerization. The mechanisms of these graft copolymerization reactions are discussed.

INTRODUCTION

Mayo and Lewis[1] in considering copolymerization developed the concept of monomer reactivity ratio, which was defined as the ratio of the rate constants for the reaction of a given radical type with corresponding monomer and with the other monomer of a given pair. For example, they showed how monomer reactivity ratios of free radicals may be used to compare reactivities in copolymerizations of binary systems of acrylonitrile and methyl methacrylate, styrene, or vinylidene chloride with benzoyl peroxide as catalyst.[2] Mark and co-workers[3] subsequently compiled an extensive list of copolymerization reactivity ratios for vinyl monomers.

Applications of these concepts to free radical-initiated copolymerization reactions of vinyl monomers and of binary mixtures of vinyl monomers with preirradiated fibrous cotton cellulose are considered here.

Modification of the macromolecular properties of fibrous cotton cellulose by free-radical-initiated graft copolymerization with vinyl monomers has been reported.[4,5] The rate and extent of the graft copolymerization reaction of different vinyl monomers from solution with fibrous cotton cellulose are dependent on the method of free-radical initiation, the monomer reactivity for the cellulosic radical, the effects of solvent on the morphology of the cellulosic fibers, and other experimental variables.[4] Copolymerization of vinyl monomers with preirradiated cellulose, which, for example, in the case of cellulose lattice type I contains long-lived or trapped free radicals on carbon C_5 of the anhydroglucose ring, has been reported.[6,7] The concentration of long-lived free radicals in preirradiated cellulose can be determined by controlling the radiation dosage.[8] It is often desirable to increase the rate and extent of grafting of a given vinyl monomer with cellulose and to copolymerize more than one type of monomer with cellulose simultaneously to impart new properties to the fibrous copolymers.

A limited number of reports on the effects of mixing unsaturated monomers in binary and ternary systems on the extent of free-radical-initiated graft copolymerization of the monomers with cellulose have been published.[9-15] Sakurada and co-workers[14,15] used cobalt 60 γ-radiation and high-energy electron radiation to initiate copolymerization reactions of mixtures of butadiene and styrene and of butadiene, styrene, and acrylonitrile with cotton cellulose. They suggested that when the ternary system was used, popcorn polymerization occurred. Rapson and Kvasnicka[12] reported the grafting of vinyl monomers from binary and ternary systems onto regenerated cellulose, initiated by the cobalt 60 simultaneous grafting technique. The effects of solvents used on the extent of graft copolymerization were usually interpreted, in these reports, as the Trommsdorff-type phenomenon[16] and/or as the swelling of the cellulosic macrostructure to increase the accessibility of the free-radical sites to the monomers. Generally, the effects of the composition of the binary and ternary systems of monomers on the composition of the grafted copolymer were not reported.

In this report, the graft copolymerization reactions of binary mixtures of selected monomers and acrylonitrile with pre-irradiated cotton cellulose in different solvent systems are reported. The extent of graft copolymerization and composition of the grafted copolymers are related to the binary mixtures of monomers and solvent systems used.

EXPERIMENTAL

Materials

Cotton cellulose fibers of the Deltapine variety were purified in the usual manner.[17] The monomers (acrylonitrile, styrene, 1,3-butylene dimeth-

acrylate, vinylpyrrolidone, vinylidene chloride, and methyl, butyl, lauryl, glycidyl, and allyl methacrylates) were obtained from commercial sources. The monomers were passed through columns of activated alumina to remove inhibitors of polymerization. Then the monomers were stored in glass bottles at about 5°C until used. The solvents (methanol, dimethyl sulfoxide, and methyl ethyl ketone) were reagent grade and were dried prior to use. Deoxygenated distilled water was used to prepare the solutions.

Methods

The SRRL ^{60}Co radiation source[18] was used. The dose rate, determined by ferrous–ferric dosimetry,[19] was about 5.4×10^{19} eV/g hr. Samples of cotton cellulose fibers, which had been dried overnight over P_2O_5 under vacuum at 50°C, were irradiated to a dosage of 5.2×10^{19} eV/g at ambient temperature in a nitrogen atmosphere.

About 24 hr after irradiation samples of cotton fibers (1.5 g) were immersed in monomer solutions (50 ml) at 25°C. The solutions had been evacuated several times and flushed with nitrogen prior to addition of the fibers. The graft copolymerization reaction was allowed to proceed at 25°C for the desired time. Then the grafted fibers were washed several times with the solvent used in the monomer solution to remove unreacted monomer. Nongrafted copolymer was removed from the grafted fibers by successive extractions of the fibers by solvents normally used for the polymer which had been formed. The extracted fibers were finally washed with distilled water and dried overnight under vacuum at 50°C. The extent of graft copolymerization of the monomers with cotton cellulose was determined as the increase in weight (% add-on) of the grafted fibers over that of control fibers similarly treated, except for the omission of the monomers. In the binary mixtures of monomers, with the exception of vinylpyrrolidone, only acrylonitrile contained nitrogen. The percentage of acrylonitrile residues in the grafted copolymer was calculated from the nitrogen content of the copolymer, determined by the macro-Kjeldahl method.[20]

RESULTS

Extent of Graft Copolymerization

The effects of the acrylonitrile/monomer mole ratio in binary mixtures in different solvents on the extent of graft copolymerization with irradiated cellulose are shown in Figures 1 and 2. The grafted polymer add-ons for all binary mixtures of acrylonitrile and styrene, vinylpyrrolidone, or 1,3-butylene dimethacrylate were greater than the add-ons from solutions of either of the monomers alone. The copolymer add-ons from solutions of acrylonitrile and vinylidene chloride were relatively constant and about the same as that from solutions of either of the monomers alone. The add-ons

from binary mixtures of acrylonitrile and methyl or glycidyl methacrylates increased sharply as the proportion of acrylonitrile decreased.

