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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Santappa, M.(1981) 'Graft Copolymers', Journal of Macromolecular Science, Part A, 16: 8, 1493 — 1508

To link to this Article: DOI: 10.1080/00222338108063250

URL: <http://dx.doi.org/10.1080/00222338108063250>

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Graft Copolymers*

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INTRODUCTION

The preparation of graft copolymers is a domain of polymer chemistry that has received considerable interest. Grafting of vinyl monomers to natural and synthetic polymers by means of chemical or radiation-initiated polymerization has been suggested as a potentially good means of altering the properties of the base polymer. Graft polymerization is different from random or block copolymerization in that it leaves the main polymeric backbone essentially intact. A graft copolymer may combine some of the characteristic properties of each polymer or have properties entirely different from either of the components. Hence such products made of selected polymer combinations can have highly specific properties tailor-made for a particular application.

Graft copolymerization can be initiated either by free radical mechanism or by ionic mechanism. Depending on the monomer to be grafted, the type of initiation may be preferred. Ionic grafting has a number of disadvantages connected with the necessity of carrying out the reaction in anhydrous medium and/or in the presence of a considerable quantity of alkali metal hydroxide. It was also observed that in ionic polymerization, more grafted chains of considerably low molecular weight are formed than in radical polymerization. In general, the free-radical technique is more promising and

*Presented as a Plenary Lecture at the International Symposium on "New Frontiers in Polymer Science and Polymer Applications," held January 8-9, 1980, Madras, India.

practical for the preparation of graft copolymers. Free radicals can be produced by both irradiation and chemical methods.

GRAFTING TECHNIQUES

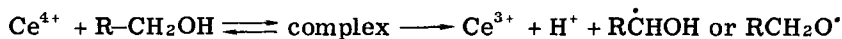
Irradiation

The techniques of graft copolymerization have been reviewed earlier by us [1] and others [2-8]. There are two techniques in irradiation: (1) Mutual irradiation and (2) pre-irradiation. The mutual technique involves irradiating the substrate in the presence of the monomer in liquid or vapor phase and, in general, the applicability of this method is limited to systems in which the radical yield from the substrate polymer must be higher than that from the monomer; otherwise excessive homopolymerization results. The pre-irradiation methods involve irradiating the substrate alone and then bringing it in contact with liquid or gaseous monomers. Grafting takes place by the reaction of the monomer with the trapped radicals. Most of the monomers can be grafted by this technique. The mutual method gives homopolymers whereas the pre-irradiation method gives mainly true graft copolymers. When ionizing radiation is used for grafting a monomer onto natural polymers, the sensitivity of the polymeric substrates toward high energy irradiation is an important factor. The natural polymers will be progressively damaged with increasing radiation dose. The low absorption energy from ultra-violet irradiation can also be utilized for grafting onto natural polymers. However, in this case the grafting is usually limited to the surface of the polymeric substrate.

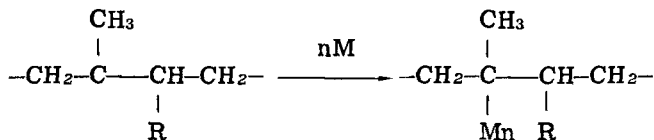
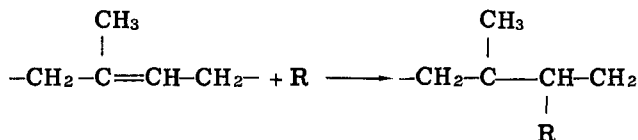
Chemical Methods

According to our viewpoint, the chemical method of producing free radicals is more accessible and may be easily carried out. Well-investigated chemical methods of synthesizing graft copolymers involve a peroxide catalyst or redox initiators for production of free radicals which may attack $>C=C<$ bonds in the backbone polymer or effect chain transfer with a reactive element in backbone polymer.

