

## Mechanical Properties and Transition Temperatures of Copolymers of *N-n*-Alkylacrylamides and Vinylidene Chloride

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### Synopsis

Mechanical and solution properties, melting transitions, torsional stiffness temperatures,  $T_f$ , and selected modulus-temperature curves are presented for copolymers of the *N-n*-alkylacrylamides with vinylidene chloride. Copolymers were prepared at 60°C across the range of compositions using as comonomers *N-n*-butyl-, octyl-, dodecyl- and oleyl-acrylamide, which have amorphous side-chains, and *N-n*-octadecyl acrylamide and *n*-octadecyl acrylate whose side-chains are crystalline. The mechanical properties reflected the effect of the decline in backbone crystallinity and the simultaneous development of strong intermolecular interactions in the amorphous stage. Copolymers were stiff or showed brittle failure across the compositional range except when intermolecular forces were reduced (with *n*-octadecyl acrylate) and side-chain crystallization eliminated (with *N*-oleylacrylamide). These systems and the *n*-dodecylacrylamide copolymers had yield strengths less than brittle strengths and substantial elongations. Backbone crystallinity was eliminated at about 15 mole % amide and side-chain crystallinity vanished at less than 10 mole % of the amide in the *N-n*-octadecylacrylamide series. No depression in side-chain melting point occurred with dilution by segments of vinylidene chloride. Over-all decline in the flex-temperature was the normal monotonic function of composition except that values increased in magnitude at high vinylidene chloride contents, the effect presumably being caused by the presence of crystallinity. An empirical equation was developed which permitted the calculation of  $T_f$  for any *N-n*-alkylacrylamide composition with any number of carbon atoms in the side-chain, above 3.

### INTRODUCTION

Little attention has been given to copolymers incorporating the higher *N-n*-alkylacrylamides except for the determination of their monomer reactivity ratios.<sup>1,2</sup> Modification of the physical properties of polyacrylonitrile by these comonomers<sup>3</sup> resulted in lowered glass temperatures, but brittle failure persisted, introduced by strong polar intermolecular interactions. This effect was aggravated by side-chain crystallization, when the side-chains had 18 carbon atoms. Polyacrylonitrile is composed of

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stiff chains and consequently has high glass and melting transitions of respectively, 104° and 317°C.<sup>4</sup> Polyvinylidene chloride, on the other hand, is composed of flexible chains in the amorphous stage ( $T_g = -17^\circ\text{C}$ ),<sup>4</sup> but its chain-segments pack readily, leading to crystallinity levels of 43%<sup>5</sup> and a  $T_m$  of 198°C.<sup>4</sup> Consequently the homopolymer is rigid and somewhat brittle. External plasticization is difficult because of the high crystallinity levels,<sup>6</sup> only the amorphous regions accepting the plasticizer. Because of this, it is usual to lower the crystallinity and melting point of polyvinylidene chloride by copolymerization,<sup>7</sup> often with vinyl chloride<sup>5,6,8</sup> or the lower acrylates.<sup>9</sup> Use of the higher acrylate esters<sup>10</sup> has yielded tough, highly flexible, resilient films, flexibility increasing with increase in the side-chain length of the acrylate ester. Vinylidene chloride copolymers are excellent gas and water barriers,<sup>8,11,12</sup> those employing comonomers with long side-chains finding use in both supported<sup>13-15</sup> and unsupported films.<sup>16-18</sup>

In this paper are presented preliminary data on the mechanical and thermal properties, together with the glass and selected melting transitions, for copolymers of vinylidene chloride with respectively, the *N-n*-butyl, octyl, dodecyl, octadecyl, oleylacrylamide and *n*-octadecyl acrylate, over the range of compositions. A broad range of composition was expected to gradually reduce crystallinity levels in the backbone,<sup>5,7</sup> while chain-stiffening through hydrogen bonding was continuously being increased. Effects on properties of amorphous side-chains (*n*-butyl, octyl, dodecyl and oleyl) could be compared with results for comonomers having crystalline side-chains (*N-n*-octadecyl acrylamide and *n*-octadecyl acrylate). Finally, effects of side-chain length and state of order could be compared with respect to the magnitude of glass temperature reduction. Of special significance should be the reduction in  $T_g$  by the three  $C_{18}$  comonomers whose homopolymers have been shown to have a common  $T_g$  of about  $-111^\circ\text{C}$ .<sup>3</sup> This temperature almost coincides with the well known  $\gamma$  transition, which has its origins in alkyl subgroup and polyethylene in-chain motions.<sup>19</sup> Consequently a glass temperature of  $-111^\circ\text{C}$  seems to represent the lower limit of vitrification temperature.<sup>3</sup>