The effects of the water content of the binary systems on the extent of graft copolymerization with irradiated cellulose are shown in Figure 3.
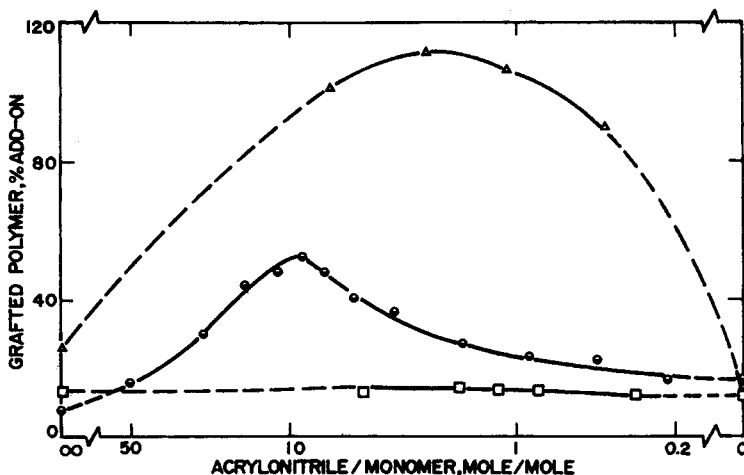

Fig. 1. Effects of acrylonitrile/monomer mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomers + 70 vol-% solvent; (□) vinylidene chloride in 20% water + 80% methanol, 3 hr; (◒) styrene in 21% water + 79% methanol, 0.5 hr; (△) vinylpyrrolidone in 20% water + 80% dimethyl sulfoxide, 3 hr.
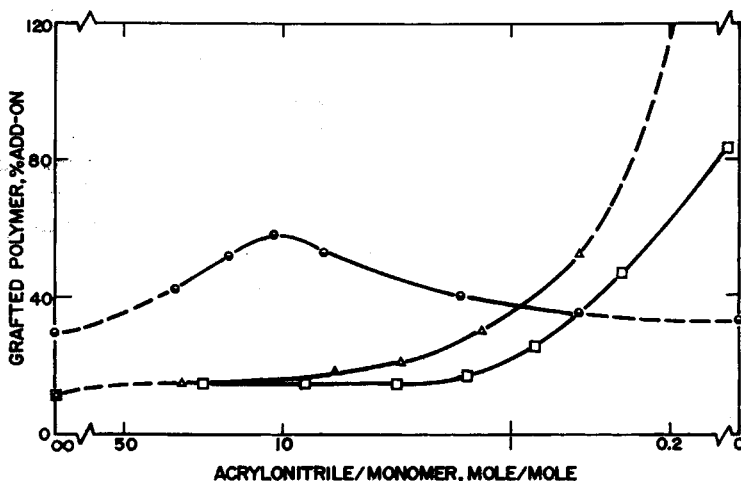

Fig. 2. Effects of acrylonitrile/monomer mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; (□) methyl methacrylate in 43% water + 57% methanol, 0.5 hr; (◒) 1,3-butylene dimethacrylate in 11% water + 89% dimethyl sulfoxide, 3 hr; (△) glycidyl methacrylate in 43% water + 57% methanol, 0.5 hr.

In the system containing acrylonitrile and glycidyl methacrylate, the co-
polymer add-ons increased with increased water content.   In the system
containing acrylonitrile and styrene, the add-on increased to a maximum
value and then decreased; in this system, when the water content was
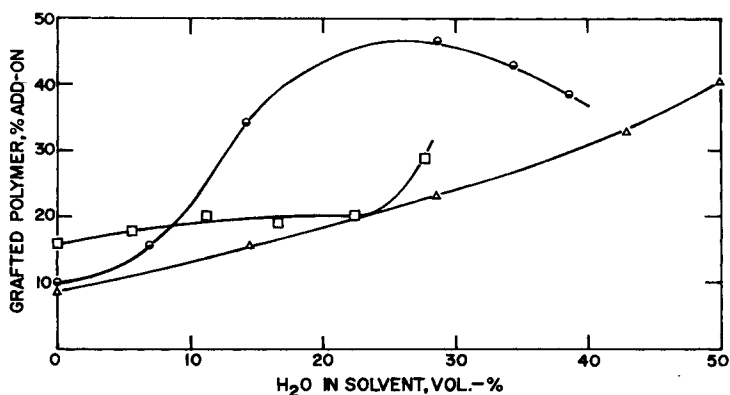greater than about 40 vol-%, the system separated into two phases.   In