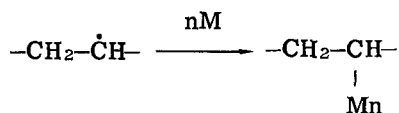
Among the many redox initiators in grafting studies, the redox system Ce^{4+} and an alcohol is a good source for free radicals:



Other redox systems involving Mn^{3+} , V^{5+} , or Ti^{3+} (a reducing agent) are also effective. E.g., initiation of grafting on natural rubber with methyl methacrylate or other monomers:

Attack on double bond:Abstraction of α -hydrogen:

In this case, the α -hydrogen atom may be attacked simultaneously which will create radical centers for grafting:

Chain transfer:

BACKBONE FOR GRAFTING

Modification of polymers by graft copolymerization of other monomers has been the subject of much discussion but only little commercialization has so far been reported. It is not intended to make detailed reference to the copious literature which has contributed to the development of this subject. The work on graft copolymers was particularly aimed at their application in the leather industry. This paper deals with some of the important graft copolymers used in the leather industry.

Chlorinated Rubber and Polyvinyl Chloride

Extensive studies, particularly from the kinetic point of view, on grafting of vinyl monomers on chlorinated rubber and PVC and bromopolystyrene have been reported [9-11] by us earlier. Chlorinated rubber is widely used as a film-forming resin and has applications in paints, printing inks, and adhesives. It forms hard, inert films which are resistant to attack by acids, alkalies and mold growth. It has the added advantage of high specific adhesion, good solvent-releasing properties, and is nontoxic and nonflammable. However, chlorinated rubber alone was not found useful in leather finishing because the film cracked on leather. An attempt was therefore made to overcome this defect by grafting acrylic polymers onto chlorinated rubber. By graft copolymerization, which has been studied extensively in our laboratories, it is possible to incorporate polymers into chlorinated rubber which may give it certain desirable properties possessed by the synthetics without detracting from the favorable properties. It was recognized earlier that chlorinated rubber backbones were susceptible to branching in chain transfer reactions involving halogen atoms of the backbone, giving fairly good yield of graft polymer.

The attempt in grafting of vinyl polymers to chlorinated rubber stemmed from expected property improvements that could be more or less permanent in nature because of the ability to deposit high molecular weight polymers in intimate contact with the basic structure. The final product was a mixture of polymer containing also ungrafted, homo-, and copolymers of the monomers used. Graft copolymerization was formed by a chain-transfer reaction involving the growing polymer radicals to the backbone of chlorinated rubber in addition to homopolymer from the monomer [9, 10]. The homopolymer was isolated from the polymer mixture by fractional precipitation, and proof of grafting was provided by infrared spectra, light-scattering, and osmometry data. Typical data on the light-scattering and osmometry studies of graft copolymers are presented in Tables 1 and 2, respectively. The isolation of graft polymers from polymer mixtures is relatively simple, since the backbone and graft side chains have different solubility characteristics. Even though unambiguous characterization was rendered difficult by the heterogeneity of the product, the presence of graft copolymers in the polymer mixture could be confirmed as shown earlier by Rao and Santappa [9, 10]. Conditions have been established to effect good results with the benzoyl peroxide system in grafting acrylic ester monomers to chlorinated rubber. However, no attempt was made to remove the ungrafted polymers from the product which was used for leather finishing, as their presence was not in any way detrimental to the finishing property. Moreover, since the acrylic copolymers are already used in the leather industry as binders and as top coat, the presence of these polymers along with the grafted products was beneficial for leather finishing.

TABLE 1. Light-Scattering Data^a

Polymer	\bar{M}_w app. $\times 10^{-6}$	A_2 $\times 10^4$	$\langle S \rangle_z^2$ $\times 10^{10}$ app. cm^2	$\frac{\langle S \rangle_z^2}{\bar{M}_w}$ $\times 10^{17}$	% of side- chain polymer
Chlorinated rubber	4.41	0.180	2.24	5.07	-
Chlorinated rubber-g-PMA	33.94	0.079	3.20	0.94	86.89
Chlorinated rubber-g-PMMA	8.15	0.36	5.00	6.13	45.86

^aSolvent: Methyl ethyl ketone. Temperature: 35°C. \bar{M}_w app. $\approx \bar{M}_w$ and $\langle S \rangle_z^2$ app. $\approx \langle S \rangle_z^2$.

TABLE 2. Osmotic Pressure Data^a

Polymer	\bar{M}_n $\times 10^{-5}$	T_2 $\times 10^{-2}$	A_2 $\times 10^4$	$\psi(1 - \theta/T)$ $\times 10^2$	% of side- chain polymer
Polyvinyl chloride	1.36	1.23	9.03	8.04	-
Polyvinyl chloride-g- PMMA	3.02	2.89	9.55	8.51	54.90
Polyvinyl chloride-g- PEMA	1.61	0.77	4.80	4.27	15.45

^aSolvent: Tetrahydrofuran. Temperature: 29°C.