## EXPERIMENTAL

### Materials

**Amines.** The amines, the purest available commercially (99% except oleyl, 97.7%) were used directly.

**Acryloyl Chloride.** A commercial product, bp 75°C at 760 mm, was used without purification.

***N-n*-Alkylacrylamides and *n*-Octadecyl Acrylate.** The preparation and purification of *N-n*-butyl-, *n*-octyl-, and *n*-octadecylacrylamide has been described.<sup>3</sup> *N-n*-Dodecylacrylamide was prepared<sup>3</sup> and the crude mixture of amide and salt were isolated by evaporation of the benzene, salt was removed by treating the residue with skellysolve B, removing the residual

salt by washing this solution twice with 10% sodium carbonate, then water until neutral; the amide was isolated by crystallization at 0°C. Recrystallization from acetone (10 ml/g) at -20°C gave the pure amide in 71.1% yield; acid number 0, mp 57-58.5°C, % carbon, calc., 75.23, found 75.24; % hydrogen, calc., 12.23, found 11.77; purity by gas-liquid chromatography, 99%. *N*-Oleylacrylamide was prepared<sup>3</sup> and the crude reaction product was dissolved in skellysolve B (3 ml/g) and washed cautiously (to prevent emulsions) with two 10% HCl washes (1 ml/ml), freed of acid and washed twice with 10% sodium carbonate; freed of alkali, and the solvent removed. Crystallization from acetone (3 ml/g) at -20°C gave the amide in 53% yield, acid number 0.27; % carbon, calc. 78.44, found 78.51; % hydrogen, calc. 12.23, found 12.21; purity by gas-liquid chromatography, 96%. The infrared spectrum showed that the amide was the equilibrium mixture of *cis* and *trans* isomer, isomerization apparently occurring during the acylation because the amine used was almost pure oleylamine. *n*-Octadecyl acrylate was obtained under special purchase from Monomer-Polymer Corporation and its physical properties have been described.<sup>10</sup> It was 95% pure by gas-liquid chromatography, with the main impurities being the lower homologs.

### Polymerization Procedure

All of the copolymers through a composition of 25 mole % of amide (or ester) were copolymerized in dispersion, in capped bottles under nitrogen, by tumbling them for 24 hr at 60°C. A 0.5% polyvinyl alcohol solution (2 ml/g based on total monomer) containing 1.5 wt % of powdered magnesium carbonate (based on water) was used as the dispersing agent. The initiator was 0.1 mole % benzoyl peroxide, based on monomer and dispersions were generally of good quality. The balance of the copolymers were prepared in *t*-butanol (4 moles of solvent per 1 mole of total comonomer), except for *n*-octadecyl acrylate which was prepared in benzene, using a 1 to 1 ratio. Benzoyl peroxide, 0.2 mole %, based on total comonomers, was employed as the initiator for the amides, except for the *N*-*n*-octadecylacrylamide series, (where 0.4 mole % was used) and bis-azo-isobutyronitrile (0.5 mole %) was employed as the initiator for the ester. All polymerizations were run for 48 hr at 60°C, except for the *n*-octadecyl acrylate series which was run for 72 hr. The purification of the dispersed copolymer was as described,<sup>10</sup> but the skellysolve treatment was omitted and 1 hour methanol extractions were used. The solution copolymers were isolated by precipitation into methanol and extracted in batches (5 ml/g) in the refluxing methanol till free of all monomer. Exceptions were the *n*-butylacrylamide copolymers of compositions greater than 25 mole % of the butylamide which were treated with a mixture of petroleum ether, 80 and ethyl ether, 20. All copolymers were dried to constant weight in thin layers under vacuum. The *N*-oleylacrylamide copolymers were lightly crosslinked; the sol-fraction was about 50%.

TABLE I  
Composition, Solution Properties, and Thermogravimetric Properties of Copolymers of Vinylidene Chloride and *N-n*-Alkylacrylamides

Copolymer	Amide content				Yield, %	Osmometric mol. wts.		Thermogravimetric data	
	Monomer mix., mole %	Copolymer		$\bar{M}_n$		$\bar{DP}_n$	Onset of decomp., °C	Onset of decomp., °C	
		Mole %	Wt %						
<i>N-n</i> -Butylacrylamide	0	0	0	0	95.2	—	—	195	210
	5	5.22	6.74	6.74	82.4	—	—	168	177
	7.5	9.23	11.77	11.77	79.8	—	—	140	165
	10	14.50	18.20	18.20	86.3	87,450	863	140	16
	12.5	13.75	17.30	17.30	90.9	67,850	671	—	—
	15	17.17	21.38	21.38	92.4	129,950	1272	140	163
	25	28.66	34.52	34.52	96.3	132,650	1256	141	162
	35	42.17	48.90	48.90	90.0	—	—	130	142
	50	56.93	63.43	63.43	79.0	—	—	138	148
	75	77.00	81.45	81.45	77.0	—	—	129	155
	5	7.10	11.61	11.61	74.2	—	—	169	182
	<i>N-n</i> -Octylacrylamide	7.5	9.22	16.12	16.12	94.0	76,850	733	140
10		11.25	19.34	19.34	91.9	81,950	768	157	172
12.5		13.77	23.20	23.20	91.4	92,350	848	—	—
15		19.09	30.85	30.85	92.1	118,400	1044	158	170
25		27.57	41.85	41.85	95.3	125,600	1040	165	172
35		40.16	55.94	55.94	82.0	62,100	472	160	166