Fig. 3. Effects of increasing water content of solvent on extent of graft copolymerization
of acrylonitrile/monomer mixtures with irradiated cellulose at 25°C.   Dosage, 5.2×10^{19}
eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent;
(□) 1,3-butylene dimethacrylate:acrylonitrile, 1:11 mole ratio in water + dimethyl
sulfoxide, 1 hr; (◒) styrene:acrylonitrile, 1:19 mole ratio in water + methanol, 0.5 hr;
(△) glycidyl methacrylate:acrylonitrile, 1:1.3 mole ratio in water + methanol, 0.5 hr.
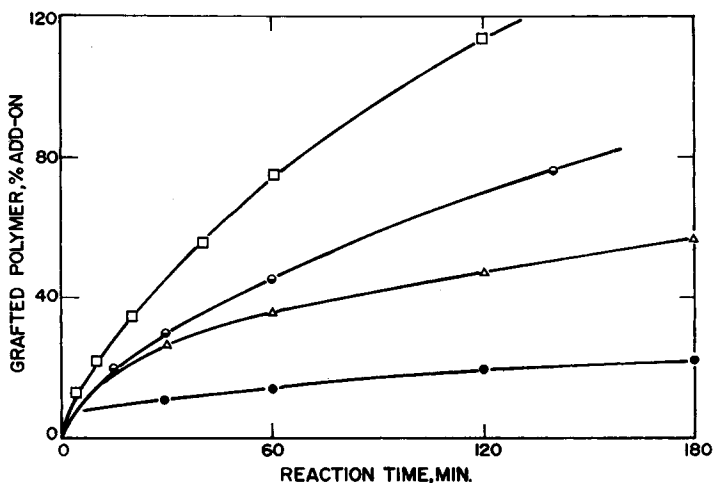

Fig. 4. Effects of reaction time on extent of graft copolymerization of acrylonitrile mo-
nomer mixtures with irradiated cellulose at 25°C.   Dosage, 5.2×10^{19} eV/g; cellulose:
solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; (□) styrene:acryloni-
trile, 1:9 mole ratio in 21% water + 79% methanol; (◒) glycidyl methacrylate:acrylo-
nitrile, 1:1.3 mole ratio in 43% water + 57% methanol; (△) 1,3-butylene dimethacryl-
ate:acrylonitrile, 1:11 mole ratio in 11% water + 89% dimethyl sulfoxide; (●) butyl
methacrylate:acrylonitrile, 1:2.4 mole ratio in 29% water + 71% methanol.

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the system containing acrylonitrile and 1,3-butylene dimethacrylate, the add-on did not change significantly, until the water content was almost high enough (about 30 vol-%) to result in the separation of the system into two phases.
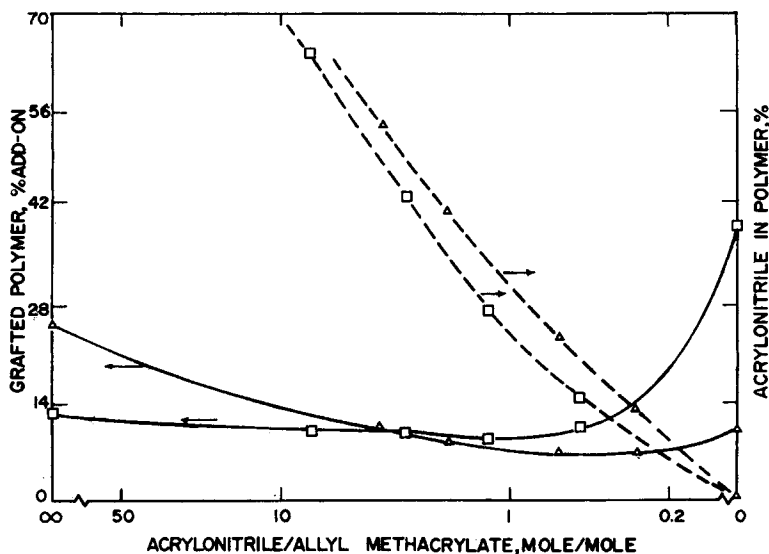

Fig. 5. Effects of acrylonitrile/allyl methacrylate mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; (□) monomers in 24% water + 76% methanol, 3 hr; (△) monomers in 13% water + 87% dimethyl sulfoxide, 0.75 hr.
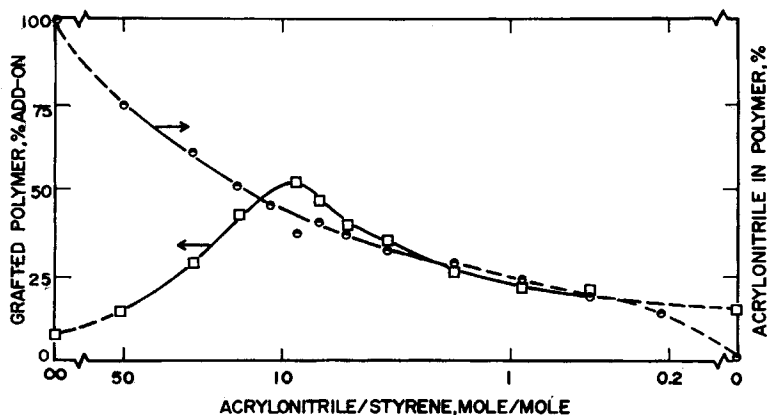

Fig. 6. Effects of acrylonitrile/styrene mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} cV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent, in 21% water + 79% methanol, 0.5 hr.

