

## Side-Chain Crystallinity. II. Heats of Fusion and Melting Transitions on Selected Copolymers Incorporating *n*-Octadecyl Acrylate or Vinyl Stearate

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### Synopsis

The heats of fusion and the melting transitions of the crystallinity present in the side chains were determined for selected copolymers incorporating *n*-octadecyl acrylate or vinyl stearate. A major purpose of this investigation was to ascertain the effect of interrupting the long ordered 18-carbon side chains by randomly interspersed amorphous side chains of various lengths. For this purpose the lower acrylate homologs ( $C_1$  through  $C_8$  and including oleyl,  $C_{18}$ ) were copolymerized over the composition range with *n*-octadecyl acrylate. It was found that simple dilution of the crystalline component (from comonomer b) by the amorphous component (from comonomer a) governed the decline in the heats of fusion and the fraction of crystallinity present. High crystallization rates were encountered because equilibrium crystallinity was nearly achieved for most of the copolymers. Melting point depression was less than theory in copolymers having short amorphous comonomer side-chain lengths, but approached the theoretical depression as these side chains became very long. Thus the outer methylene sequences (the crystalline sequences) of the fatty co-units could bridge the smaller amorphous units, giving rise to larger crystal sizes than theory specified. Main-chain stiffness, when present in the melt, had a small effect on the distribution of crystallite sizes but exhibited a much larger influence in preventing the attainment of equilibrium crystallinity, especially at high amorphous comonomer compositions. However, crystallinity was still high compared with that of copolymers described in the literature crystallizing through their main-chain units. When long blocks of crystalline segments were present (as in compositionally heterogeneous vinyl stearate copolymers), melting point depression was small and followed the theoretical probability sequence function.

### INTRODUCTION

Much interest has centered<sup>1a,2</sup> on the crystallization phenomenon in copolymers in which one co-unit of the main chain is capable of crystallizing. The Flory theory of the equilibrium crystallization of polymers<sup>3</sup> required that sequence length distribution, and not the chemical nature of the amorphous component, determined the melting point depression. A very broad distribution of crystal sizes and lowered crystallinities were

postulated to be present in copolymers. Consequently, melting was predicted to occur over a wide temperature range. Theory<sup>4</sup> further required that equilibrium crystallization could only be attained in the limit of infinite time. The extent of realizable crystallinity would reside somewhere between this unattainable limit, and the equally unattainable limit of zero time imposed by cold crystallization.<sup>4</sup> In copolymers the development of crystallinity would be expected to be much slower than in homopolymers, and its extent greatly reduced by the presence of noncrystallizable units.

Many experimental studies<sup>1a,2</sup> have been directed toward confirming these predictions. Copolymers of polyethylene have received the most attention.<sup>1a,5-12</sup> While the data supported most of the features of Flory's theory, melting point depressions and decline in crystallinity were greater than predicted. Both deviations are attributable to failure to approach a sufficiently high state of equilibrium crystallization.<sup>4</sup>

Crystallinity in polyesters and polyamides and in copolymers formed from a single monomer by varying the syndiotactic and isotactic placements, has been reviewed.<sup>1a</sup> The sterically-ordered copolymers usually exhibited low crystallinities with only one stereoisomer crystallizing. In contrast, each component of the polyesters and polyamides could generally crystallize, leading to crystallinity over all compositions.<sup>1a,13</sup> The latter systems often exhibited isomorphism. Again, the broad features of the theory<sup>3</sup> were experimentally supported, but the anomalies already discussed tended to appear.<sup>4</sup>

All of these investigations have considered only copolymer systems in which the crystallizing component is part of the main chain. The special case of crystallization involving units having side chains has received relatively little attention. Some qualitative studies have been made, however. Melting points, obtained by refractometry, for copolymers of vinyl stearate and vinyl acetate, decreased progressively with increase in vinyl acetate,<sup>14</sup> while those for copolymers of poly-*N-n*-octadecylacrylamide with acrylonitrile<sup>15</sup> or vinylidene chloride,<sup>16</sup> by differential scanning calorimetry, showed little depression. Main-chain crystallinity of vinylidene chloride segments was apparent over a limited composition range in the last system<sup>16</sup> as was that of the vinyl alcohol units in copolymers with vinyl stearate.<sup>17</sup> Copolymers of *n*-octadecyl and *n*-tetradecyl methacrylate showed isomorphic replacement.<sup>18</sup> The melting points of the side chains in copolymers of *n*-octadecyl and methyl methacrylate were diffuse, but were little depressed by the short methyl branches.<sup>18</sup>

The general aim of this investigation was to study quantitatively the decline in side-chain crystallization and the depression of melting point for a variety of copolymer systems. The thermodynamic data were obtained by differential scanning calorimetry. In the first paper of this series<sup>19</sup> the thermodynamic properties of homopolymers of the higher poly-*(n-alkyl acrylates)*, poly-*N-n-alkylacrylamides*, and poly(vinyl esters) were studied. It was shown that only the outer methylene units in the side chains form a crystal lattice in these systems. The critical side-chain

length required to maintain a stable nucleus varied among these homologous series. For the poly(*n*-alkyl acrylates) it was above 9.2 carbon atoms.