The formulation standardized with grafted chlorinated rubber for top finish has been found to be good with regard to the extensibility of the finish, gloss, dry and wet rub resistance, and also as per the test reports of the tanners who have tested the product in their tanneries; see, for example, Table 3.

PVC and its copolymers with vinyl acetate are widely used in industrial applications. Kennedy et al. [12-15] have investigated the ionic grafting of a number of monomers onto PVC and its copolymers.

TABLE 3. Results of Physical Tests Conducted on Leathers Treated with Chlorinated Rubber Finishes

Solution	Flexural endurance	Water vapor permeability (mg/cm ² /h)	Color fastness		Gloss
			Dry rub	Wet rub	
Control 1. Nitrocellulose lacquer	Not affected after 100,000 flexings	1.26	Very good	Very good	Very good
Control 2. Acrylic polymer solution	Finish peeled off at 30,250 flexings	1.13	Very good	Very good	Very good
Chlorinated rubber graft copolymer solution	Not affected after 100,000 flexings	2.14	Very good	Very good	Very good

Graft copolymerization of vinyl monomers onto PVC and its copolymers using free-radical initiators have been reported by us [9, 11]. At present, the applications of these graft copolymers in the leather industry are being explored.

Collagen

Collagen Fibers

Investigations [16-34] have been made at CLRI in the preparation/characterization and some of the properties of graft copolymers involving collagen backbone and vinyl monomers.

Among known methods available for grafting, the ceric ion redox system was selected in view of its leading to minimum degradation accompanied by a high percentage of grafting. Polar monomers such as acrylonitrile, acrylamide, and methyl methacrylate can be readily grafted into the collagen substrates [16]. Table 4 gives the details of grafting reactions. The effect of different experimental factors such as time, temperature, and the concentrations of monomer and initiator on the composition of collagen-PMMA graft copolymer was investigated. The number of grafting sites and the molecular weights (\bar{M}_n) of the grafted PMMA branches obtained under different polymerization conditions indicated that the branch length and the grafting sites were considerably influenced by all these factors.

TABLE 4. Grafting of Vinyl Monomers onto Collagen by Ceric Ion^a

Graft copolymer	Amino acid	Amino acid (g/100 g)	% in graft copolymer		% Grafting
			Collagen	Monomer	
Collagen-g-PAN	Argenine	5.35	62.15	37.85	60.87
	hydroxy proline	7.75	56.62	43.38	
Collagen-g-PAA	Argenine	6.81	79.14	20.86	26.36
	hydroxy proline	7.81	57.82	42.82	
Collagen-g-PMMA	Argenine	4.10	48.00	52.00	108.30
	hydroxy proline	5.00	37.00	63.00	

^a[Ce(IV)] = 5×10^{-3} mol/L; [collagen] = 0.5 unit mol/L; [monomer] = 1.0 mol/L; time = 3 h; temperature = 30°C. Dispersion medium: For AN and AA, H₂O; DMF (1:1); for MMA, water.

For an unambiguous characterization of collagen vinyl graft copolymers the grafted side chains were isolated and proof of grafting was provided by several methods [20, 21]. The grafted vinyl polymer chains were isolated by both acid and enzymatic hydrolysis of the collagen backbone in order to characterize the graft copolymers. Proof of grafting was obtained through the detection of amino acid end groups in the grafts isolated by both methods. The grafts isolated gave the characteristic blue color with ninhydrin normally associated with the presence of amino acids. The presence of amino acid end groups was further confirmed by dinitrophenylation of the isolated grafts. The absorption spectra of dinitrophenylated (DNP) grafts showed absorption maximum in the ultraviolet region of $\lambda = 340\text{--}360$ m μ , characteristic of DNP-amino acids. The turbidometric titration behavior of the grafts and their general behavior of swelling in different solvents also provided additional proof of grafting. The graft copolymers were also characterized by infrared spectra and electron microscopy.