The effect of reaction time on the extent of graft copolymerization of acrylonitrile–monomer mixtures with irradiated cellulose are shown in Figure 4. The rate of copolymerization and maximum copolymer add-on were dependent on the monomer added to solutions containing acrylonitrile. In all cases the add-on increased with increased reaction time.
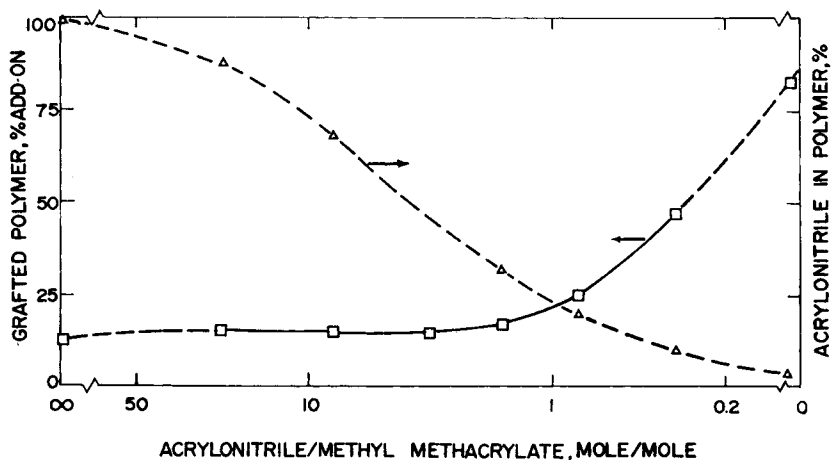

Fig. 7. Effects of acrylonitrile/methyl methacrylate mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent, in 43% water + 57% methanol, 0.5 hr.
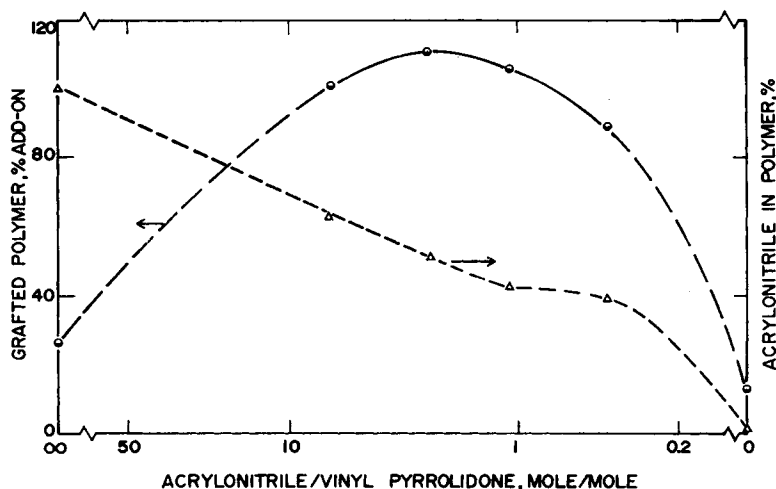

Fig. 8. Effects of acrylonitrile/vinylpyrrolidone mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; monomers in 20% water + 80% dimethyl sulfoxide, 3 hr.

Composition of Grafted Copolymer

The effects of acrylonitrile/monomer mole ratio in binary mixtures in different solvents on the composition of the grafted copolymer, as related to the polymer add-on, are shown in Figures 5, 6, 7, 8, 9, and 10. The addition of allyl methacrylate to acrylonitrile in water–methanol did not change the polymer add-on. In water–dimethyl sulfoxide, the addition of allyl methacrylate to acrylonitrile decreased the polymer add-on (Fig. 5).