Three different lines of investigation of the side-chain crystallinity in copolymers were pursued. The first, constituting a major purpose of this work, was to test the effect of interrupting the long, ordered 18-carbon side chains in poly(*n*-octadecyl acrylate) by randomly interspersed amorphous side chains of various lengths. For this purpose each of the lower *n*-alkyl acrylates (C<sub>1</sub> through C<sub>8</sub>) was selected for copolymerization with *n*-octadecyl acrylate over the complete range of composition. With this selection complete randomness in sequence lengths<sup>20</sup> would be assured. Because of its amorphous nature<sup>16</sup> and similar reactivity ratios<sup>21</sup> oleyl acrylate was also chosen as an example in this series. All of these copolymers would be expected to have low glass transition temperatures. The second line of investigation inquired into the effect of using stiff amorphous comonomers having high glass transition temperatures and small side groups on the decrease in crystallinity and melting point with decrease in *n*-octadecyl acrylate. Finally, the third line of investigation took up the case of non-random copolymers in which blocks of crystalline side chains would be present. In the paper immediately following this,<sup>22</sup> the influence of developing crystallinity on the glass transition temperatures of these copolymers will be presented.

## EXPERIMENTAL

### Lower *n*-Alkyl Acrylates, Methyl Methacrylate, and Acrylonitrile

All were the purest monomers from commercial sources. The acrylates were treated with aqueous alkali to remove the inhibitor and dried; methyl methacrylate and acrylonitrile were distilled immediately before use.

### Higher Fatty Comonomers

The preparation and purification of *n*-octadecyl acrylate has been described.<sup>19</sup> Oleyl acrylate was prepared and purified by the procedure used for *n*-dodecyl and *n*-tetradecyl acrylate,<sup>19</sup> except that a single acetone crystallization (3 ml/g) was employed at  $-60^{\circ}\text{C}$  as the final purification step. The yield was 52%, and the ester was 99.4% octadecenyl acrylate by gas-liquid chromatography but contained about 20% elaidyl acrylate by infrared analysis.

ANAL. Calcd: C, 78.20%; H, 11.88%. Found: C, 78.40; H, 11.66%.

Vinyl stearate<sup>23</sup> was obtained from the White Chemical Company. It was purified by four crystallizations from acetone (10 ml/g) at  $-20^{\circ}\text{C}$ . The yield was 59% and the purity was 98.8% by gas liquid chromatography.

### Polymerization Procedure

All polymerizations were conducted in sealed vessels, under nitrogen, in benzene solution (4 mole benzene/mole of total monomer), for 48 hr at

60°C, using 0.2 mole-% bis-azo isobutyronitrile as the initiator. Exceptions were *n*-octadecyl acrylate copolymers with, respectively, methyl methacrylate and oleyl acrylate, where the benzene monomer ratio was 1, and with *n*-butyl acrylate and acrylonitrile, where the ratio was 3. Vinyl stearate-methyl methacrylate copolymers were made at 60°C for 72 hr using a solvent to comonomer mole ratio of unity. Most yields were between 85 to 95%. Some low yields were encountered in the mid-composition range of the vinyl stearate-methyl methacrylate copolymers (39-70%). The copolymers were purified by extraction with hot methanol (or petroleum ether, when soluble in methanol) till free of all monomers. They were then dried in thin layers. Copolymer compositions, determined from elementary analyses, agreed with feed compositions within experimental error. Consequently, to reduce experimental scatter, the thermodynamic data were correlated with feed compositions. Exceptions were the vinyl stearate copolymers, where copolymer compositions derived from elemental analysis were used.

### Calorimetric Procedures

The procedures of Jordan et al.<sup>19</sup> were followed exactly. Hard, brittle samples and hard, waxy samples were ground to powders or small granules and weighed on a Cahn balance in regular sample cups; soft sticky polymers were weighed (Cahn balance) into the crimped solvent cups provided with the instrument. Minimum sample weights (usually 1-2 mg) were used for melting point. The ends of the fusion curves were taken as the temperature of melting. As will be seen from the text, this interpretation was the only feasible one. This interpretation is justified by the principle<sup>18,5</sup> that the final disappearance of crystallinity, under equilibrium conditions, is the thermodynamic melting point. In this work, where equilibrium was only approached, the melting points are necessarily approximate. Melting points of the side-chain crystallites of homopolymers by differential scanning calorimetry do seem to be close to equilibrium values, however.<sup>19</sup> Maximum sample weights (14-25 mg) were employed for the fusion endotherms. Methanol or other liquid treatments were not used in this series to increase the extent of crystallization because of the varied solubilities of these copolymers. A computer (IBM 1130) was used for all calculations.

### Molecular Weight Measurements

The osmometric procedure was described.<sup>15</sup> The solvent was toluene.

## RESULTS AND DISCUSSION

### Thermodynamic Quantities and Molecular Weight Measurements

The heats of fusion, melting transitions, and molecular weight measurements for all of the copolymer systems studied in this investigation are listed in Table I. In this paper designation b will refer to crystalline units derived from *n*-octadecyl acrylate or vinyl stearate in the chain, while

