

Hydroxyaliphatic Acids in Branched Copolymers With Acyl Chloride-Terminated Long Side Chains: A New Shrink-Resist Treatment for Wool

M.J. DIAMOND, H.L. NEEDLES,¹ C.A. ELLIGER, D.J. KERTESZ,² E.N. FRANKEL³ and G. FULLER, Western Regional Research Laboratory,⁴ Berkeley, California

Abstract

Two synthetic routes were followed to prepare graft copolymers with long side chains containing acyl chloride terminal groups. In the first of these methods acryloxy aliphatic acyl chlorides were synthesized from ricinoleic acid, 12-hydroxystearic acid and 10-hydroxydecanoic acid and then polymerized with other acrylate ester comonomers. In the second procedure, a prepolymer was formed by copolymerizing acryloyl chloride with acrylate esters. The prepolymer then was treated with 12-hydroxystearic acid or 9(10)-hydroxymethylstearic acid to produce polymers with side chains having terminal carboxylic acid groups. These polymers were made more reactive by conversion to acid chlorides. The active polymers were applied to wool fabrics; the imparted shrink-resistance was durable under an accelerated wash test procedure. An added advantage of the treatment is a soft "hand" or feel resulting from internal plasticization of the polymer coating.

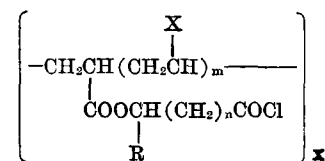
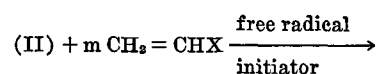
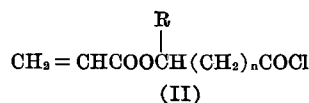
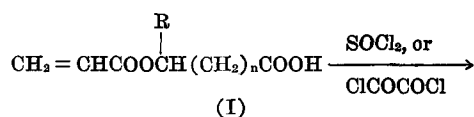
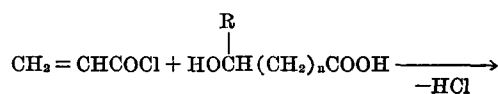
Introduction

Monofunctional long chain acrylate esters have been prepared and investigated as internal plasticizers (1), and several laboratories have described bifunctional long chain acrylate esters with the following end groups: carboxyl (2-7), carbomethoxy (8-11) and amide (12,13). However, we wished to prepare acrylic monomers with more highly reactive end groups capable of reacting rapidly with hydroxyl or amine functions. The intended monomers, acryloxyaliphatic acyl chlorides, could form graft polymers containing long side chains terminated with reactive groups capable of forming covalent linkages with natural proteinaceous or cellulosic products to produce durable coatings.

Several polymer formulations with reactive groups attached directly to the polymer backbone have been produced and applied to wool (14-16). The treated wool fabric was shrink resistant and machine washable, but had a harsh "hand" or feel (17). Increasing the distance between the polymer backbone and the reactive chloride group is a modification which we expected to yield treated fabrics with softer hand, because the polymer is internally plasticized.

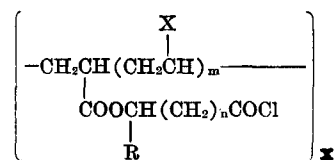
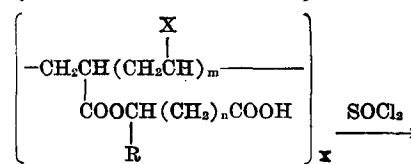
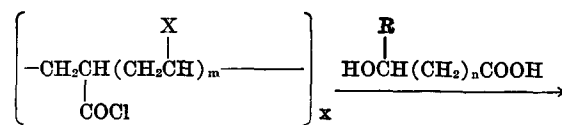
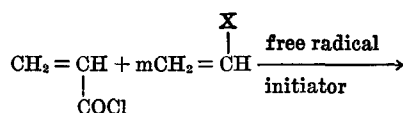
The first preparative route investigated is represented by the following series of reactions in which

chemical modification of the monomers is completed before polymerization is performed as the final step.



R = H, or alkyl
X = -COOR' where R' = alkyl
m, n and x = integers

An alternate route with polymerization as the first step in the series is represented by the following reactions.