Fig. 9. Effects of acrylonitrile/1,3-butylene dimethacrylate mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; monomers in 11% water + 89% dimethyl sulfoxide, 3 hr.
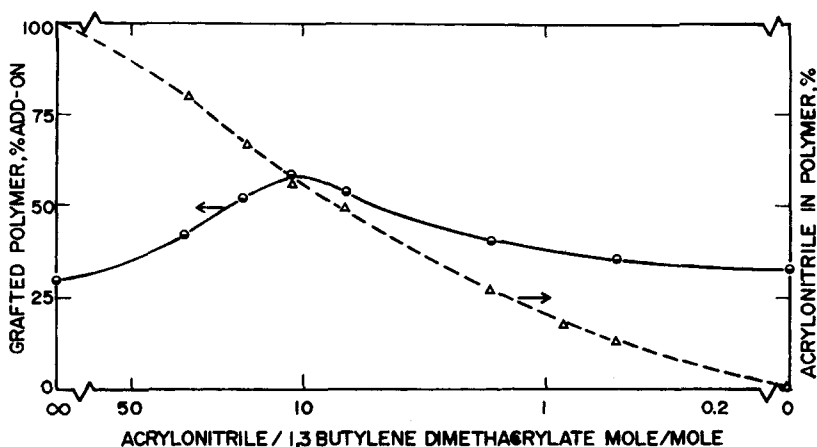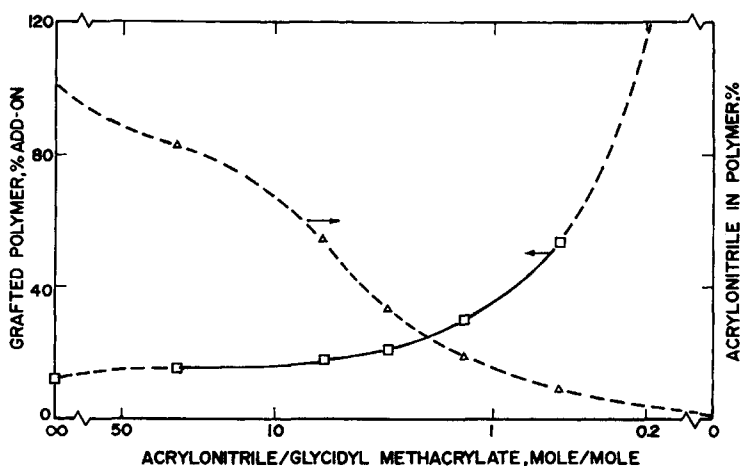
Fig. 10. Effects of acrylonitrile/glycidyl methacrylate mole ratio on extent of graft copolymerization with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; monomers in 43% water + 57% methanol, 0.5 hr.

The addition of styrene to acrylonitrile in water–methanol increased the polymer add-on (Fig. 6).   The addition of methyl methacrylate to acrylonitrile in water–methanol did not significantly change the polymer add-on, until the molar amount of methyl methacrylate in the mixture was greater

Fig. 11. Effects of increasing water content of solvent on extent of graft copolymerization of acrylonitrile–styrene mixtures with irradiated cellulose at 25°C and on composition of the grafted polymer.   Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; styrene:acrylonitrile, 1:9 mole ratio in water + methanol, 0.5 hr.   Dotted line indicates maximum concentration of water at which one phase was obtained.

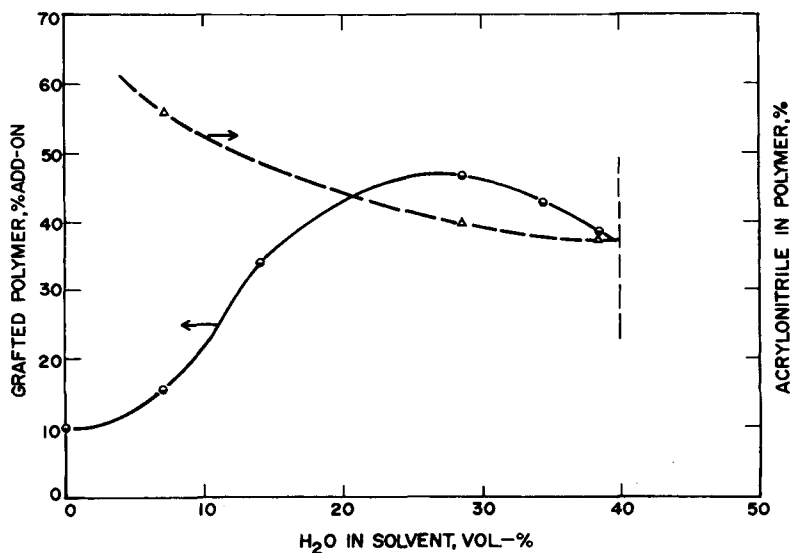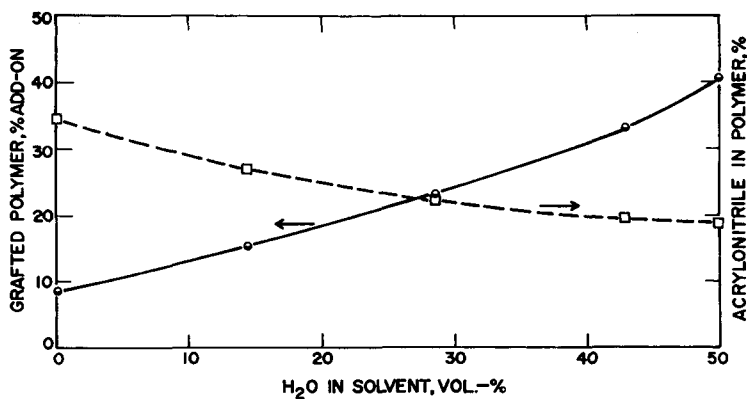Fig. 12. Effects of increasing water content of solvent on extent of graft copolymerization of acrylonitrile–glycidyl methacrylate mixtures with irradiated cellulose at 25°C and on composition of the grafted polymer. Dosage, 5.2×10^{19} eV/g; cellulose:solution, 1:33; solution, 30 vol-% monomer + 70 vol-% solvent; glycidyl methacrylate:acrylonitrile, 1:1.3 in water + methanol, 0.5 hr.