<i>N-n</i> -Dodecylacrylamide									
50	56.99	71.48	83.0	106,500	729	153	164		
65	69.21	80.96	94.0	144,500	922	149	165		
75	77.97	87.00	95.0	228,200	1389	150	167		
5	7.17	16.01	68.4	74,900	699	170	185		
7.5	9.79	21.15	85.6	51,600	465	—	—		
10	12.23	25.59	95.8	151,500	1325	162	174		
12.5	15.11	30.54	96.4	—	—	165	175		
15	17.81	34.87	97.0	124,700	1019	160	169		
25	27.34	48.17	98.6	146,400	1047	150	163		
35	46.97	68.63	51.2	59,200	361	158	161		
50	59.80	78.50	57.9	77,700	503	164	169		
65	72.52	86.70	67.9	115,200	575	167	173		
75	80.77	91.21	77.6	147,100	694	165	175		
100	100.0	100.0	91.0	420,000	1754	185	230		
<i>N-n</i> -Octadecylacrylamide									
5	6.89	19.81	58.6	75,950	675	183	188		
7.5	9.59	26.14	68.8	126,800	1069	167	179		
10	11.82	30.91	74.3	149,300	1207	170	179		
12.5	14.64	36.39	89.7	150,700	1158	155	174		
15	18.82	43.82	94.1	162,900	1167	165	175		
25	34.91	64.15	66.9	172,200	978	158	169		
35	42.70	71.32	86.0	72,200	373	155	160		
50	59.50	86.06	77.0	133,000	574	155	163		
65	71.43	89.30	92.0	98,600	381	161	167		
75	80.50	93.23	93.0	294,200	1053	150	165		

(Continued)

TABLE I (continued)

Copolymer	Amide content				Yield, %	Osmometric mol. wt.		Thermogravimetric data	
	Monomer mix., mole %	Copolymer		$\bar{M}_n$		$\bar{DP}_n$	Onset of decomp., °C	Onset of decomp., °C	
		Mole %	Wt %						
N-Oleylacrylamide	5	8.41	23.34	45.3	(62,200) <sup>a</sup>	—	135	165	
	7.5	10.72	28.47	43.3	—	—	—	—	
	10	13.78	34.64	43.9	(36,250) <sup>a</sup>	292	141	165	
	12.5	17.64	41.53	44.1	(35,950) <sup>a</sup>	271	—	—	
	15	21.20	47.16	33.8	(38,150) <sup>a</sup>	275	137	159	
	25	25.81	53.57	32.7	(55,750) <sup>a</sup>	291	124	145	
	35	34.71	57.30	71.2	40,600	170	115	135	
	100	100.0	100.0	96.0	(50,600) <sup>a</sup>	157	139	139	
	n-Octadecyl acrylate	5	4.90	14.70	90.3	—	—	—	—
		7.5	7.56	21.48	87.6	—	—	—	—
10		9.86	26.80	88.1	128,650	1078	—	—	
12.5		12.33	32.01	91.6	116,300	930	—	—	
15		15.18	37.47	92.1	119,050	905	—	—	
20		20.02	45.59	92.1	126,250	886	—	—	
30		31.93	61.09	92.4	71,550	422	—	—	
40		40.02	69.08	95.2	77,000	409	—	—	
50		51.64	78.14	97.2	100,050	466	—	—	
60		61.51	84.25	97.0	124,950	527	—	—	
75	74.92	90.91	99.8	—	—	—	—		

<sup>a</sup>  $\bar{M}_n$  in parentheses determined in another copolymer series prepared using the same experimental conditions. The 35 mole % copolymer in this other series had a molecular weight of 37,800.

### Mechanical Properties

Test specimens were prepared by molding small samples between chrome plates protected by cellophane at temperatures between 140°F and 310°F and pressures of 20 to 50 tons. No additives were added; color ranged from amber to clear. All specimens were equilibrated at 23°C and 50% R.H. for at least 1 week, far in excess of the time necessary to develop full crystallinity in both backbone and side-chain.<sup>6,20,21</sup> The tensile data was obtained with the use of an Instron tensile tester and the ASTM procedure for rigid materials (D638-61T). Flexural data were obtained using an Instron tensile tester with a flexural accessory according to the ASTM procedure D790-61. Flexural strengths were measured at 5% strain. Torsional stiffness temperatures were determined by the method of Clash and Berg, ASTM standards designation D1043-61T.

### Melting Temperatures, Thermogravimetric Data and Solution Properties

The procedures and instruments have been described.<sup>3</sup> The solvent for osmometry was usually toluene. Dioxane was used for the following through the listed mole fraction feed compositions; *N-n*-dodecyl, 0.125; octyl and butyl, 0.25; oleyl, 0.05.

### Calculations by Computer

The parameters of eqs. (1), (4) and (5) were evaluated by an IBM 1130 computer using program designation VGM58 and were generally carried through 5 degree polynomials. Programs for the remaining calculations were written for insertion in a general calculation sub-routine designated QREAD.

## RESULTS AND DISCUSSION

### Copolymer Compositions, Thermal and Solution Properties

In Table I are listed the compositions, conversions, solution properties and thermogravimetric data for all of the copolymers studied in this investigation. While conversions were high, the reactivity ratios of *N-n*-octadecylacrylamide ( $M_1$ ) and vinylidene chloride ( $M_2$ )<sup>1</sup> ( $r_1 = 1.37$ ,  $r_2 = 0.44$ ), indicated only gradual compositional drift with conversion for this system and its homologs. This was confirmed by a determination of the heterogeneity index by light scattering of one *N-n*-octadecylacrylamide-vinylidene chloride copolymer,<sup>22</sup> where the mole fraction of amide in the feed was 0.25. In general, the degree of polymerizations ( $\overline{DP}_n$ ) were higher than the critical level affecting mechanical properties.<sup>23</sup> Mechanical properties appear to depend on an average between weight and number-average molecular weight.<sup>23</sup> In the light scattering determination just described,  $\overline{M}_w$  was accurately 662,000 and  $\overline{M}_w/\overline{M}_n$  was 3.9.<sup>22</sup> Polydispersity indices by gel permeation chromatography for selected *N-n*-octa-