**TABLE I**  
Composition, Degrees of Polymerization, Heats of Fusion, and  
Melting Points for the Copolymers

Experiment number	Fatty ester in copolymer <sup>a</sup>		DP <sub>n</sub>	Crystallinity properties			
	Mole fraction	Weight fraction		$\Delta H_f$ , cal/g	$x_c^b$	$x_c/x_{cmax}^c$	$T_m$ , °C
<b>MONOMER</b> <i>n</i> -Octadecyl acrylate and methyl acrylate							
1	0.050	0.166	1596	0.564	0.01	0.159	17.0
2	0.075	0.234	1660	1.17	0.03	0.234	27.0
3	0.100	0.295	1704	2.62	0.05	0.416	33.0
4	0.125	0.350	1886	7.25	0.13	0.971	42.0
5	0.150	0.399	1394	7.31	0.13	0.859	39.0
6	0.200	0.485	1226	8.77	0.16	0.847	42.0
7	0.300	0.618	1113	12.50	0.22	0.948	52.0
8	0.400	0.715	950.6	15.39	0.27	1.01	47.0
9	0.500	0.790	962.9	17.42	0.31	1.03	48.0
10	0.600	0.850	862.7	17.49	0.31	0.964	51.0
11	0.700	0.898	792.5	18.94	0.34	0.988	52.0
12	1.000	1.000	852.9	21.34	0.38	1.00	56.0
<i>n</i> -Octadecyl acrylate and ethyl acrylate							
13	0	0	1221	0	0	0	—
14	0.050	0.146	1321	1.96	0.03	0.629	17.0
15	0.100	0.265	1845	4.75	0.08	0.840	30.0
16	0.125	0.317	1278	6.07	0.11	0.897	28.0
17	0.150	0.364	1020	6.55	0.12	0.843	34.0
18	0.200	0.448	863.5	8.93	0.16	0.934	39.0
19	0.300	0.582	680.2	11.50	0.21	0.926	43.0
20	0.400	0.684	688.3	14.70	0.26	1.01	45.0
21	0.500	0.764	628.8	16.22	0.29	0.995	46.0
22	0.600	0.829	583.9	17.42	0.31	0.985	47.0
23	0.750	0.907	594.2	19.11	0.34	0.987	51.0
<b>MONOMER</b> <i>n</i> -Octadecyl acrylate and <i>n</i> -butyl acrylate							
24	0	0	1938	0	0	0	—
25	0.050	0.118	1591	1.63	0.03	0.647	-12.0
26	0.075	0.170	1452	1.28	0.02	0.353	1.0
27	0.100	0.219	1497	3.37	0.06	0.721	10.0
28	0.125	0.266	1407	4.09	0.07	0.721	16.0
29	0.150	0.309	1202	5.68	0.10	0.861	22.0
30	0.200	0.387	1425	6.97	0.12	0.844	28.0
31	0.300	0.519	1543	9.54	0.17	0.861	35.0
32	0.400	0.628	1357	12.70	0.23	0.948	42.0
33	0.500	0.719	—	14.37	0.26	0.937	44.5
34	0.750	0.883	916.7	18.40	0.33	0.977	50.0
<i>n</i> -Octadecyl acrylate and <i>n</i> -octyl acrylate							
35	0	0	826.5	0	0	0	—
36	0.050	0.085	776.3	0.73	0.01	0.402	-13.0
37	0.075	0.125	790.0	1.26	0.02	0.472	-6.0
38	0.100	0.164	768.0	2.24	0.04	0.640	0
39	0.125	0.201	758.2	3.09	0.06	0.720	6.0
40	0.150	0.237	734.0	3.17	0.06	0.627	9.0
41	0.200	0.306	684.8	5.32	0.09	0.815	15.0
42	0.300	0.430	631.3	8.44	0.15	0.920	26.0
43	0.400	0.540	589.1	10.80	0.19	0.937	33.0
44	0.500	0.638	575.5	11.61	0.21	0.853	40.0
45	0.750	0.841	457.1	15.04	0.27	0.838	47.0

TABLE I (continued)

Experiment number	Fatty ester in copolymer <sup>a</sup>		Crystallinity properties				
	Mole fraction	Weight fraction	DP <sub>n</sub>	$\Delta H_f$ , cal/g	$x_c^b$	$x_c/x_{cmax}^c$	$T_m$ , °C
<i>n</i> -Octadecyl acrylate and 2-ethylhexyl acrylate							
46	0	0	385.8	0	0	0	—
47	0.050	0.085	380.6	0.52	0.01	0.287	-13.0
48	0.075	0.125	382.0	1.17	0.02	0.439	-5.0
49	0.100	0.164	378.2	1.72	0.03	0.492	-9.0
50	0.125	0.201	393.0	2.07	0.04	0.483	-1.0
51	0.150	0.237	371.6	2.70	0.05	0.534	10.0
52	0.200	0.306	352.3	4.79	0.09	0.734	16.0
53	0.300	0.430	379.1	7.95	0.14	0.866	27.0
54	0.400	0.540	387.7	10.13	0.18	0.879	32.0
55	0.500	0.638	400.9	11.51	0.21	0.845	38.0
56	0.600	0.725	406.1	12.68	0.23	0.820	41.0
57	0.750	0.841	425.6	15.09	0.27	0.841	47.0
<i>n</i> -Octadecyl acrylate and <i>n</i> -dodecyl acrylate							
58	0	0	930.6	8.75	0.16	1.00	12.0
59	0.050	0.067	677.1	8.40	0.15	0.876	13.0
60	0.075	0.099	614.1	8.71	0.16	0.872	20.0
61	0.100	0.131	602.9	8.90	0.16	0.839	17.0
62	0.125	0.162	815.9	9.11	0.17	0.845	22.0
63	0.150	0.193	762.9	9.56	0.17	0.856	21.0
64	0.200	0.253	665.6	10.30	0.19	0.863	24.0
65	0.300	0.367	553.8	11.10	0.20	0.831	27.0
66	0.400	0.474	561.2	11.54	0.21	0.785	32.0
67	0.500	0.574	520.8	12.52	0.22	0.784	36.0
68	0.600	0.670	475.8	13.27	0.24	0.772	40.0
69	0.750	0.802	352.9	16.94	0.33	0.980	47.0
MONOMER	<i>n</i> -Octadecyl acrylate and oleyl acrylate <sup>d</sup>						
70	0.075	0.076	—	0	0	0	-8.0
71	0.100	0.101	—	0.90	0.02	0.418	-3.0
72	0.125	0.126	—	1.50	0.03	0.558	-1.0
73	0.150	0.151	—	1.47	0.03	0.456	3.0
74	0.200	0.201	—	2.42	0.04	0.564	12.0
75	0.300	0.301	—	5.15	0.09	0.802	22.0
76	0.400	0.402	—	7.14	0.13	0.832	30.0
77	0.500	0.502	101.2	8.44	0.15	0.788	37.0
78	0.600	0.602	81.1	10.84	0.19	0.844	40.0
79	0.750	0.751	88.3	12.62	0.23	0.748	46.0
<i>n</i> -Octadecyl acrylate and methyl methacrylate							
80	0	0	1452	0	0	0	—
81	0.050	0.146	1189	0	0	0	—
82	0.075	0.208	1012	0	0	0	—
83	0.100	0.265	1014	0.504	0.01	0.089	44.0
84	0.125	0.317	1067	0.721	0.01	0.107	46.0
85	0.150	0.364	1053	1.43	0.03	0.184	47.0
86	0.200	0.448	1027	2.28	0.04	0.239	49.0
87	0.300	0.582	1008	4.63	0.08	0.373	52.0
88	0.400	0.683	1148	7.15	0.13	0.491	52.0
89	0.500	0.764	1200	9.59	0.17	0.588	53.0
90	0.600	0.829	1054	15.09	0.27	0.853	54.0
91	0.750	0.907	—	17.45	0.31	0.902	56.0