R = H, or alkyl
X = -COOR', where R' = alkyl
m, n and x = integers

¹ Present address: Department of Consumer Sciences, University of California, Davis, Calif. 95616.

² Present address: Syntex Laboratories, Inc., Palo Alto, Calif.

³ No. Market. Nutr. Res. Div., ARS, USDA.

⁴ W. Market. Nutr. Res. Div., ARS, USDA.

Polymer solutions were obtained by both procedures, diluted to desired concentrations with perchloroethylene and applied directly to wool fabric. The treated wool fabrics then were subjected to an "Accelerator" accelerated wash test (18). Area shrinkage was measured and the hand of the fabrics was rated by sensory evaluation on a hedonic scale (19).

Experimental Procedures

Materials

Acryloyl chloride purchased from Aldrich Chemical Co., and Monomer-Polymer Laboratories, Borden Chemical Co., was redistilled prior to use. Oxalyl chloride and thionyl chloride, purchased from J.T. Baker Chemical Co., were redistilled before reaction. Ricinoleic acid was prepared by saponification of methyl ricinoleate (Baker Castor Oil Co.) which had been purified by fractional distillation at reduced pressure (20). 12-Hydroxystearic acid was similarly prepared from commercial methyl 12-hydroxystearate (20).

Purified methyl ricinoleate was cleaved with hot alkali in 2-octanol to yield 10-hydroxydecanoic acid (21,22). Methyl 9(10)-formylstearate was prepared by reaction of oleic safflower oil methyl esters with carbon monoxide and hydrogen in the presence of a rhodium-containing catalyst (23). The formyl derivatives were hydrogenated to methyl 9(10)-hydroxymethylstearate over Raney nickel at 1000 psig and 100–120 C. The product was distilled in vacuo and saponified.

Analytical Techniques

IR spectra were determined from films on NaCl plates with a Perkin-Elmer Infrared Spectrophotometer, Model 257.

NMR spectra were obtained using a Varian NMR Spectrometer, Model HA100, from solutions in CCl_4 containing tetramethylsilane as an internal standard.

Synthetic Routes To Graft Polymers With Long Side Chains

Route I: Chemical Modification of Monomers Followed by Copolymerization

One hundred grams of 10-hydroxydecanoic acid, 1.5 g Ionox-330 inhibitor and 400 ml chloroform (previously eluted through alumina to remove ethanol traces) were mixed in a 1-liter reaction flask fitted with a stirrer, thermometer, pressure-equalized dropping funnel, nitrogen capillary inlet, and reflux condenser connected through calcium chloride drying tube to a pressure-controlled vacuum system. The flask contents were warmed in a water bath and stirred under sufficient vacuum to maintain reflux at 54 C, while 60.1 g acryloyl chloride was added dropwise during 40–50 min; then the mixture was allowed to reflux 20–30 min more. The solvent and excess acryloyl chloride were removed with aspirator vacuum followed by mechanical pump vacuum at approximately 1 mm pressure while maintaining bath temperature under 55 C. One hundred fifty grams of crude 10-acryloxydecanoic acid was obtained.

Similarly, 12-acryloxystearic acid, 12-acryloxyoleic acid and 9(10)-acryloxymethylstearic acid were prepared from acryloyl chloride and the respective hydroxyaliphatic acids. The products exhibited the expected IR spectra with major absorption at 3000–3400 (inflection), 2925, 2850, 1725, 1710, 1635 and 1620 cm^{-1} .

A 2 g portion of crude 10-acryloxydecanoic acid was purified by column chromatography. The sample was dissolved in a few milliliters benzene and deposited on a column prepared from a benzene slurry of 70 g silicic acid. The column then was eluted successively with benzene containing increasing amounts of methanol (from 0% to 10%), and finally with diethyl ether.