than that of acrylonitrile (Fig. 7).   The addition of vinylpyrrolidone to acrylonitrile in water-dimethyl sulfoxide increased the polymer add-on to a maximum amount at a vinylpyrrolidone-to-acrylonitrile mole ratio of about 1:10 (Fig. 8).   The addition of 1,3-butylene dimethacrylate to acrylonitrile in water–dimethyl sulfoxide increased the polymer add-on to a maximum amount at a mole ratio of about 10 (Fig. 9).   The addition of glyc-

Fig. 13. Effects of reaction time on extent of graft copolymerization of acrylonitrile–monomer mixtures with irradiated cellulose at 25°C and on composition of the grafted polymer.   Dosage, 5.2×10^{19} eV/g;   cellulose:solution, 1:33;   solution, 30 vol-% monomer + 70 vol-% solvent;   (□) 1,3-butylene dimethacrylate:acrylonitrile, 1:11 mole ratio in 11% water + 89% dimethyl sulfoxide;   (◐) styrene:acrylonitrile, 1:9 mole ratio in 21% water + 79% methanol.
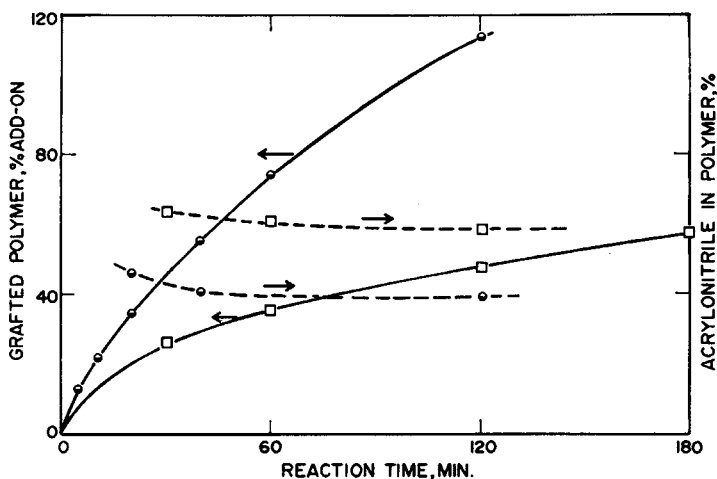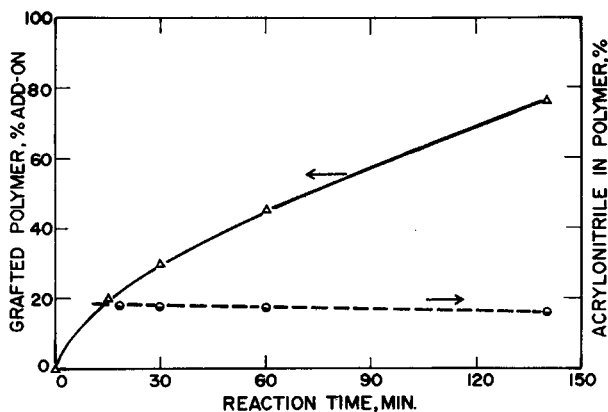

Fig. 14. Effects of reaction time on extent of graft copolymerization of acrylonitrile–glycidyl methacrylate mixtures with irradiated cellulose at 25°C and on composition of the grafted polymer.   Dosage, 5.2×10^{19} eV/g;   cellulose:solution, 1:33;   solution, 30 vol-% monomer + 70 vol-% solvent;   glycidyl methacrylate:acrylonitrile, 1:1.3 in 43% water + 57% methanol.

idyl methacrylate to acrylonitrile in water–methanol increased the polymer add-on, particularly when the amount of glycidyl methacrylate exceeded the amount of acrylonitrile in the mixture (Fig. 10).

The effects of increasing the water content of the methanol–water solvent for acrylonitrile–styrene and acrylonitrile–glycidyl methacrylate mixtures on the composition of the grafted copolymer, as related to the polymer add-on, are shown in Figures 11 and 12, respectively. In the mixture containing styrene, the polymer add-on increased to a maximum amount at about 30 vol-% water and 70 vol-% methanol; however, the proportion of acrylonitrile in the copolymer decreased with increased water content. (Fig. 11). In the mixture containing glycidyl methacrylate, the polymer add-on increased and the proportion of acrylonitrile in the copolymer decreased with increased water content (Fig. 12).

The effects of reaction time for acrylonitrile–1,3-butylene dimethacrylate and acrylonitrile–styrene mixtures and acrylonitrile–glycidyl methacrylate mixture on the composition of the grafted copolymer, as related to polymer add-on, are shown in Figures 13 and 14, respectively. In each system, the polymer add-on increased with increased reaction time and the proportion of acrylonitrile in the copolymer was relatively constant.

DISCUSSION

The effects of acrylonitrile monomer mole ratios and solvents on the extent of graft copolymerization could be interpreted as the Trommsdorff-type effect[16] of the solvents, which in each case would include the monomers. The acrylonitrile/monomer mole ratio in the solvents is compared with the polyacrylonitrile/polymonomer in the grafted copolymer, as shown in Table I. Generally, in all cases, except when lauryl methacrylate and vinylidene chloride were mixed with acrylonitrile, the proportion of acrylonitrile in the grafted copolymer was less than that in the binary monomer mixture. However, for some solvent–monomer mixtures, the proportion of acrylonitrile in the copolymer exceeded that in the monomer mixture, for example, allyl methacrylate and vinylpyrrolidone.