TABLE II  
 Mechanical Properties and Torsional Modulus  $T_t$ , Temperatures of the Copolymers of Vinylidene Chloride and the  $N$ - $n$ -Alkylacrylamides

Copolymer	Acrylamide in copolymer mole %	Tensile properties			Flexural properties			Clash berg $T_t$	
		Strength, psi	Modulus, psi	Elongation, %	Strength, psi	Modulus, psi	Found	Calc. <sup>a</sup>	
<i>N</i> - <i>n</i> -Butylacrylamide	0	1270	96,000	0	3650	197,000	—	—	
	5.2	2830	103,600	10	1875	103,800	41	64	
	9.2	2690	71,300	20	1450	82,400	27	62	
	14.5	2740	46,100	65	1350	71,700	14	59	
	13.8	3000	38,800	75	1100	55,200	16	59	
	17.2	3580	49,700	30	1100	58,100	18	58	
	28.7	4180	114,100	3	2440	135,000	46	53	
	42.2	1500	63,400	20	1600	88,000	39	47	
	56.9	2250	99,800	4	1830	99,500	41	42	
	77.0	2870	93,100	3	1600	96,000	30	36	
100.0	—	—	—	—	—	46	32		
<i>N</i> - <i>n</i> -octylacrylamide	7.1	1650	112,500	1	1940	90,700	30	20	
	9.2	2990	45,700	10	875	48,000	11	18	
	11.3	1660	44,900	20	690	39,400	10	15	
	13.8	1370	27,500	30	390	21,700	-6	13	
	19.1	1720	11,500	350	330	20,000	-1	7	
	27.6	2440	59,500	10	930	48,500	-1	-1	
	40.2	2270	47,100	6	960	54,400	-20	-13	
	57.0	2850	50,400	10	860	46,800	-22	-26	
	69.2	2500	41,000	10	660	36,100	-40	-35	
	78.0	1860	49,200	10	630	31,000	-53	-41	
100.0	—	—	—	—	—	-53	-53		



<i>N-n</i> -Dodecylacrylamide	7.2	4020	83,300	30	1070	55,500	1	3
	9.8	2860	24,300	20	460	24,300	-6	-1
	12.2	2000	23,400	325	320	18,000	-8	-5
	15.1	1420	14,300	290	150	8,700	-17	-9
	17.8	1330	1,830	300	10	500	-21	-13
	27.3	1050	11,150	340	170	8,500	-41	-26
	47.0	1420	32,900	5	390	21,700	—	—
	59.8	1400	35,900	5	470	21,700	-67	-57
	72.5	930	27,700	5	330	18,000	-70	-64
	80.8	990	24,000	5	300	17,500	-68	-68
	100.0	670	23,300	5	370	15,700	-75	-72
	6.9	1500	54,000	3	900	51,200	10	-11
	9.6	1550	35,300	10	680	35,900	-3	-17
11.8	1910	24,800	30	500	27,600	-11	-22	
14.6	1940	25,700	10	420	23,300	-20	-28	
18.8	2750	42,100	15	460	25,500	-16	-37	
34.9	1770	54,500	4	575	34,900	-37	-65	
42.7	400	34,700	2	460	27,800	-54	-75	
59.5	410	34,500	2	610	37,000	-43	-94	
71.4	460	32,100	2	710	42,000	-62	-103	
80.5	560	31,900	2	610	36,500	-72	-107	
100.0	150	28,400	—	540	32,500	-99	-111 <sup>b</sup>	

(continued)

TABLE II (continued)

Copolymer	Acrylamide in copolymer mole %	Tensile properties			Flexural properties			Clash berg $T_f$	
		Strength, psi	Modulus, psi	Elongation, %	Strength, psi	Modulus, psi	Found	Calc. <sup>a</sup>	
N-Oleylacrylamide	8.4	2370	21,600	30	430	25,900	-12	-15	
	10.7	2530	14,200	10	125	7,500	-15	-20	
	13.8	1490	7,480	90	75	4,100	-32	-26	
	17.6	425	1,130	100	30	1,400	-37	-34	
	21.2	450	700	400	10	440	-50	-41	
	25.8	525	2,400	140	20	800	-70	-50	
	34.7	345	2,240	80	10	500	-85	-64	
	100.0	550	3,500	40	110	5,700	-97	-111 <sup>b</sup>	
	n-Octadecyl acrylate	4.9	2340	52,400	10	700	36,600	-4	-6
		7.6	2340	19,000	35	275	17,400	-22	-13
9.9		1570	12,400	315	170	11,200	-18	-18	
12.3		1150	7,900	235	100	5,960	-22	-23	
15.2		550	3,300	280	45	2,600	-20	-20	
20.0		325	3,140	720	28	1,700	-18	-39	
31.9		350	11,450	3	175	11,150	-52	-59	
40.0		135	21,100	1	530	33,600	-47	-72	
51.6			Too brittle to test		690	39,600	-60	-86	
61.5			Too brittle to test		630	36,900	-69	-95	
74.9		Too brittle to test		790	46,900	-75	-105		
100.0		Too brittle to test		—	—	-111 <sup>b</sup>	-111 <sup>b</sup>		

<sup>a</sup> Using eq. (6).<sup>b</sup>  $T_f$  from reference 3.

decylacrylamide-vinylidene chloride copolymers were: feed composition as mole fraction, index; 0.10, 4.6; 0.25, 5.4; 0.50, 5.3; 0.75, 7.4. It was concluded that while compositional distributions were fairly narrow for these systems, molecular weight distributions were broad.