TABLE I (continued)

Experiment number	Fatty ester in copolymer <sup>a</sup>		DP <sub>n</sub>	Crystallinity properties			
	Mole fraction	Weight fraction		$\Delta H_f$ , cal/g	$x_c$ <sup>b</sup>	$x_c/x_{cmax}$ <sup>c</sup>	$T_m$ , °C
<i>n</i> -Octadecyl acrylate and acrylonitrile							
92	0	0	346.2 <sup>e</sup>	0	0	0	—
93	0.050	0.244	342.9 <sup>e</sup>	0	0	0	—
94	0.075	0.331	343.2 <sup>e</sup>	0	0	0	—
95	0.100	0.405	331.6 <sup>e</sup>	—	0	0	35.0
96	0.125	0.466	310.9 <sup>e</sup>	1.71	0.03	0.172	37.0
97	0.150	0.519	331.6 <sup>f</sup>	2.75	0.05	0.248	39.0
98	0.200	0.604	491.4 <sup>f</sup>	4.40	0.08	0.341	45.0
99	0.300	0.724	520.4 <sup>f</sup>	6.40	0.11	0.414	56.0
100	0.400	0.790	593.3	9.88	0.18	0.586	56.0
101	0.500	0.860	558.3	11.73	0.21	0.639	55.5
102	0.600	0.903	554.8	15.43	0.28	0.801	57.0
103	0.750	0.941	640.1	20.11	0.36	1.00	57.0
Vinyl stearate and methyl methacrylates <sup>g</sup>							
104	0.024	0.070	1257	0	0	0	—
105	0.036	0.104	1112	0.62	0.01	0.303	56.0
106	0.046	0.129	1020	0.43	0.01	0.167	58.0
107	0.076	0.203	958.8	1.17	0.02	0.291	57.0
108	0.158	0.368	906.5	3.18	0.06	0.436	58.0
109	0.183	0.410	728.1	6.39	0.11	0.786	58.0
110	0.197	0.433	613.5	6.13	0.11	0.714	58.0
111	0.377	0.622	449.8	11.30	0.20	0.917	59.0
112	0.414	0.687	411.8	9.34	0.16	0.686	58.0
113	0.375	0.650	275.3	9.13	0.16	0.709	57.0
114	0.744	0.900	265.6	16.56	0.29	0.928	57.0
115	0.902	0.966	254.6	17.93	0.32	0.937	56.0
116	0.950	0.983	230.0	19.95	0.35	1.02	57.0
117	1.00	1.00	157.5	19.82	0.38	1.00	58.0
Vinyl stearate and 2-ethylhexyl acrylates <sup>g</sup>							
118	0.043	0.070	403.5	0	0	0	—
119	0.054	0.088	416.0	0	0	0	—
120	0.076	0.121	476.4	0	0	0	—
121	0.062	0.099	491.9	0	0	0	—
122	0.130	0.201	487.2	0	0	0	—
123	0.116	0.181	637.2	0.464	0.01	0.129	47.0
124	0.213	0.314	617.6	0.937	0.02	0.151	55.0
125	0.282	0.398	449.6	3.30	0.06	0.418	58.0
126	0.333	0.457	405.4	5.56	0.10	0.614	58.0
127	0.523	0.649	276.1	9.24	0.16	0.718	57.0
128	0.730	0.820	245.9	13.41	0.24	0.825	56.0

<sup>a</sup> Feed composition; found compositions by elemental analysis agreed within experimental error.

<sup>b</sup> Equation (8).

<sup>c</sup> Equation (7).

<sup>d</sup> Partially crosslinked. Sol fraction was about 10% in experiments 77-79.

<sup>e</sup> Dimethylformamide used.

<sup>f</sup> Dimethylformamide-toluene (50/50) used.

<sup>g</sup> Copolymer compositions are from elemental analysis.

other co-units will receive the designation a. All of these except *n*-dodecyl acrylate were amorphous. The degrees of polymerization  $DP_n$  were calculated from osmometric molecular weights by using a weighted average of the molecular weights for the two comonomers. Degrees of polymerization generally fell with increasing b component. This probably reflects transfer to monomer.<sup>24</sup> Notable exceptions were the copolymers of *n*-octadecyl acrylate and acrylonitrile, where the trend was reversed. No ready explanation is offered for this phenomenon except that it seems to occur in precipitation copolymerization<sup>15</sup> incorporating acrylonitrile. Not surprisingly,<sup>24</sup> the decline in molecular weights with increasing oleyl acrylate is marked.