The grafted copolymers could include grafted chains composed of one monomer and, less likely, grafted block polymers. After acid hydrolysis of the cellulosic fraction of the copolymer, attempts to dissolve the grafted polymer residues were unsuccessful. Also, attempts to fractionate the grafted polymer residues by extraction with different solvents were unsuccessful. Strong interaction between two types of grafted polymers and/or formation of grafted block copolymers are indicated. We reported earlier that when solutions containing only one monomer were copolymerized with cellulose under similar conditions, the polymer formed could be separated from the cellulose fraction and dissolved.[21]

Addition of water to the solvents generally increased the extent of graft copolymerization, usually accompanied by a decrease in the proportion of acrylonitrile in the grafted polymer. The interaction of water with

the cellulose would tend to increase the accessibility of the free-radical sites to the monomers and consequently the extent of copolymerization with cellulose.   Through chain transfer, it would also be possible to form block or grafted copolymers of the monomers.   Also, water was probably a poorer solvent for the polymers being formed than the organic solvents

TABLE I

Effects of Acrylonitrile/Monomer Mole Ratio and Solvent on Polyacrylonitrile/ Poly(M) Ratio in Copolymer Grafted onto Irradiated Cellulose at 25°C[a]

Acrylonitrile/ monomer in solvent, mole/mole	Solvent	Reaction time, min	Copolymer add-on, %	Poly(AN)/poly(M) in copolymer, mole/mole
	Acrylonitrile–Methyl Methacrylate			
23	43% H₂O, 57% MeOH	30	14	12
8.0		30	14	4.0
1.6		30	16	0.85
0.80		30	25	0.45
0.32		30	47	0.21
0.11		30	82	0.076
	Acrylonitrile–Butyl Methacrylate			
34	23% H₂O, 77% MeOH	30	11	13
12		30	11	7.7
2.4		30	10	1.7
1.2		30	12	0.84
0.49		30	16	0.43
	Acrylonitrile–Lauryl Methacrylate			
9.2	32% MEK, 68% DMSO	240	21	57
4.6		240	17	16
2.3		240	16	4.1
2.3		180	17	5.4
2.3		1140	35	1.7
	Acrylonitrile–Glycidyl Methacrylate			
28	43% H₂O, 57% MeOH	30	15	12
5.9		30	18	3.1
3.0		30	21	1.3
1.3		30	27	0.70
0.50		30	68	0.27
	Acrylonitrile–Allyl Methacrylate			
3.7	13% H₂O, 87% DMSO	45	10	2.8
1.8		45	8	1.7
0.61		45	7	0.72
0.28		45	7	0.36
1.8	0% H₂O, 100% DMSO	45	7	2.3
1.8	20% H₂O, 80% DMSO	45	20	1.3
1.8	23% H₂O, 77% DMSO	45	10	1.5

TABLE I (*continued*)

Acrylonitrile/ monomer in solvent, mole/mole	Solvent	Reaction time, min.	Copolymer add-on, %	Poly(AN)/poly(M) in copolymer, mole/mole
|Acrylonitrile–1,3-Butylene Dimethacrylate			
31	11% H₂O, 89% DMSO	180	42	17
17		180	52	8.3
11		180	57	5.6
6.8		180	53	4.3
1.7		180	40	1.6
0.85		180	37	0.88
0.52		180	36	0.65
11		30	27	7.4
11		60	36	6.7
11		120	47	6.0
	Acrylonitrile–Styrene			
50	21% H₂O, 79% MeOH	30	14	5.8
24		30	28	3.0
16		30	43	2.0
11		30	45	1.6
8.7		30	52	1.2
6.9		30	46	1.3
5.2		30	40	1.2
3.5		30	35	0.93
1.8		30	26	0.76
8.7		10	21	1.7
8.7		40	56	1.4
8.7		120	114	1.3
8.7	7% H₂O, 93% MeOH	30	16	2.5
8.7	28% H₂O, 72% MeOH	30	47	1.3
8.7	39% H₂O, 61% MeOH	30	39	1.2
	Acrylonitrile–Vinylidene Chloride			
4.8	20% H₂O, 80% MeOH	180	13	7.0
1.8		180	14	3.7
1.2		180	13	2.9
0.81		180	12	1.9
0.30		180	11	0.73
	Acrylonitrile–Vinylpyrrolidone			
6.6	20% H₂O, 80% DMSO	180	102	3.5
2.5		180	112	2.2
1.1		180	105	1.6
0.41		180	89	1.4

ᵃ AN = Acrylonitrile; M = monomer shown with AN; DMSO = dimethyl sulfoxide.

used in the mixtures. The decrease in proportion of the acrylonitrile in the grafted polymer could also indicate that two different polymers were being formed during the graft copolymerization reaction.

