

Copolymers of Vinyl Chloride and Vinylidene Chloride With Some Acid Chlorides

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Synopsis

Vinyl chloride and vinylidene chloride were copolymerized with 10-acryloxydecanoyl chloride and 12-acryloxystearoyl chloride by use of free-radical initiator in solution to obtain copolymers with active chlorine groups. Alternative routes for making such copolymers which consisted of making the corresponding acrylic acid or acrylyl chloride copolymers, followed by reaction with hydroxy acid and finally conversion to the acid chloride by treatment with thionyl chloride, were investigated. The monomer reactivity ratios for the radical copolymerization of vinyl chloride (VCl) and vinylidene chloride (VCl_2) with acrylic acid (AA) and acrylyl chloride (ACl) were determined: VCl-AA, $r_1 = 0.025$, $r_2 = 6.40$; VCl-ACl, $r_1 = 0.017$, $r_2 = 2.65$; VCl_2 -AA, $r_1 = 0.46$, $r_2 = 1.26$; VCl-ACl, $r_1 = 0.50$, $r_2 = 1.12$.

INTRODUCTION

Polymers and copolymers possessing acid chloride groups show high reactivity, which makes it possible to prepare from them many polymeric derivatives. Inclusion of only a small percentage of acid chloride in a copolymer provides sites which can be used for the attachment of grafts or crosslinking.^{1,2}

Increasing popularity of synthetic fibers in the textile industry led to expanded research for improving the properties of wool. Significant advances in solving the problem of shrinkage and pilling have now been made.³

It is the purpose of this work to describe the preparation of some acid chloride copolymers useful for application in shrinkproofing wool. The scope of the work includes the preparation of the copolymers with active chloride groups on the side chains; uses of the finished copolymers will be discussed elsewhere.⁴

EXPERIMENTAL

Materials

Vinyl chloride was commercial grade and was used without further purification.

Vinylidene chloride was distilled through a 1-ft Widmar column under nitrogen from the commercial grade immediately before use.

Acrylic acid was purified by distillation at reduced pressure.

Acrylyl chloride was freshly distilled at atmospheric pressure under nitrogen just before use.

10-Acryloxydecanoic acid and 12-acryloxystearic acid were prepared by reaction of the hydroxy acids with acrylyl chloride to give acryloxy acids. These products were treated with excess oxalyl chloride to yield the corresponding acryloxy acid chlorides.⁴

AIBN was recrystallized from methanol and then from chloroform.

All the solvents used were analytical grade and were dried and purified by the usual methods.

Copolymerization of Vinyl Monomers with Acryloxy Acid Chloride

The copolymerizations were carried out in ethylene chloride with 1% AIBN as initiator in polymerization tubes at 50°C. The required amounts of acid chloride, solvent, initiator and comonomer were placed under nitrogen in a pressure tube fitted with a neoprene-lined cap. With vinyl chloride an excess was used; the polymerization tube was chilled and some vinyl chloride was allowed to boil out, thus removing air from the vapor space. The tube was placed in a bath controlled by a thermostat within $\pm 0.1^\circ\text{C}$. After the polymerization period, the polymer solution was precipitated in a large amount of dry petroleum ether (bp 40–70°C), filtered under nitrogen atmosphere, and dried to constant weight under vacuum. The compositions of the copolymers thus obtained were determined by elemental analyses.

Acrylic Acid Copolymers

The polymerizations were carried out in dioxane under normal pressure in a three-necked flask equipped with stirrer, Dry Ice-acetone reflux condenser, and nitrogen inlet. In order to avoid heterogeneous polymers the reaction was achieved by adding the acrylic acid to the vinyl monomer solution at about the rate at which the acrylic acid is incorporated into the polymer. Thus, 300 g of vinyl chloride previously liquified in a Dewar flask was dissolved in 2 liters of dioxane and 5 g of acrylic acid and 6 g of AIBN were added. The mixture was heated to 50°C and allowed to react during the period of 30 hr. Additional 5-g portions of acrylic acid were added every 5 hr until a total of 30 g had been added. The copolymer was isolated by evaporation of the solvent. The yield was 78.9 g of copolymer, η_{inh} (30°C, ca. 0.2% solution in dioxane) 0.23, with 65.8% of vinyl chloride.