The fractions eluted by 10% methanol in benzene were evaporated to dryness, and the residue was recrystallized twice from ether-petroleum ether at 10 C to provide a sample suitable for analysis. Calculated for $\text{C}_{13}\text{H}_{22}\text{O}_4$: C, 64.4%; H, 9.09%. Found: C, 64.6%; H, 9.32%. The NMR spectrum of purified 10-acryloxydecanoic acid displayed the expected characteristics: $\delta = 1.2\text{--}1.8$ (mult., broad, 14 H) $-(\text{CH}_2)_n-$; 2.30 (t, $j = 7$ cps, 2 H) $-\text{CH}_2\text{COOH}$; 4.08 (t, $j = 7$ cps, 2 H) $-\text{COOCH}_2-$; and 5.68–6.46 (complex mult., 3 H) α,β -unsaturated carbonyl.

For preparation of acryloxydecanoyl chloride, 150 g of crude 10-acryloxydecanoic acid was dissolved in 250 ml benzene in the same apparatus as described above. The reaction mixture first was stirred and warmed to 40–45 C, and then 150 g oxalyl chloride or thionyl chloride (24–29) was added dropwise during 1 hr. The solution was stirred at 45 C for 1 hr longer; then the solvent and excess oxalyl chloride were removed by distillation at reduced pressure, first with aspirator vacuum and then with mechanical pump using a bath temperature below 55 C. One hundred seventeen grams of yellow crude 10-acryloxydecanoyl chloride was obtained, which was redistilled twice using an ASCO Rota-Film Molecular Still at 20 μ pressure and 170 C jacket temperature. Ordinary distillation of the bulk product resulted in gum formation. Sixty grams of colorless 10-acryloxydecanoyl chloride was obtained. The acid chlorides of the longer chain acryloxy acids were prepared in a similar manner.

Again, IR spectra were consistent with the expected structures. The elemental analyses of a series of acryloxyacyl chlorides are summarized in Table I.

The NMR spectra of purified 10-acryloxydecanoyl chloride and 9(10)-acryloxymethylstearoyl chloride were consistent with the expected structures. However, in the cases of 12-acryloxystearoyl chloride and 12-acryloxyoleoyl chloride, additional peaks at $\delta = 2.30$ and 3.70 ppm indicated the presence of as much as 40% β -chloropropoxy derivative (30). The NMR results for the latter two compounds are corroborated by the high values for chlorine and low values for carbon reported in Table I.

The free radical polymerization procedure (31) is represented by the following example. A solution containing 100.0 g *n*-butyl acrylate, 20.0 g 12-acryloxystearoyl chloride and 1.0 g azobisisobutyronitrile (AIBN) in 500 ml toluene was heated under nitrogen atmosphere at reflux, 112 C, for 2 hr.

TABLE I
Analysis of Acryloxyacyl Chlorides

Compound	Per cent calculated			Per cent found		
	C	H	Cl	C	H	Cl
10-Acryloxydecanoyl chloride, $\text{C}_{13}\text{H}_{22}\text{O}_3\text{Cl}$	59.9	8.1	13.6	60.0	8.3	13.0
12-Acryloxyoleoyl chloride, $\text{C}_{21}\text{H}_{38}\text{O}_3\text{Cl}$	68.0	9.5	9.6	66.7	9.4	11.4
12-Acryloxystearoyl chloride, $\text{C}_{21}\text{H}_{38}\text{O}_3\text{Cl}$	67.6	10.0	9.5	65.2	9.8	12.9
9(10)-Acryloxymethylstearoyl chloride, $\text{C}_{22}\text{H}_{38}\text{O}_3\text{Cl}$	68.4	10.2	9.2	67.9	10.2	9.5

TABLE II
Shrink Resistance of Wool From Acryloyl Acyl Chloride Copolymer Treatments^a