Graft polymerization of methyl methacrylate on a number of modified collagens was studied in order to elucidate the mechanism of the oxidation of collagen and to determine the grafting sites on collagen using the ceric ion technique [18]. The number of grafting sites obtained in the case of unmodified collagen indicated that the grafting reactions involved only a small proportion of fiber molecules. None of the modifications of the different functional groups of collagen could completely eliminate grafting, except dinitrophenylation. In this case complete inhibition of grafting was due to the presence of aromatic

TABLE 5. Grafting of MMA onto Modified Collagen^a

Nature of modification	% Grafting	\bar{M}_n of grafted PMMA $\times 10^{-5}$	No. of grafting sites (mol/mol)
Untreated collagen	159.60	20.75	0.23
Acetylated collagen	93.28	16.94	0.17
Methylated collagen	159.40	11.48	0.42
N-Acetylated collagen	156.00	22.70	0.21
Deaminated collagen	51.07	7.55	0.20
Dinitrophenylated collagen	Nil	Nil	Nil
Cyanoethylated collagen	183.00	14.16	0.39
Thiolated collagen	146.00	2.95	1.49
N-Brominated collagen	108.40	6.29	0.52
Vinylated (maleic anhydride treated) collagen	301.90	18.32	0.49

^a[Ce(IV)] = 0.25×10^{-3} mol/L; [collagen] = 0.25 unit mol/L; [MMA] = 0.5 mol/L; time = 3 h; temperature = 30°C.

nitro compounds. Collagen was also modified by thiolation, vinylation, bromination, and cyanoethylation in order to introduce new functional groups which will subsequently enter into the polymerization reaction. The number of grafting sites significantly increased when collagen was thiolated, N-brominated, vinylated, cyanoethylated, or methylated. The general trend of the results obtained with modified collagen samples indicates that hydroxy groups and the peptide backbone may provide sites for initiation of the grafting reaction. The extent of grafting, number-average molecular weights, and the number of grafting sites of PMMA with various modified collagen are given in Table 5.

Skins/Hides

The usual methods followed for the grafting of vinyl monomers on collagen powder and collagen solution were, however, found to be unsuitable for grafting on skins which have a three-dimensional network structure. In this case, an emulsion polymerization technique using suitable wetting agents and surfactants was finally found to give successful results [23]. Some of the physical properties of the leathers

obtained with skins/hides grafted with different vinyl monomers are superior to those of the leathers obtained without any pretreatment. These improved properties were: increased elongation, enhanced resistance to chemicals, resistance to mold growth, and decreased water absorption in addition to the desired "fullness." The hygienic properties of leather such as water-vapor permeability and air permeability are retained even after grafting. The results obtained in the present study show that grafting with PAN, PMA, PBA, and PMMA could be accomplished and combine the good qualities of both synthetics and natural fibers without loss to any degree of the favorable properties of natural leathers as represented in Table 6.

Leathers

Methods evolved for the grafting of vinyl monomers onto collagen fibers, hides, and skins have also been successfully employed for grafting on certain types of leathers with suitable experimental conditions: The grafted leathers were full and showed improved properties [27, 28]. The methods developed in this laboratory for grafting of vinyl monomers on skins and leathers have been tried in the tannery on a larger scale using a number of skins and leathers. It has been found that the laboratory methods can be successfully extrapolated to the tannery scale.

Grafting onto Cellulose Nitrate

Heterogeneous Medium

Cellulose has the distinction of being among the first polymer substrates to be used for grafting, and this technique has also been successfully applied to cellulose derivatives such as cellulose acetate [35], methyl cellulose [36], carboxy methyl cellulose [37], cellulose phosphonate [38], and aldehyde cellulose [39]. However, very little attention has been paid to the grafting of synthetic monomers onto cellulose nitrate in spite of its versatile applications. Lacquers of cellulose nitrate (or nitrocellulose as it is commercially known) are widely used in the surface coating industries. At present cellulose nitrate is made flexible by the addition of plasticizers. The drawback with the plasticizer is its migration on aging which makes the film brittle. Moreover, properties such as poor adhesion, poor resistance to microorganisms, and the yellowing nature of cellulose nitrate need some attention. Envisaging graft copolymerization as a potentially good means of altering the properties of cellulose nitrate, grafting of various vinyl monomer on the latter has been tried [40]. Our results have shown that grafting of acrylates and methacrylates can be carried out in a heterogeneous medium by the ceric ion initiation technique. Using MMA as a model monomer, the effect of such parameters as monomer concentration, initiator concentration, cellulose nitrate concentration, and reaction time on the grafting reactions have been