The first five and the seventh system in Table I provide data relevant to the first line of investigation called for in the introduction. These are the all-acrylate copolymers having amorphous side chains of various lengths and low glass transition temperatures. They will be referred to as series 1 in the discussion below. The next two systems in Table I have high glass transition temperatures and thus satisfy the second aim of the introduction. These will be called series 2. The last two are nonrandom copolymers, as in the third specification, and will be labeled series 3.

Melting points and the heats of fusion for all of the systems (Series 1, 2, 3, Table I) declined in a regular fashion from the values for the respective crystalline homopolymers (expts. 12 and 117) as the content of b units decreased. The melting point depression will be treated in detail below. From thermodynamic data on homopolymers,<sup>19</sup> the heats of fusion were

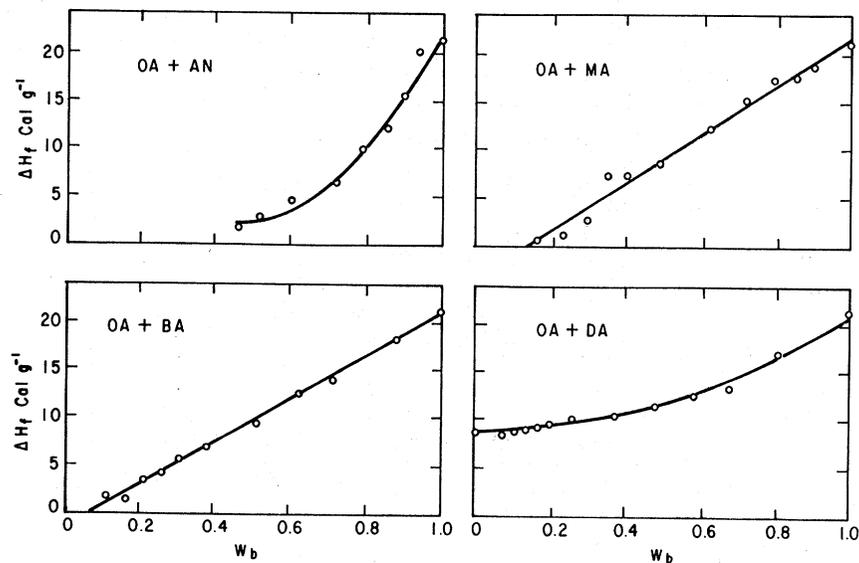


Fig. 1. Heats of fusion vs. the weight fraction  $w_b$  of *n*-octadecyl acrylate for several typical copolymer systems. Designations are: OA, *n*-octadecyl acrylate; AN, acrylonitrile; MA, methyl acrylate; BA, *n*-butyl acrylate; DA, *n*-dodecyl acrylate.

found to be proportional to the crystallinity present. This proportionality would be expected to be followed by the copolymers. The slope for the decline of the heat of fusion with decreasing  $w_b$  was relatively small for the copolymers made using the amorphous  $n$ -alkyl acrylate homologs (series 1, expts. 1-57 and 70-79). This is illustrated in Figure 1 for the  $n$ -octadecyl acrylate-methyl acrylate system (OA + MA) and for the  $n$ -octadecyl acrylate-butyl acrylate system (OA + BA). In all of these entirely acrylate systems the glass temperatures of the copolymers at low  $n$ -octadecyl acrylate content were low (all were below  $-10^\circ\text{C}$ ), indicating that chain mobility of the molten copolymers was high.<sup>25</sup> Thus the low glass temperatures permitted rapid crystallization<sup>1b</sup> at the low supercooling employed. In contrast, copolymers with relatively high values of  $T_g$ , approximately  $26^\circ\text{C}$ , (series 2, Table I), showed larger decreases in  $\Delta H_f$  with decreasing  $w_b$  and equally large decreases in crystallinity. The slopes of the  $\Delta H_f$ -composition curves at high  $w_b$  were therefore considerably greater. Examples are copolymers of  $n$ -octadecyl acrylate with methyl methacrylate (expts. 80-91) and acrylonitrile (expts. 92-103), respectively. This is also illustrated in Figure 1 for the  $n$ -octadecyl acrylate-acrylonitrile system (OA + AN). Changes in the programmed rate of cooling and heating had little effect on the areas under the fusion curves or on the melting temperature. Thus the fusion phenomena for these samples were comparatively insensitive to details of their thermal history. Consequently the development of metastable crystallites requiring rapid heating rates for their preservation<sup>26-28</sup> and the complications of multiple peaks arising from different cooling rates<sup>29</sup> were absent in this work.

The heats of fusion for copolymers of  $n$ -octadecyl and  $n$ -dodecyl acrylate (expts. 58-69), where each component is crystalline,<sup>19</sup> fell between the values for the respective homopolymers. This can be seen (OA + DA) in Figure 1. Their melting transitions have already been shown<sup>19</sup> to be linear with composition. Consequently the crystallinity here is a good example of solid solution formation involving the methylene groups in the side chains.<sup>18,19</sup> They resemble certain polyamide systems in retaining crystallinity over all composition ranges<sup>1a</sup> and in exhibiting isomorphism.<sup>1a,18</sup>

As overall crystallinity declined with dilution by a units, the melting peaks traced by differential scanning calorimetry became increasingly broad for all of the copolymers in Table I. Such broadening of melting peaks has provided qualitative indication of broadening distribution of crystal sizes in representative cases.<sup>30,31</sup> Typical curves found for all of the copolymer systems in Table I are shown in Figure 2. The scanning curves increased in breadth from the lowest number to the highest as  $w_b$  declined for all of the copolymers. The melting range increased from about  $22^\circ\text{C}$  for curve 1 to about  $45^\circ\text{C}$  for curve 4, but was very wide ( $50$ - $70^\circ\text{C}$ ) for curves 3 and 4 of the higher amorphous acrylate systems. In the all-acrylate systems (series 1), an increase in amorphous side-chain length of