Temperatures of 1% decomposition (Table I, last column) were low and were generally insensitive to the length of the alkyl side-chain. On this basis segmental distribution seems to affect decomposition temperature more than other factors, the distribution of segments being similar for the comonomers regardless of side-chain length. Color present in the molded sheets at high vinylidene chloride compositions suggests that blocks of 5 or more conjugated units appear in these copolymers.<sup>9</sup> It is not known why the temperature of decomposition dropped somewhat at the higher amide levels. The amides had been found to have good thermal properties<sup>3</sup> as homopolymers.

### Mechanical Properties

Tensile and flexural strengths and their moduli, % elongations, and torsional stiffness temperature,  $T_f$ , are listed in Table II for all copolymers. In general, the strengths and moduli in tensile and flexure decreased for each system as the length of the side chain increased. The oleyl and *n*-dodecylacrylamide copolymers (where side-chain crystallinity was absent) and the *n*-octadecyl acrylate copolymers (where reductions in intermolecular interactions occurred) were flexible. Most of these copolymers had yield strengths less than brittle strengths over a wide composition range and substantial elongations. The *N*-*n*-butyl, octyl and octadecyl copolymers were stiff and many compositions showed brittle failure. Presumably this was caused by hydrogen bonding and side-chain crystallinity increasing stress concentration beyond a critical level. This behavior had been found to a greater extent with these same comonomers and acrylonitrile.<sup>3</sup>

Within each system, tensile and flexural strengths dropped steadily, reaching the low values of waxes for the two systems having a saturated side-chain length of 18 carbon atoms. Tensile and flexure moduli generally went through a minimum between 10 and 20 mole % of amide. This minimum would seem to reflect the decline in backbone crystallinity and lowered  $T_g$  and the corresponding increase in stiffness through hydrogen bonding and (where present) side-chain crystallinity as composition changes. Even the flexible copolymers (those containing dodecyl- and oleylacrylamide and octadecyl acrylate) developed weakness at high amide contents.

### Crystalline Melting Transitions

Differential scanning calorimetry was used to monitor the side-chain melting transitions of all of the amide copolymers; backbone melting temperatures were determined for the *N*-*n*-octadecylacrylamide system, only. Side-chain melting transitions,  $T_m$ , for the *N*-*n*-octadecylacrylamide

copolymers were: mole fraction of amide in the feed,  $T_m$  °C; 0.75, 45°; 0.65, 48°; 0.50, 49°; 0.35, 46°; 0.25, 49°; 0.15, 54°; 0.125, 48°; 0.10, 49°. Thus no melting point depression was found through a vanishing peak area below 10 mole % amide. This indicates that the size of the chlorine sub-groups were ineffective in reducing crystallite sizes<sup>7</sup> even when the side-chains were no longer the continuous phase. The side-chain melting point of poly-octadecyl acrylate was also about 50°C. This again demonstrates the structural insensitivity of the side-chain melting transition for the linear 18 carbon alkyl group<sup>3</sup> and implies that blocks of methylene segments of fairly constant average length are present in the side-chain crystals.

Backbone melting temperatures of the vinylidene chloride segments (a second peak in DSC) for the copolymers incorporating *N-n*-octadecylacrylamide were: mole fraction of amide in the feed,  $T_m$  °C; 0.05, 157°; 0.075, 103°; 0.10, 106°; 0.125, 103°; 0.15, 105°. The disorderly nature and extent of depression of the melting transition from the value for pure polyvinylidene chloride, 198°C, did not reflect the normal mole fraction dependence found for random copolymers.<sup>7</sup> Reasons for this behavior are unknown. On the basis of peak area disappearance, these copolymers, below 85 mole % vinylidene chloride, were amorphous as to backbone crystalline order. Crystalline order was destroyed at a much lower comonomer composition than was found for Saran copolymers,<sup>5</sup> where crystallinity was retained to a composition below 0.56 mole fraction of vinylidene chloride. However, it has been noted that Saran copolymers have a tendency to form in blocks<sup>5,24</sup> and therefore would retain their crystallinity over a wider range of composition.<sup>7</sup> It is pertinent that copolymers of vinylidene chloride (80 mole %) and acrylonitrile (20 mole %), whose copolymerization parameters predict greater randomness than for Saran type copolymers, were found to be amorphous.<sup>25</sup>

No side-chain melting was found for any of the copolymers including those containing *N-n*-dodecyl- and oleylacrylamide from -80°C through 80°C. This finding for the *N*-oleylacrylamide is especially noteworthy. The presence of the double bond in the 9-10 position appears to be all that is required to eliminate side-chain ordering. However, the oleylacrylamide used in these experiments was the equilibrium *cis-trans* mixture. The occurrence of both configurations may act to depress melting to lower temperatures than would be found for either pure geometric configuration. However, melting points for the mixed *cis-trans* butadienes lie between the melting points for each comonomer,<sup>26</sup> suggesting that the amorphous state for either oleyl or elaidyl side-chains is a characteristic property.

### Torsional Modulus and Flex Temperatures

The flex temperatures,  $T_f$ , for all of the copolymers are listed in Table II. The flex temperature is the value of Young's modulus at 135,000 lbs in.<sup>-2</sup> ( $0.9308 \times 10^{10}$  dynes cm.<sup>-2</sup>). In this work it was obtained as the 5 sec shear modulus,  $\log 3G$ ,<sup>5</sup> using the Clash-Berg torsional modulus apparatus.