TABLE 6. Physical Test Data for Goat Pelts Grafted with Vinyl Polymers

Sample	Grafting (%)	Air permeability (s)	Tongue tear resistance (kg/cm thickness)	Tensile strength (kg/cm ²)	Elongation at break (%)	Strength tear resistance (kg/cm ² thickness)
Control	-	86	12.6	134.5	75.0	64.5
Grafted with PMMA	86.88	92	11.9	150.3	62.5	40.1
Control	-	85	37.1	202.7	75.0	-
Grafted with PMA	75.84	50	22.1	170.2	68.7	-
Control	-	83	13.6	144.4	68.7	90.9
Grafted with PBA	182.10	122	22.7	209.7	131.2	68.1
Control	-	49	13.3	179.9	62.5	60.6
Grafted with PAN	71.10	50	9.5	100.5	43.7	56.8

^aControl: Goat pelts directly chrome tanned, Treated sample: Goat pelts chrome tanned after grafting.

TABLE 7. Comparison of Grafting Reactions onto Cellulose Nitrate

	Heterogeneous	Homogeneous
1. Medium	Aqueous	Nonaqueous
2. Reaction type	Suspension	Solution
3. Molecular weights (\overline{M}_n) of grafted chains	2.0×10^5	1.0×10^4
4. Percent grafting	25	60
5. Grafting site	Residual -OH groups on AGU	Unsaturation created in AGU

studied. The molecular weights of the grafted chains were measured after isolating them from the backbone. Oxidation of cellulose nitrate with ceric ion conducted under identical conditions of grafting in the absence of monomer has shown that more ceric ion was consumed for the graft reaction than for the oxidation process. The probable mechanism of grafting may be at the α -carbon atom of primary alcohol or at a C₂-C₃ glycol group of the anhydroglucose unit (AGU) or at the hemiacetal group of the end unit of cellulose nitrate, as cellulose nitrate is formed by the partial nitration of cellulose.

Homogeneous Medium

Reactions of grafting onto cellulosic materials in a homogeneous medium are very few. We have carried out grafting of vinyl monomers onto cellulose nitrate in a solvent medium by using free radical initiators like benzoyl peroxide (Bz₂O₂) [41, 42] and azobisisobutyronitrile (AZBN) [44]. The effects of reaction conditions on the grafting efficiency and percent grafting were determined. AZBN was found to be more efficient than Bz₂O₂ in initiating graft copolymerization of vinyl monomers onto cellulose nitrate. Pure graft copolymers were isolated from the unreacted backbone and homopolymer by selective solvent extraction. A comparison of the graft copolymerization of MMA in heterogeneous and homogeneous medium is presented in Table 7.

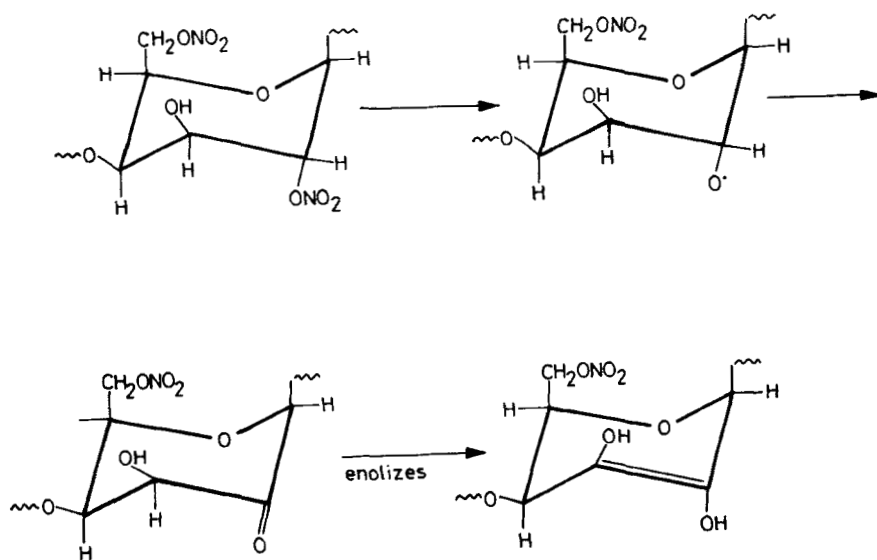
The molecular weights of the grafted chains were determined after isolating them by acid hydrolysis. The effects of various reaction conditions on the molecular weights of the grafted chains were also studied. Nitrogen in cellulose nitrate and graft polymers was estimated by (1) the volumetric method and (2) the colorimetric method since the conventional nitrometer method and Kjeldahl methods were not suitable.