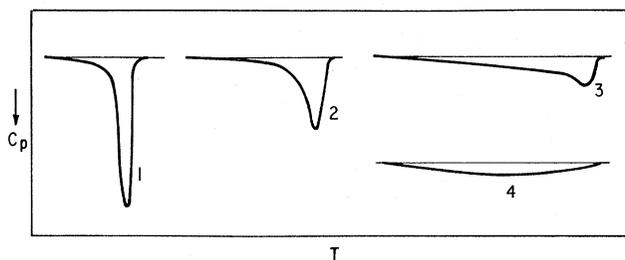


Fig. 2. Typical fusion endotherms for the copolymers by differential scanning calorimetry. *n*-Octadecyl acrylate-ethyl acrylate copolymers, selected as representative and listed in Table I, gave endotherm traces as follows: (1) experiment 23; (2) experiment 20; (3), experiment 18; (4) experiment 14.

the a component produced a broader crystallite distribution at higher values of  $w_b$ . With copolymers having a high  $T_g$  (series 2), broadening also was found even at a high proportion of fatty comonomer. This probably occurred because the segmental restraints imposed on the main chain prevented much perfection of the phase in finite times.<sup>4</sup> A similar situation has already been encountered in the bulk annealing of the poly-*N*-*n*-alkylacrylamide homopolymers,<sup>19</sup> whose  $T_g$  was relatively high. It can be readily seen from these curves why the ends of the fusion curves were designated as the melting points in Table I.

Values of the heats of fusion  $\Delta H_f$  for the pertinent data in Table I, versus the weight fraction,  $w_b$ , of the b comonomer (selectively illustrated in Fig. 1) were curve fitted using the computer. The relationship was

$$\Delta H_f = \Delta H_{f0'} + k_1 w_b + k_2 (w_b)^2 \quad (1)$$

where  $\Delta H_{f0'}$  is the intercept and  $k_1$  and  $k_2$  are the constants of the parabolic curve. The computed constants are given in Table II. Equation (1) was linear ( $k_2 = 0$ ) for the entirely *n*-alkyl acrylate copolymers (series 1), containing noncrystallizing a co-units (first five and the seventh system in Table II). Values of  $k_1$  were close to the limiting value of 21.3 cal/g (with  $\Delta H_{f0'}$  the origin) required for equilibrium crystallization<sup>4</sup> for the last three systems; the first three approached that value less closely. The constants for the other systems have no obvious physical meaning other than to permit computation of smoothed data.

The marked retention of crystallinity as the mole fraction  $m_b$  or the weight fraction  $w_b$  of *n*-octadecyl acrylate (or vinyl stearate) decreased in all of the copolymers in Table I stood in striking contrast to the rapid reduction in crystallinity usually found for copolymers of polyethylene<sup>1a,5-12</sup> and for other copolymers.<sup>1a</sup> With ethylene copolymers values of  $k_1$  [eq. (1)] three to six times those in Table II are frequently encountered<sup>9,32,33</sup> with different foreign inclusions in the chain. In fact, the extent of crystallinity of the copolymers of the present study lies close to the equilibrium limit,<sup>4</sup> especially for series 1 copolymers (Fig. 1). The data permit

TABLE II  
Curve Fitting Parameters for the Various Equations

System <sup>a</sup>	Equation (1)			Equation (10)		
	$\Delta H_{f0}'$	$k_1$	$k_2$	Intercept $\times 10^4$	$R/\Delta H_{f0} \times 10^4$	$\Delta H_{f0}$ , cal/mole
OA + MA	-3.58	25.5		0.065 <sup>b</sup>	-1.019	19,500
OA + EA	-1.35	22.8		0.087	-1.251	15,890
OA + BA	-1.81	22.9		-0.283 <sup>b</sup>	-2.144	9,269
OA + OCA	-1.32	21.4		-0.092	-2.764	7,190
OA + EHA	-1.86	21.5		-0.071 <sup>b</sup>	-2.662	7,465
OA + DA	8.79	0.029	12.2			
OA + OLA	-1.65	21.4		0.111	-2.917	6,812
OA + MMA	9.24	-37.7	51.0	-0.00012	-0.5044	39,400
OA + AN	16.6	-62.8	68.3	-0.181	-1.020	19,480
VS + MMA	-0.830	10.0	10.4	0.0864	0.00911	—
VS + EHA	-1.87	8.07	13.5	-0.250	-0.4556	43,620

<sup>a</sup> Arranged as in Table I.

<sup>b</sup> One or two data points were out of line; these were not included.

an estimation of the extent that experimental crystallinity approaches this limit.