It is close to the glass temperature,  $T_g$ , ( $10^{10}$  dynes  $\text{cm}^{-2}$ )<sup>27</sup> for amorphous polymers and copolymers. The found values of  $T_f$  (Table II), especially for the higher acrylamides above 10 mole % of amide, suggest that the compositions should be flexible with large elongations at use temperature. As was just demonstrated, however, the amide copolymers were stiff, and

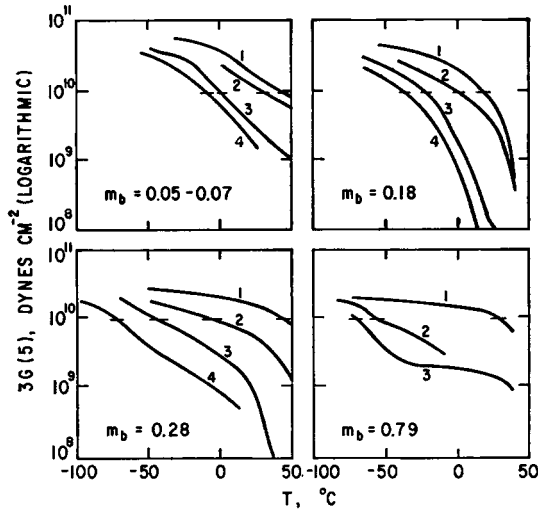


Fig. 1. Torsional modulus versus temperature for the amorphous side-chain acrylamide copolymers. Numerical designations are: 1-*N-n*-butyl; 2-*N-n*-octyl; 3-*N-n*-dodecyl; 4-*N*-oleyl.

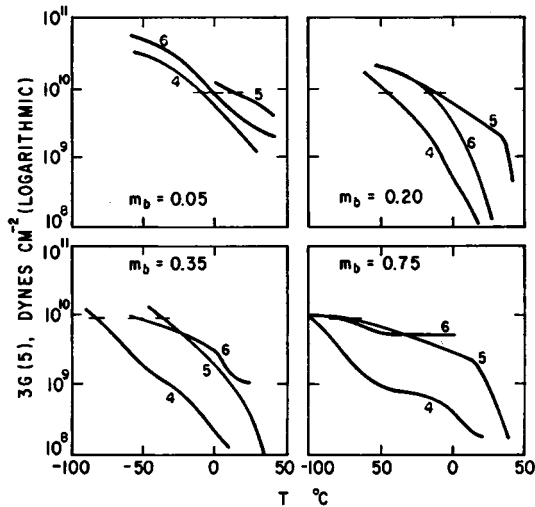


Fig. 2. Torsional modulus versus temperature for the  $C_{18}$  crystalline side-chain acrylamide copolymers and for amorphous *N*-oleylacrylamide copolymers. Numerical designations are: 4-*N*-oleylacrylamide; 5-*N-n*-octadecylacrylamide; 6-*n*-octadecyl acrylate.

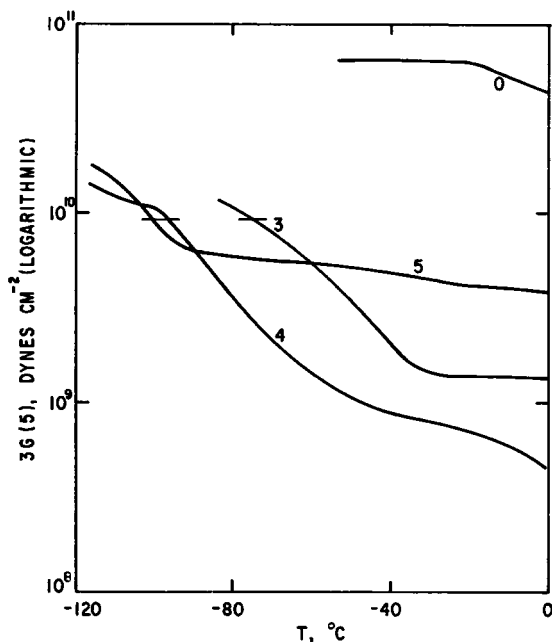


Fig. 3. Torsional modulus versus temperature for selected homopolymers. Numerical designations are the same as in Figure 1 and 2, except that 0 indicates polyvinylidene chloride.

some even brittle. An examination of the modulus-temperature curves suggests a possible reason for this behavior. Curves for the copolymers having amorphous side-chains are shown in Figure 1. They demonstrate that the rate of change of modulus with temperature, above  $T_f$ , was small for the lower amides especially at high amide comonomer contents. The quantity  $m_b$ , given in the figure, indicates the approximate mole fraction of amide in the copolymers. These curves in no way resemble those for amorphous copolymers<sup>27</sup> but are similar to those found for certain polyethylene ionomers,<sup>28</sup> for graft copolymers of methyl methacrylate on natural rubber<sup>29</sup> and for poorly externally plasticized vinylidene chloride compositions.<sup>30</sup> When crystallinity is present in the side-chains (Fig. 2) the slopes are similar to the oleylacrylamide copolymers at low amide contents, but, as side-chain crystallinity develops along with hydrogen bonding, the slopes become lower than for any of the copolymer studied. The extremes of this behavior are shown in Figure 3 for selected homopolymers.