ANAL. Calcd: C, 42.39%; H, 5.10%; Cl, 37.33%. Found: C, 42.69%; H, 5.64%; Cl, 37.33%.

The preparation of acid chlorides of the acrylic acid copolymers was carried out by using a three-necked flask fitted with a well-sealed stirrer, dropping funnel, a thermometer, and a water-cooled condenser with CaCl_2 trap. The above acrylic acid copolymer (100 g) was dissolved in 500 ml of dry dioxane, and a solution composed of 200 ml of ethylene chloride and 50

ml of thionyl chloride was added dropwise during 2 hr. The mixture was allowed to react an additional 6 hr, and the excess of thionyl chloride was removed under vacuum. The yield was 108.2 g of copolymer, η_{inh} (30°C, chloroform) 0.14.

ANAL. Calcd: C, 39.88%; H, 4.25%; Cl, 49.80%; Found: C, 39.48%; H, 4.66%; Cl, 48.96%.

Acrylyl Chloride Copolymers

The same procedure described above was used, and the results are shown in Table V.

Reaction of Acrylyl Chloride Copolymers with Hydroxy Acids

The same apparatus described in the preparation of acrylic acid chlorides was used. The solution of acrylyl chloride copolymer in ethylene chloride was added dropwise to the solution of equimolar amount of corresponding hydroxy acid in dioxane at 60°C. The mixture was allowed to react under stirring while bubbling dry nitrogen through the mixture during a period of about 20 hr until no more hydrogen chloride was evolved. The copolymer thus obtained was precipitated with dry methanol.

Preparation of Acid Chlorides of the Acryloxy Acid Copolymer

The same procedure described above was used, with addition of a two-fold excess of thionyl chloride solution in ethylene chloride to the dioxane solution of acryloxy acid copolymer. The reaction was allowed to proceed under stirring while bubbling dry nitrogen through the mixture for 8 hr. The solvent was evaporated under reduced pressure and the excess of thionyl chloride was distilled off. The solvent was removed by distillation, and the polymer was washed with ethylene chloride.

RESULTS AND DISCUSSION

Copolymerization of Acryloxyacid Chlorides with Vinyl Monomers

Vinyl chloride (VCl) and vinylidene chloride (VCl_2) were copolymerized with 10-acryloxydecanoyl chloride (ADCl) and 12-acryloxystearoyl chloride (ASCl) in ethylene chloride with AIBN in polymerization tubes at 50°C. The infrared spectrum of the copolymers showed absorption at 1735 cm^{-1} due to the ester group, at 1805 cm^{-1} due to acid chloride group, and at 690 to 625 cm^{-1} due to C-Cl bond.⁶ The solubility in organic solvents (THF, chloroform, ethylene chloride) of the copolymers increased with increasing acid chloride content and the copolymers of vinylidene chloride with less than 30% acid chloride were insoluble.

The compositions of the copolymers were determined by elemental analysis (C, H, Cl). All chlorine analyses on these copolymers are in good agreement with the theoretical values, although they are consistently a few tenths of a per cent low, which might be explained by the formation of a small amount of anhydride between adjacent carboxylic acid groups.

TABLE I
 Copolymerization of Vinyl Chloride with 10-Acryloxydecanol Chloride (ADCl) and
 12-Acryloxystearoyl Chloride (ASCl) in Solution at 50°C^a

Run no.	VCl, %	Comonomer		Polymerization time, hr	Conversion, %	Cl found, %	Copolymer		
		Type	%				VCl, %	Comonomer, %	η_{inh}^c
1	90	ADCl	10	22	58.0	49.52	83.00	17.00	0.25
2	70	ADCl	30	25	53.8	32.82	46.30	53.70	0.18
3	50	ADCl	50	45	75.6	28.69	35.28	64.72	0.16
4	30	ADCl	70	45	62.1	16.42	7.87	92.13	0.15
5	80	ASCl	20	25	62.2	44.76	75.10	24.90	0.24
6	70	ASCl	30	40	54.8	39.92	65.90	34.10	0.18
7	60	ASCl	40	40	47.7	38.13	61.64	38.35	0.17
8	20	ASCl	80	70	34.2	10.82	5.97	94.03	0.19

^a The polymerizations were conducted in 50 ml of ethylene chloride at 50°C with the use of 1% AIBN and 10.0 g of comonomers.