Under equilibrium conditions<sup>4</sup> the crystallinity  $x_{cmax}$  for each mole of crystalline b units is

$$x_{cmax} = m_b = (m_b/w_b)[W_b/(W_b + W_a)] \quad (2)$$

where  $W_b$  is the weight of all b units and  $W_a$  is the weight of the a units. In like manner  $m_b$  and  $w_b$  are the respective mole and weight fractions of b units. When each crystallizing b unit is only partially crystalline, that is, crystalline in a portion only of its side chain,<sup>19</sup> then eq. (2) becomes

$$x_{cmax} = x_{c0}m_b = x_{c0}(m_b/w_b)[W_b/(W_b + W_a)] \quad (3)$$

where  $x_{c0}$  is the fraction crystallinity of the b homopolymer unit.<sup>19</sup> Molecular weights of the a and b units are often dissimilar, as in the present systems. It is conceivable that, in special cases, when the molecular weight of b units exceeds that of a units, the crystallinity in a copolymer system would correspond to simple dilution of the b by a units, thus

$$x_{cmax} = x_{c0}w_b \quad (4)$$

In such cases, however, each crystallizing unit would be required to contribute a multiplicity of segments to the crystalline phase, except in the trivial case where  $m_b = w_b$ . Under these circumstances, then

$$x_{cmax} = C_1m_b - C_2(m_b)^2 + \dots \quad (5)$$

Also under these circumstances, the maximum heat of fusion (in cal/g) would likewise correspond to simple dilution; thus

$$\Delta H_{fmax} = w_b\Delta H_{f0} \quad (6)$$

because  $x_{c0}$  is proportional to  $\Delta H_{f0}$ , the heat of fusion of the crystalline homopolymer.<sup>19</sup> The ratio of the experimental crystallinity of a crystallizable unit to the maximum attainable by the unit, on a weight basis would then be

$$x_c/x_{c\max} = \Delta H_f/\Delta H_{f\max} \quad (7)$$

where  $x_c$  is the experimental crystallinity and  $\Delta H_f$  is the observed heat of fusion. The ratio is a measure of the extent of attainment of equilibrium crystallization.<sup>34</sup>

These requirements are met by the copolymers of this investigation. Figure 1 shows that the decline in the heat of fusion is governed largely by dilution by a units, especially in series 1 copolymers. Because the molecular weight for b units is greater than for a units, each crystalline unit must contribute a block of side-chain methylene groups to the crystal lattice.<sup>19</sup> In turn, sequences of side chains are segmentalized by the interruption of a units. The extent of interruption should be determined, then, by both the frequency of occurrence of a units and by their lengths. Short a unit lengths, extending from an amorphous, and, hence, somewhat conformationally free, main chain could permit b side-chain crystal lattices to bridge the a units. Experimental crystallite sizes and perfection would then be higher and melting point depression less than required by theory.<sup>3</sup> Rates of crystallization would be increased because of the conformational freedom conferred by the amorphous main chain. Higher rates would also result from crystal growth intramolecularly initiated in local volume elements, which can proceed without the segmental sorting of main chains characteristic of ordinary crystallizing copolymers.<sup>3,4</sup> Consequently, equilibrium conditions could be approached in finite times at high b unit concentrations. The formation of stable nuclei would be prevented at low  $w_b$  so that  $x_c/x_{c\max}$  would rapidly decline. The extent to which these predictions are fulfilled by the available data will constitute the main emphasis of the balance of this paper.

With these requirements met, the experimental crystallinity  $x_c$  becomes

$$x_c = (x_c/x_{c\max})(w_b x_{c0}) \quad (8)$$

Values of the extent of equilibrium crystallinity  $x_c/x_{c\max}$  and the experimental crystallinity  $x_c$  are listed in Table I. As a generalization, the ratios are much higher than would be found for ordinary crystalline copolymers.<sup>9,32,33</sup> The ratios follow the trends previously discussed for the heats of fusion. A small decline in the ratio with decrease in  $w_b$  can be observed for the entirely acrylate copolymers, whose glass transitions are low. A more rapid decline was found in the ratio for the copolymers of higher  $T_g$  (series 2), where chain stiffness in the melt was prevalent. Even in stiff chains, conformational adjustments can apparently occur in short enough times to produce greater crystallinity than is found in copolymers crystallizing through main-chain units. Moreover, the degree to which  $x_c/x_{c\max}$  approaches unity with increasing  $w_b$  is restricted more by main-chain

stiffness than by interference by sequences of a units. For example, at  $w_b = 0.30$ ,  $x_c/x_{cmax}$  for *n*-octadecyl acrylate-oleyl acrylate (expt. 75) is 0.80 and for the *n*-octadecyl acrylate-methyl methacrylate (expt. 84) copolymer the ratio is only 0.11. On a mole base, the ratios are closer, being 0.80 and 0.37 respectively, but still remain higher for the system of lower glass transition. It may be concluded that the ability of each crystallizing co-unit to contribute several units to a side-chain lattice facilitates attainment of equilibrium, but that main-chain stiffness opposes its attainment.

In copolymers of *n*-octadecyl acrylate with *n*-dodecyl acrylate (expts. 58 and 59), the ratio  $x_c/x_{cmax}$ , viewed as a function of  $w_b$ , decreased from unity and went through a shallow minimum. This suggests that some disordered regions were present in this isomorphic system.

Blocks of sequences of vinyl stearate units would be expected in the two sets of vinyl stearate copolymers (series 3, Table I). This would result from the compositional heterogeneity imposed by the divergent copolymerization parameters for the comonomer pairs. In spite of the block character of these systems, the slope of the curve  $x_c/x_{cmax}$  against  $w_b$  for vinyl stearate copolymerized with methyl methacrylate was similar to that of *n*-octadecyl acrylate with the same comonomer. An averaging of the contributions from the crystalline and amorphous blocks seemed to produce these results. The rapid decline of  $x_c/x_{cmax}$  with decreasing  $w_b$  for the 2-ethylhexyl acrylate copolymers with vinyl stearate suggests that in this case the influence of the amorphous blocks predominates.