Values of  $T_f$ , like  $T_g$ , might be expected to be a monotonic junction of composition.<sup>19</sup> They should therefore lie between the  $T_g$  of vinylidene chloride ( $-17^\circ\text{C}$ )<sup>4</sup> and those of the *N-n*-alkylacrylamides (estimated from (3) as *N-n*-butyl,  $32.2^\circ$ , octyl,  $-53^\circ$ , dodecyl,  $-72^\circ$ , octadecyl and oleyl,  $-111^\circ\text{C}$ ). However in saran copolymers, when the comonomer is a lower acrylate (31), and for other systems,<sup>31,32</sup> a maximum or minimum in  $T_g$  is

often observed. A minimum was found in this work for the *N-n*-butylacrylamide copolymers (Table II), although developing backbone crystallinity here may have caused the phenomena. The  $T_f$  values for the higher amides and ester do, in fact, decline monotonically. However, the observed  $T_f$  values of copolymers richer in vinylidene chloride are much higher than the  $T_g$  of vinylidene chloride. This probably reflects the stiffening introduced by the crystallization of vinylidene chloride segments, the effect decreasing as amide content increases. At high amide contents, the  $T_f$  values of the amide homopolymers are approached.

In spite of the scatter of the  $T_f$  data (Table II) and the perturbations caused by crystallinity and accumulated intermolecular interactions, it would be desirable to be able to estimate  $T_f$  values for copolymers of any side-chain length. To do this, distortions in  $T_f$ , particularly in the region of high vinylidene chloride content, would have to be accounted for mathematically, and amorphous  $T_f$  values increased by this amount. Accordingly data for the flex temperatures in Table II, plotted as a function of mole fraction of amide in the polymer, were curve fitted by computer using the equation below

$$T_{fc} = T_{fo} + \alpha(m_b) + \beta(m_b)^2 + \gamma(m_b)^3 + \delta(m_b)^4 \quad (1)$$

where  $T_{fo}$  is the smoothed  $T_f$  value,  $m_b$  is the mole fraction of amide, and  $T_{fo}$  is the intercept. Coefficients are listed in Table III. If the vinylidene

TABLE III  
Curve Fitting Coefficients for the Relationship between  $T_f$  and the Mole Fraction of the *N-n*-Alkylacrylamides

Acrylamide	$T_{fo}$	$\alpha$	$\beta$	$\gamma$	$\delta$
<i>N-n</i> -Butyl	56.78	-519.2	2383	-3660	1787
<i>N-n</i> -Octyl	67.57	-735.3	2462	-3467	1620
<i>N-n</i> -Dodecyl	24.11	-329.8	399.9	-168.7	0
<i>N-n</i> -Octadecyl	25.75	-340.9	548.2	-333.5	0
<i>N</i> -Oleyl	35.37	-393.9	937.9	-476.2	0
<i>n</i> -Octadecyl <sup>a</sup>	-8.63	-98.73	0	0	0

<sup>a</sup> *n*-Octadecyl acrylate.

chloride segments were amorphous it is reasonable that the  $T_f$  data would have been distributed around a line between  $T_{g(\text{vinyl})}$  and  $T_{g(\text{amide})}$ <sup>32</sup> and thus obey the relation

$$T_{fd} = T_{fa} + km_b \quad (2)$$

where  $T_{fd}$  is the flex-temperature for copolymers with an amorphous backbone and  $k = T_{fb} - T_{fa}$ , the *a* and *b* subscripts referring to vinylidene chloride and amide respectively and  $m$  = mole fraction. Each observed  $T_f$  was corrected for backbone crystallinity using

$$T_{fe} = T_f - [T_{fc} - (T_{fa} + km_b)] \quad (3)$$

and the values so reduced inserted into the familiar Fox relation<sup>33</sup> in terms of mole fraction (3)

$$1/T_{fe} = (1/T_{fa})_e + k_e m_b \quad (4)$$

where  $k_e = 1/T_{fb} - 1/T_{fa}$ . Temperatures are in degrees Kelvin. The Fox coefficients were generated by computer as first degree polynomials and these were plotted as a function of chain length,  $n$ , where they obeyed the relation

$$k_e = k_{e0} + K_e(n) \quad (5)$$

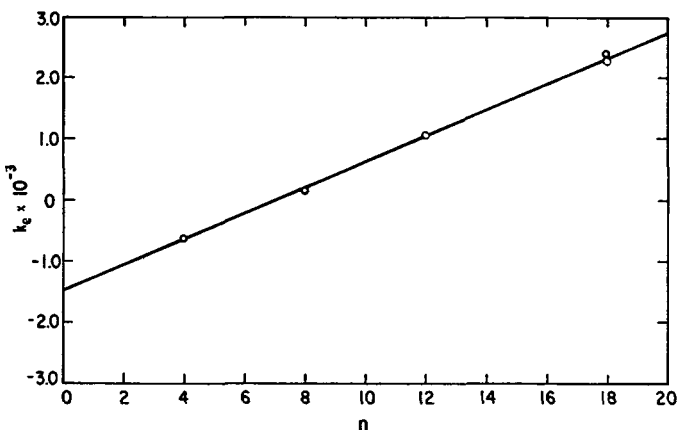


Fig. 4. Regression coefficients of the Fox equation versus the number of carbon atoms in the side-chain,  $n$ . Slope =  $K_e = 2.10 \times 10^{-4} \text{ }^\circ\text{K}^{-1}$ . Intercept =  $k_{e0} = -1.49 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ .

Data are plotted in Figure 4, and  $K_e$  and  $k_{e0}$  are listed. To calculate  $T_f$  values, corrected for crystallinity distortions, for any side-chain length from  $C_4$  through  $C_{18}$ , the empirical equation below was developed,

$$T_{fc}' = 1.0 / [(k_{e0} + K_e(n))m_b + 1/T_{fa}] - \frac{273.0 + A(m_b) + B(m_b)^2 + \frac{315}{n}}{n} \quad (6)$$

where  $A = -100$ ,  $B = -[1.0/(k_{e0} + K_e(n)) + 1/T_{fa}] + 273.0 - 315/n + T_{fb} - A$  (or where  $B \approx 100 - 315/n$ ).  $T_{fb}$  may be calculated using eq. (19) in reference (3). The  $T_f$  values listed in the last column of Table II were computed using eq. (6). Except for the  $n$ -butyl series, where  $T_f$  goes through a pronounced minimum,<sup>31,32</sup> the calculated values are reasonably close for this type of data. For very long side-chain lengths, eq. (6) simplifies to eq. (5). This suggests that eq. (4) would apply in predicting  $T_f$  values to systems having long side-chains grafted randomly to polyvinylidene chloride.



## CONCLUSION

Mechanical properties, flex temperatures and modulus-temperature curves were determined on copolymers of vinylidene chloride and *N-n*-butyl, octyl, dodecyl and oleylacrylamide where the side-chains are amorphous and for *N-n*-octadecylacrylamide and *n*-octadecyl acrylate, where the side-chains are crystalline. The over-all decline in flex-temperature was the normal monotonic function of composition. The data emphasized the marked efficiency of the 18 carbon comonomers in reducing  $T_g$ . However, the development of stiffening through intermolecular interactions, this property being important with the amides, and the propagation of crystallinity through the side chains of the saturated 18 carbon comonomers, produced compositions having brittle strengths less than yield strength, and led to brittle failure. This behavior was reflected in the modulus-temperature curves. For these reasons copolymer containing *n*-octadecyl acrylate and *N-n*-dodecyl and oleylacrylamide, had the best overall viscoelastic and mechanical properties but only in the low amide (or ester) composition range.

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## References

1. E. F. Jordan, Jr. and A. N. Wrigley, *J. Appl. Polym. Sci.*, **8**, 527 (1964).
2. J. F. Bork, D. P. Wyman and L. E. Coleman, *J. Appl. Polym. Sci.*, **7**, 451 (1963).
3. E. F. Jordan, Jr., G. R. Riser, W. E. Parker and A. N. Wrigley, *J. Polym. Sci.*, Pt. A-2, **4**, 975 (1966).
4. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, N. Y. (1962), pp. 16-35.
5. K. Okuda, *J. Polym. Sci.*, Pt. A, **2**, 1749 (1964).
6. R. C. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).
7. P. J. Flory, *Trans. Faraday Soc.*, **51**, 848 (1955).
8. S. H. Pinner, *Modern Packaging Films*, Butterworths, London (1967), pp. 120-142.
9. D. M. Woodford, *Chem. Ind. (London)*, 316 (1966).
10. E. F. Jordan, Jr., W. E. Palm, L. P. Witnauer and W. S. Port, *Ind. Eng. Chem.*, **49**, 1695 (1957).
11. P. W. Morgan, *Ind. Eng. Chem.*, **45**, 2296 (1953).
12. A. W. Myers, C. E. Rogers, V. Stannett and M. Szwarc, *Mod. Plast.*, **34**, No. 9, 157 (1957).
13. H. W. Ackerman, Jr., U. S. Patent 2,819,984 (1958).
14. W. G. MacPherson, U. S. Patent 3,297,666 (1967).
15. Borden and Company, Brit. Patent 1,009,486 (1965). CA64:8491c.
16. A. Trofimow, P. K. Isaacs and D. Goodman, U. S. Patent 3,006,902 (1961).
17. Solvay and Cie, Neth. Patent Appl. 6,406,960 (1964). CA62:16481e.
18. K. Mayumi, S. Yoshikawa and S. Iwazuki, Japan Patent 26,569 (1963). CA60:8206e.
19. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).
20. G. Niser, W. S. Port and L. P. Witnauer, *J. Polym. Sci.*, **36**, 543 (1959).
21. G. Riser and L. P. Witnauer, *SPE Trans.*, **2**, 7 (1962).

22. E. F. Jordan, Jr., *J. Polym. Sci. A-1*, **6**, 2209 (1968).
23. F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Interscience Publishers, New York (1962), p. 210.
24. J. L. McClanahan and S. A. Previtera, *J. Polym. Sci., Pt. A*, **3**, 3919 (1965).
25. B. Bennett, C. W. Cooper and M. Luttinger, *J. Appl. Polym. Sci.*, **6**, S23 (1962).
26. L. Mandelkern, *Crystallization of Polymers*, McGraw-Hill Book Co., New York (1964), pp. 92-95.
27. I. Yannas, *J. Polym. Sci., Pt. A-2*, **6**, 687 (1968).
28. *Encycl. of Polymer Sci. and Technolog.*, Interscience, New York, **6** (1967), p. 421.
29. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold Publishing Co., New York (1962), pp. 176-177.
30. C. B. Havens, *Ind. Eng. Chem.*, **42**, 315 (1950).
31. K. H. Illers, *Kolloid Z.*, **190**, 16 (1963).
32. K. H. Illers, *Ber. Bunsenges. Physik. Chem.*, **70**, 353 (1966). CA64: 17732a.
33. T. G. Fox, *Bull. Am. Phys. Soc. [2]*, **1**, 123 (1956). CA51: 11751g.

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