^b Based on carbon, hydrogen, and chlorine analysis.

^c Viscosities were determined on ca. 0.2% chloroform solutions at 30°C.

TABLE II
Copolymerization of Vinylidene Chloride with 10-Acryloxydecanoyl Chloride and
12-Acryloxyoctadecanoyl Chloride in Solution at 50°C^a

Run no.	VCl, %	Comonomer		Polymerization time, hr	Conversion, %	Cl, %	Copolymer		
		Type	%				VCl, %	Comonomer, %	η_{inh}^e
1	80	ADCl	20	23	42.5	52.44	65.00	35.00	— ^d
2	70	ADCl	30	10	30.3	43.18	50.96	49.04	0.14
3	70	ADCl	30	45	73.0	51.67	64.18	35.82	0.12
4	60	ADCl	40	45	67.2	45.59	54.00	46.00	0.20
5	70	ASCl	30	70	64.4	55.13	72.60	27.40	0.12
6	60	ASCl	40	70	54.9	50.19	64.62	35.38	0.14
7	50	ASCl	50	92	51.1	43.77	54.47	45.53	0.15
8	40	ASCl	60	92	43.2	37.28	44.43	55.57	0.16

^a The polymerizations were conducted in 50 ml of ethylene chloride at 50°C with the use of 1% AIBN and 10.0 g of comonomers.

^b Based on carbon, hydrogen, and chlorine analyses.

^c Viscosities were determined on ca. 0.2% chloroform solutions at 30°C.

^d Insoluble copolymer was obtained.

The polymerization conditions, the compositions and the inherent viscosity of the copolymers are shown in Tables I and II.

The high reactivity of acid chloride groups toward water made it necessary to keep all materials anhydrous before, during, and after polymerization.

Determining the Reactivity Ratios

To better understand the course of copolymerization, the monomer reactivity ratios have been determined. The copolymerization of vinyl chloride and vinylidene chloride with acrylic acid were carried out in polymerization tubes in about 20% solution in dioxane at 50°C with the use of AIBN as the initiator. Obtained polymers were precipitated in petroleum ether. Reactivity ratios calculated by the method of Fineman and Ross⁶ from the analytical data, are: VCl-AA, $r_1 = 0.025$, $r_2 = 6.40$; VC12-AA, $r_1 = 0.46$; $r_2 = 1.26$. Results are presented in Tables III and IV.

Monomer reactivity ratios of acrylyl chloride have been determined in ethylene chloride solution using 0.5% AIBN and using the same procedure as described above. Since the vinyl chloride-acrylyl chloride copolymers very easily undergo hydrolysis, the copolymer compositions were obtained from the analytical data of completely hydrolyzed products. The hydrolyses have been done in dioxane with about 20% of water in which solvent the vinyl chloride-acrylyl chloride copolymers are not soluble, and hydrolyzed product is completely soluble. The reactivity ratios are: VCl-ACl, $r_1 = 0.017$, $r_2 = 2.65$; VCl₂-ACl, $r_1 = 0.50$, $r_2 = 1.12$, and the analytical data are presented in Tables V and VI.

TABLE III
Copolymerization of Vinyl Chloride (M₁) and Acrylic Acid (M₂)

Run no.	Molar ratio M ₁ /M ₂ in feed	Conversion, %	Cl in copolymer, %
1	0.493	14.0	3.32
2	0.768	10.0	4.75
3	1.15	8.5	6.94
4	1.73	4.9	9.32
5	2.68	4.0	11.68

TABLE IV
Copolymerization of Vinylidene Chloride (M₁) and Acrylic Acid (M₂)

Run no.	Molar ratio M ₁ /M ₂ in feed	Conversion, %	Cl in copolymer, %
1	0.318	7.3	17.38
2	0.494	7.1	23.20
3	0.743	3.2	29.38
4	1.115	3.0	36.72
5	1.735	3.0	41.52
6	2.967	2.5	50.42

TABLE V
Copolymerization of Vinyl Chloride (M_1) and Acrylyl Chloride (M_2)

Run no.	Molar ratio M_1/M_2 in feed	Conversion, %	Cl in copolymer, % ^a
1	0.62	3.0	7.34
2	0.97	4.4	13.68
3	2.17	6.1	16.30
4	3.37	6.7	19.15
5	5.80	8.9	22.43

^a Found in hydrolyzed product.