Polymer No.	Copolymer formulation		Ratio of monomer-monomer A:B ^b		Polymer uptake by fabric, wt %	Hand or feel ^c	Area shrinkage of fabric, %
	Monomer A	Monomer B	Weight basis	Molar basis			
1	<i>n</i> -Butyl acrylate	12-Acryloxystearoyl chloride	5:1	14.5:1	8.3	4	6.9
2	<i>n</i> -Butyl acrylate	12-Acryloxystearoyl chloride	10:1	29:1	8.7	4	20.0
3	<i>n</i> -Butyl acrylate	10-Acryloxydecanoyl chloride	5:1	10:1	11.2	4-	2.0
4	<i>n</i> -Butyl acrylate	12-Acryloxyoleoyl chloride	5:1	14.5:1	7.4	4-	5.1
5	Methyl acrylate	10-Acryloxydecanoyl chloride	5:1	15:1	8.5	4-	12.4
6	Methyl methacrylate	10-Acryloxydecanoyl chloride	5:1	13:1	8.1	3+	20.1
7	<i>n</i> -Butyl acrylate	None	Homopolymer		9.8	4+	30.6
8	None	None (untreated fabric)	Control		0	5	45.4

^a Polymers were applied from 10% perchloroethylene solution; "Accelerator" wash test was used.

^b Prior to polymerization.

^c Rating scale: 1, boardy, unacceptable; 2, stiff, dry, rough, unacceptable; 3, some stiffness, greasy, tacky, borderline acceptable; 4, barely perceptible change in wool-like hand, acceptable; 5, treated hand indistinguishable from untreated wool.

After cooling, the resulting viscous copolymer solution was diluted with toluene or perchloroethylene to provide 10 g of polymer per 100 ml solution. This solution was used to treat fabrics as described below. A series of polymer solutions with varied monomers and monomer ratios were prepared as described above and listed in Table II.

Treatment of Fabrics. Samples of wool fabric (6.4 oz/yd², undyed, plain weave) were treated with solutions of the polymers, diluted with perchloroethylene to 10% polymer concentration, using the following technique. A weighed fabric sample was immersed in the polymer solution, then removed and pressed between pad rolls to remove excess liquid, dried in air, and then cured in an oven at 150 C for 10 min. Evolution of HCl at this stage indicated reaction took place with the fabric. The sample was then weighed to determine the polymer uptake, and tested for shrinkage by the "Accelerator" test method (18). Samples of the untreated fabric were also subjected to these tests. The results are presented in Table II.

Route II: Copolymerization of Acryloyl Chloride Followed by Reactions of Prepolymer with Hydroxy Acids

Acryloyl chloride was copolymerized (31) in various proportions with a series of alkyl acrylates.

In a typical run, a 1000 ml flask was charged with 400 ml anhydrous benzene, 9.05 g (100 mmoles) acryloyl chloride, 51.2 g (400 mmoles) *n*-butyl acrylate and 0.48 g (2.0 mmoles) of dibenzoyl peroxide. The apparatus was purged with dry nitrogen and the temperature was raised to reflux. After 14 hr the IR spectrum in benzene showed absence of conjugated olefinic absorption (1616 and 1634 cm⁻¹) as well as shift of absorption from 1760 cm⁻¹ (conjugated unsaturated acyl chloride) to 1790 cm⁻¹ (saturated aliphatic acyl chloride).

The above polymer solution in benzene was allowed to cool to 30 C and 30.0 g (100 mmoles) of 12-hydroxystearic acid was added in one portion. The mixture was warmed again to reflux and reaction was allowed to proceed for 7 hr. The IR spectrum indicated the absence of acid chloride absorption at 1790 cm⁻¹. Heating was discontinued and the contents of the flask were cooled to room temperature. A 12.5 g quantity (105 mmoles) of thionyl chloride was added in one portion to the total polymer solution. Heating at reflux was maintained for 14 hr, after which the IR spectrum indicated the absence of free carboxyl groups (2800-3500 cm⁻¹, broad) and the reappearance of a new acid chloride absorption at 1795 cm⁻¹. Nitrogen gas was passed through the warm solution to remove the residual hydrogen

TABLE III
Wool Shrink Resistance From Acryloyl Chloride-Acrylate Ester Prepolymers Modified With Long Chain Hydroxy Acids and Thionyl Chloride^a