In these copolymerization reactions, the relative reactivities of the different monomers with cellulose radicals were estimated by comparing the number of molecules of monomer copolymerized with preirradiated cellulose with the number of molecules of acrylonitrile copolymerized with preirradiated cellulose under identical experimental conditions. With acrylonitrile reactivity with cellulose radicals reported as 1.00, the relative reactivities for the several monomers with preirradiated cellulose are shown in Table II.
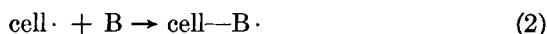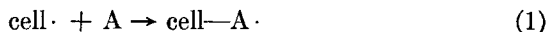
TABLE II

Relative Molecular Reactivity of Monomer for Cellulosic Radical as Compared with Reactivity of Acrylonitrile for Cellulosic Radical Under Identical Experimental Conditions[a]

Monomer	Solvent	Reaction time, min	Relative reactivity[b]
Acrylonitrile			1.00
Styrene	21% H_2O, 79% MeOH	30	1.02
Methyl methacrylate	43% H_2O, 57% MeOH	30	9.45
Vinylidene chloride	20% H_2O, 80% MeOH	180	0.45
Butyl methacrylate	23% H_2O, 77% MeOH	30	2.07
Lauryl methacrylate	32% MEK, 68% DMSO	240	0.29
Glycidyl methacrylate	43% H_2O, 57% MeOH	30	7.57
Allyl methacrylate	13% H_2O, 87% DMSO	45	0.17
1,3-Butylene dimethacrylate	11% H_2O, 89% DMSO	180	0.26
Vinylpyrrolidone	20% H_2O, 80% DMSO	180	0.24

[a] Solvent system, reaction time, and temperature used were the same for each of the monomers listed when number of moles monomer reacted with preirradiated cellulose was determined.

[b] Moles monomer reacted/moles acrylonitrile reacted.

In the binary monomer mixtures, the following types of free-radical reactions could occur with preirradiated cellulose:

$$\text{cell} \cdot + A \rightarrow \text{cell—A} \cdot \qquad (1)$$

$$\text{cell} \cdot + B \rightarrow \text{cell—B} \cdot \qquad (2)$$

$$\text{cell—A} \cdot + A \rightarrow \text{cell—AA} \cdot \qquad (3)$$

$$\text{cell—A} \cdot + B \rightarrow \text{cell—AB} \cdot \qquad (4)$$

$$\text{cell—B} \cdot + A \rightarrow \text{cell—BA} \cdot \qquad (5)$$

$$\text{cell—B} \cdot + B \rightarrow \text{cell—BB} \cdot \qquad (6)$$

where cell· is cellulose radical in preirradiated cellulose, A is acrylonitrile, and B is the other monomer of the binary mixture.

Lewis and co-workers[2] reported that in copolymerizations of styrene with acrylonitrile there was a tendency for the monomers to alternate in entering the copolymer, since the monomer reactivity ratios were less than 1. These monomer reactivities for cellulosic radicals were about equal (see Table II); the concentration of acrylonitrile in the grafted copolymer was decreased as compared with the concentration of acrylonitrile in the monomer solution (see Table I). This effect can be explained in these cases (see Table I) on the basis of the tendency of the monomers to alternate in the copolymer. Also, the reactivities of styrene and acrylonitrile for the radical on the end of the growing copolymer chain appeared to be greater than that for the cellulosic radical, as shown by the dependence of polymer add-on on acrylonitrile/styrene ratio in the monomer solution.

Similarly, in copolymerization of vinylidene chloride with acrylonitrile, the monomer reactivity ratios are less than 1,[2] so that alternation of the monomers in the copolymer would be suggested. However, the reactivity of vinylidene chloride for the cellulosic radical is less than that of acrylonitrile (see Table II). The polymer add-on was independent of the acrylonitrile/vinylidene ratio in the monomer solution (see Table I). The concentration of acrylonitrile in the copolymer was therefore increased as compared with the concentration of acrylonitrile in the monomer solution.

In the copolymerization of methyl methacrylate with acrylonitrile, the monomer reactivity ratio for methyl methacrylate is greater than unity and that for acrylonitrile is less than unity, so that both radical types prefer to react with the same monomer.[2] The reactivity of methyl methacrylate for the cellulosic radical is much greater than that of acrylonitrile (see Table II). The polymer add-on was dependent on the acrylonitrile ratio in the monomer solution and increased as the relative concentration of methyl methacrylate in the solution increased. The concentration of acrylonitrile in the copolymer was decreased as compared with that of acrylonitrile in the monomer solution. These changes can be explained by consideration of the monomer reactivity ratios and relative reactivities of the monomers for the cellulosic radical.

Copolymerization of binary mixtures with preirradiated fibrous cellulose can be used to control the extent of copolymerization of vinyl monomers with preirradiated cellulose and to determine the composition of the grafted copolymer. The initial concentration of free radicals in the preirradiated cellulose can be determined by controlling the radiation dosage.[4–6,8] Consequently, rates of copolymerization of preirradiated cellulose with different monomer systems can be readily compared. The effects of monomer reactivity ratios, monomer reactivity for the cellulosic radical, and solvents on the morphology of the preirradiated fibrous cellulose to increase the accessibility of the cellulosic radical to monomers and the Trommsdorff-type effects of the monomer solutions on the copolymerization reactions have been reported here and elsewhere.[4,5] We hope to extend these investigations to relate more quantitatively these and other factors in the macromolecular modification of the properties of fibrous cotton cellulose.

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