The graft copolymers of cellulose nitrate were characterized by different instrumental analyses. IR and NMR spectra of the graft

copolymers were recorded and compared with the homopolymers. Gel permeation chromatography was used as a technique for the differentiation between the homopolymers, polymer mixture, and graft copolymer. The graft copolymers were analyzed with differential scanning calorimeter and compared with the homopolymers. The mechanical properties of the cellulose nitrate graft copolymers were significantly altered as compared to the untreated cellulose nitrate [43].

The energy activation for the AZBN-initiated polymerization was found to be ~ 18 kcal/mol. The rate of polymerization was found to depend on monomer concentration, on the square root of the initiator concentration, and was independent of the cellulose nitrate concentration at low conversions.

Based on the experimental results, a mechanism has been proposed for the graft copolymerization of vinyl monomers onto cellulose nitrate in homogeneous medium [42]. It is believed that unsaturation occurs in the AGU under the grafting conditions due to molecular rearrangements. The primary radicals from the initiator may attack the double bond, creating radical centers for grafting.



A variety of graft copolymers were prepared using different combinations of vinyl monomers and applied as top-coat finishes for leather. The film-forming properties of these graft copolymers revealed that improvement in adhesion, gloss, and elongation could be achieved by the graft copolymerization of vinyl monomers onto cellulose nitrate.

TABLE 8. Affected Amino Acids in Casein During Graft Copolymerization

Amino acid	Amount in 100 g of control	Unaffected part in graft	Affected part in graft
Cystine	1.94	0	1.94
Glycine	24.90	18.24	6.66
Lysine	67.31	50.51	13.80
Serine	56.14	48.54	7.60
Threonine	38.62	34.98	3.65
Valine	76.43	65.48	10.96

Grafting onto Casein

Casein is used as a binder in glaze finishing of leathers. The principal drawbacks limiting its use in general are: (1) inflexibility, (2) water sensitiveness, and (3) susceptibility to attack by microorganisms. These drawbacks, in turn, result in brittleness and poor wet-rub resistance of the films, All these can be obviated in one stroke by grafting synthetic polymers onto casein.

Preliminary experiments were carried out for screening the initiation systems and to study the ideal conditions for grafting using MMA as a representative monomer [45]. Among the 10 systems studied, the potassium persulfate-sodium metabisulfite redox system was found to lead to maximum grafting without detriment to the quality of casein. The best reaction conditions were: temperature 60°C, persulfate 5%, metabisulfite 0.6%, and emulsifier (sodium lauryl sulfate) 4% (all on a casein basis).

The casein vinyl graft copolymers were also characterized to gain further insight into the grafting process. The grafted chains were isolated by hydrolyzing the casein backbone, and the molecular weights of these isolated grafted chains were determined. The average D.P. was found to be only about 10.

These results were further confirmed by the amino acid analysis of the grafted casein samples. Data on the amino acid analysis of the grafted casein are presented in Table 8. Amino acid analysis also indicated the active sites for grafting. ϵ -Amino groups of lysine served as sites for grafting in the basic medium. Glycine, serine, threonine, and valine were also involved in the grafting reactions. In the acid medium the carboxyl groups of the two acidic amino acids aspartic and glutamic were indicated as probable sites in addition to the four nonbasic acids indicated above. The reason for the short chain length cannot be explained clearly.

Casein-MMA grafts prepared in the casein-MMA ratio of 1:1, 2:1, and 4:1 were all found unglazeable. Similar compositions prepared using acrylonitrile could be glazed. Among them the 2:1 composition proved satisfactory in flexure tests as the leather withstood 90,000 flexes as compared to 80,000 flexes for the control. All the casein acrylonitrile graft compositions could be stored in bottles for well over 3 months without settling and putrefication. The moisture absorption of these graft copolymers was slightly less than that of untreated casein-based leather finishes.

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Accepted by editor November 17, 1980
Received for publication December 8, 1980