Polymer No.	Copolymer formulation		Ratio ^b of acrylate ester-acryloyl chloride, w/w	Polymer solution concentration, %	Polymer uptake by fabric, % by weight	Hand, ^c or feel	Shrinkage of fabric, area %
	Acrylate ester	Hydroxy acid					
8	None	None	Untreated control	...	0	5	45.4
9	<i>n</i> -Butyl acrylate	12-Hydroxystearic acid	4:1	5	4.5	2+	1.0
10	<i>n</i> -Butyl acrylate	None	4:1	3	3.1	4	3.0
				10	9.2	2	36.9
11	<i>n</i> -Butyl acrylate	12-Hydroxystearic acid	9:1	5	6.2	3-	34.5
				10	8.8	4-	16.3
				5	6.5	4	27.8
12 ^d	<i>n</i> -Butyl acrylate	12-Hydroxystearic acid	4:1	3	5.3	4+	28.7
				10	9.1	3	2.0
				5	6.0	3+	13.5
13	<i>n</i> -Butyl methacrylate	12-Hydroxystearic acid	4:1	3	4.1	4-	11.7
				10	7.7	2	0
				5	5.0	2+	0
14	<i>n</i> -Butyl acrylate	9(10)-Hydroxymethyl-stearic acid	4:1	3	4.1	3-	4.0
				10	7.4	3+	1.0
				5	4.0	4-	11.6
				3	2.6	4	26.9

^a Prepolymers were applied from perchloroethylene solution; "Accelerator" wash test was used.

^b Prior to polymerization.

^c See Table II for rating scale.

^d Polymerized undistilled monomers under air atmosphere.

chloride and the mixture was allowed to cool to room temperature. Evaluation of polymer performance on wool was determined, as previously described, after diluting the solutions to the desired concentration with technical perchloroethylene. Table III presents the shrinkage properties of wool fabric treated with polymers prepared by the acryloyl chloride copolymerization route. In a similar manner, 9(10)-hydroxymethylstearic acid was substituted for 12-hydroxystearic acid and *n*-butyl methacrylate was substituted for *n*-butyl acrylate to provide the desired types of polymers.

Results and Discussion

Acrylation of primary hydroxyaliphatic acids, such as 10-hydroxydecanoic acid and 9(10)-hydroxymethylstearic acid, with acryloyl chloride in the absence of a basic HCl-acceptor yields acryloxyaliphatic acids with negligible amounts of β -chloropropoxy ester by-products. However, acrylation of secondary hydroxyaliphatic acids, such as 12-hydroxystearic acid and ricinoleic acid, yields acrylates containing larger amounts of β -chloropropoxy derivatives. The reaction between acryloyl chloride and a hydroxy acid in the presence of an inorganic or organic HCl-acceptor resulted in formation of salts which were removed with difficulty. Treatment of the acryloxyacids with oxalyl chloride or thionyl chloride produces acryloxyacyl chlorides. Molecular distillation of crude long chain acrylic monomers is required to obtain a product suitable for copolymerization. However, the presence of β -chloropropoxy ester does not interfere with subsequent copolymerization. There is considerable loss of desired product during the distillation operation, which renders this approach unattractive. The acryloxyacyl chlorides have been copolymerized with several acrylic esters, and the deposition of these copolymers on wool produces fabrics with acceptable soft hand and durable shrink resistance (Table II, polymer Nos. 1-6). Butyl acrylate homopolymer (Table II, No. 7) containing no reactive end groups on side chains imparts no significant improvement in shrink resistance, since the polymeric coating is removed during washing. An untreated control sample of wool fabric (Table II, No. 8) shrinks at least 45% under the conditions of the wash test.

Table III contains data on the shrink resistance of wool fabric treated with similar type coatings prepared by the alternate acryloyl chloride polymerization route. The copolymers were applied at several different concentrations and the shrink resistance is comparable to the best results reported in Table II. This alternate prepolymerization synthetic route has the added economic advantage that all

reactions can be performed consecutively in a single vessel without intermediate purification. These polymers are not directly comparable to those from the same comonomers in Table II because larger proportions of hydroxyaliphatic acids are incorporated in the second set. The desirable improvements in the properties of wool treated with the reported new polymers indicate that similar improvements may be achieved in the treatment of a wide variety of other substrates such as cellulose, wood, paper, metals and plastics. The investigations are being continued to study the effects of substituting the simple acrylate ester by other acrylic and vinylic comonomers, and substituting the acyl chloride by other reactive groups.

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