TABLE VI
Copolymerization of Vinylidene Chloride (M_1) and Acrylyl Chloride (M_2)

Run no.	Molar ratio M_1/M_2 in feed	Conversion, %	Analyses		
			C, %	H, %	Cl, %
1	0.233	7.1	37.38	3.40	45.36
2	0.467	9.3	35.63	3.14	48.31
3	0.622	9.9	34.85	3.12	49.91
4	0.777	8.1	34.26	3.15	52.50
5	1.404	9.2	32.33	2.92	56.49
6	2.178	9.5	31.40	3.05	60.04

Preparation of Acryloxy Acid Chloride Copolymers from Acrylyl Chloride Copolymers

Under the conditions described in the Experimental Section and results shown in Tables VII and VIII, conversion of the acrylyl chloride copolymers to the corresponding acryloxy acid chloride copolymers proceeded according to the scheme of eqs. (1).

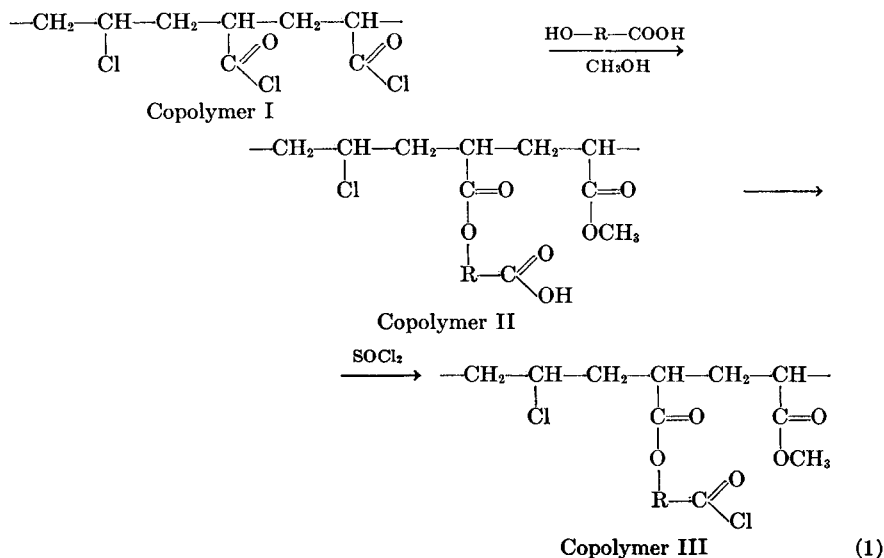


TABLE VII
Preparation of Acrylyl Chloride Copolymers (Copolymer I)^a

Run no.	ACl, %	Polymeriza- tion		Conversion, %	ACl, % ^b	Comonomer, %	Copolymer I				
		Type	%				η_{inh}^c	Analysis			
								C, %	H, %	Cl, %	
1	10	VCl	90	40	58.5	16.15	83.85	0.26	38.24	4.64	53.30
2	30	VCl	70	70	94.5	31.35	68.65	0.40	38.58	4.57	50.84
3	20	VCl	80	75	83.2	23.70	76.30	0.35	38.60	4.55	52.35
4	25	VCl	75	75	81.1	29.68	70.32	0.41	38.97	4.54	51.73
5	20	VCl	80	65	65.5	31.12	68.88	0.34	38.66	4.45	51.00
6	30	VCl	70	75	76.3	36.27	63.73	0.30	40.04	4.29	49.92
7	10	VCl ₂	90	90	62.8	15.38	84.62	0.35	27.23	2.37	68.38
8	40	VCl ₂	60	115	92.6	42.93	57.07	0.23	31.39	2.77	59.06

^a The polymerizations were carried out in 50 ml ethylene chloride at 50°C with the use of 1% AIBN and 10.0 g of comonomers.

^b Based on carbon, hydrogen, and chlorine analyses.

^c Viscosities were determined on ca. 0.2% chloroform solutions at 30°C.

TABLE VIII
Preparation of Acryloxy Acid Chloride Copolymers (Copolymer II and III)

Run no.	Copolymer II						Copolymer III		
	Comonomer		Hydroxy acid type	DS	Analysis		η_{inh}^b	Cl found, %	η_{inh}^c
	Type	% ^a			C, %	H, %			
1	VCl	69.45	HDA	81.3	45.80	6.07	0.40	42.02	0.56
2	VCl	57.97	HDA	47.8	48.17	6.39	0.41	36.34	0.40
3	VCl	51.91	HSA	79.1	53.09	7.60	0.48	33.07	0.55
4	VCl	42.85	HSA	84.7	57.58	8.52	0.43	25.65	0.47
5	VCl	47.49	HSA	66.4	54.43	7.72	0.24	29.16	0.39
6	VCl	38.67	HSA	77.5	58.22	8.44	0.35	26.67	0.41
7	VCl ₂	74.35	HDA	60.7	33.21	3.65	0.39	55.15	0.66
7d	VCl ₂	77.07	HSA	30.5	32.38	3.31	0.38	57.10	0.48
8	VCl ₂	53.45	HDA	19.3	40.26	4.68	0.42	40.34	0.38
8d	VCl ₂	50.06	HSA	25.0	42.77	5.29	0.53	37.88	0.40

^a Calculated from the chlorine analysis.

^b Determined on ca. 0.2% dioxane solution at 30°C.

^c Determined on ca. 0.2% chloroform solution at 30°C.

^d Prepared from samples 7 and 8 respectively, Table VII.

To prepare the corresponding acryloxyacid chloride copolymers with vinyl chloride or vinylidene chloride, the first step was to prepare the acrylyl chloride copolymers.^{8,9} As shown in the Experimental Section, such copolymers could be prepared from the acrylic acid copolymers or directly from the acrylyl chloride. As the chemical reactions on the polymers usually do not proceed quantitatively we report here the results obtained starting with acrylyl chloride copolymers. The high reactivity of acid chloride groups toward water made it necessary to keep all material anhydrous before, during and after polymerization. Acrylic anhydride would be formed by the reaction of acrylyl chloride and acrylic acid from the hydrolysis of the acid chloride and would result in anhydride-crosslinked, usually insoluble copolymers. The acrylyl chloride copolymers were obtained in ethylene chloride at 50°C, using AIBN as initiator. The polymerization condition, the inherent viscosity, the compositions of the copolymers and the analytical data are shown in Table VII.

The reaction of acrylyl chloride copolymers with the hydroxy acids was carried out by adding dropwise the ethylene chloride solution of the copolymer to the dioxane solution of the corresponding hydroxy acid. The copolymer obtained was precipitated with methanol to remove the excess of the hydroxy acid. The results (Table VIII, copolymer II) showed that the reaction led to formation of acryloxy acid copolymers in good yield when vinyl chloride copolymers were used. The conversion of vinylidene chloride-acrylyl chloride copolymer is less successful as the obtained degree of substitution (DS) is lower.

The degree of conversion of acrylyl chloride to the acryloxy acid expressed as number of substituted acrylyl units per hundred acrylyl units was calculated from the per cent of vinyl chloride (vinylidene chloride) in the copolymer according to the following formula:

$$DS = [(VCl_I - VCl_{II})/VCl_I - VCl_{III}] \times 100$$

where VCl_I denotes the percentage of vinyl chloride with no substitution, VCl_{II} denotes the percentage of vinyl chloride found, and VCl_{III} denotes the percentage of vinyl chloride in the case of complete conversion of acrylyl chloride to corresponding acryloxy acid.

The chlorination of copolymer¹⁰ prepared in this way was performed by adding a thionyl chloride solution in ethylene chloride to the dioxane solution of the vinyl chloride acryloxy fatty acid copolymer.

Acid chloride copolymers thus obtained usually showed higher inherent than the starting acrylyl chloride copolymers, probably due to formation of some acid anhydride connections between the chains.

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