### Melting Point Depression

The equation for the melting point depression of copolymers in which only one component crystallizes is given by the general theory of Flory<sup>3</sup>

$$(1/T_m) - (1/T_{m0}) = (-R/\Delta H_f) \ln p \quad (9)$$

where  $T_m$  and  $T_{m0}$  are the equilibrium melting points of, respectively, the copolymers and the homopolymer and  $p$  is the probability that a crystallizable b unit will be succeeded by another b unit. The heat of fusion  $\Delta H_f$  is the value for the entirely crystalline phase of the b comonomer and should equal the quantity obtained from the homopolymer by using a diluent.<sup>1c</sup> That it rarely does so is attributed to the experimental impossibility of detecting the melting of the extremely small fraction of large crystallites actually present in copolymers.<sup>1a,c,3,4</sup> For a random copolymer,  $p$  becomes indistinguishable with the mole fraction of b units, designated  $m_b$ . Thus,

$$(1/T_m) - (1/T_{m0}) = (-R/\Delta H_f) \ln m_b \quad (10)$$

Consequently, plots of  $(1/T_m) - (1/T_{m0})$  versus  $\ln m_b$  should yield  $\Delta H_f$  from the slope.

The melting points, listed in Table I, were inserted into eq. (10) and treated by regression analysis by using the computer. The appropriate

constants are given in Table II. Values of  $\Delta H_{f0}$  are also listed in column 7 of this table. The apparent heat of fusion,  $\Delta H_{f0}$ , for the copolymers containing *n*-octadecyl acrylate decreases as the side-chain length  $n_a$  of the amorphous a co-unit becomes greater (series 1 and 2). It appears to reach a limiting value when  $n_a$  is 18 carbon atoms. This is close to the value of  $\Delta H_{f0}$  for poly(*n*-octadecyl acrylate),<sup>19</sup> which was 6925 cal/mole. Values of the slope,  $(R/\Delta H_{f0})$  in eq. (10) (Table II) indicate that the rate of melting point depression decreases as the length of the a unit decreases.  $R/\Delta H_{f0}$  approaches a constant value as  $n_a$  becomes very great. It would seem, at least across short ranges of  $n_a$ , that

$$R/\Delta H_{f0} = (R/\Delta H_{f0})_0 + \delta(\ln n_a) \quad (11)$$

The appropriate constants (Table II) are plotted against  $\ln n_a$  in Figure 3. The parameters are given in the figure. Substituting eq. (11) into eq. (10) and rearranging yields

$$T_m = 1/\{[(R/\Delta H_{f0}) + \delta(\ln n_a)] - \ln m_b\} + (1/T_{m0}) \quad (12)$$

Melting points calculated by using eq. (12) are compared with found values in Table III. Thus, melting points of random copolymers having co-units composed of crystallizing 18-carbon side chains and  $n_a$  of any magnitude between 1 and at least 20 can be calculated by eq. (12) by employing only the constants of Figure 3.

It may be concluded that sequence distribution produces a melting-point depression of theoretical magnitude, as in eq. (10), only when the length of the amorphous a units equals or exceeds the length of the crystallizing side chains. Then, and only then, do the crystallite lengths fully correspond to sequence distances as required.<sup>3</sup> In contrast to copolymers crystallizing through the main chain, the amorphous main chains and immediately adjacent side-chain methylene groups<sup>19</sup> of the present copoly-

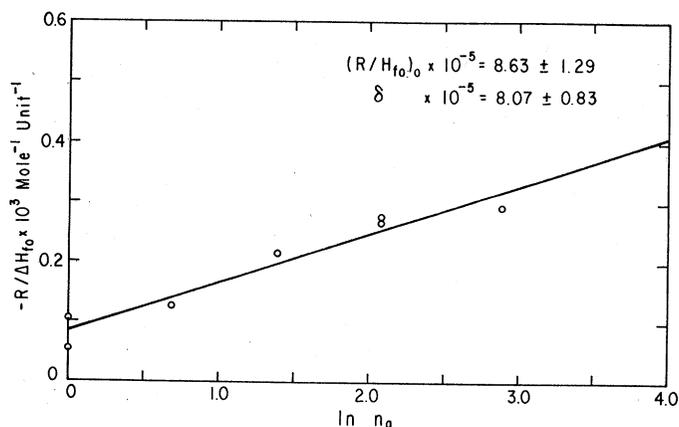


Fig. 3. Relationship between the quantity  $R/\Delta H_{f0}$  and the number of methylene groups in the side chain of amorphous comonomer a.

TABLE III  
Comparison of Melting Points Calculated by Equation (12) with Experimental Values

Mole fraction <sup>a</sup>	Melting point, °K							
	OA + MA		OA + BA		OA + OCA		OA + OLA	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
0.050	304	290	276	261	264	260		
0.075	307	300	282	274	271	267	259	265
0.100	310	306	287	283	277	273	266	270
0.15	313	312	294	295	285	282	275	276
0.20	316	315	299	301	291	288	282	285
0.30	319	325	306	308	300	299	293	295
0.40	322	320	311	315	307	306	301	303
0.50	324	321	316	318	312	313	308	310
0.60	325	324					313	313
0.75	327 <sup>b</sup>	325 <sup>b</sup>	324	323	322	320	320	319
1.00	330	330	330	330	330	330	330	330

<sup>a</sup> Feed composition.

<sup>b</sup> Mole fraction of fatty ester was 0.70.

mers enjoy greater freedom; the localized availability of crystallizable outer-chain methylene groups then results in crystallization at rates high enough to approach equilibrium values. Consequently, when a units reach a critical length of about 18 carbon atoms, the calculated  $\Delta H_{f0}$  approaches the value found for homopolymers.<sup>1c,3,4</sup> Main-chain stiffness in the melt (as in series 2 copolymers) makes little contribution to  $T_m$  depression but does affect rates of crystallization at high a-unit content. Thus, the experimental observations obey the requirements specified earlier in this paper for copolymers crystallizing through side chains.

Melting points of vinyl stearate copolymers (series 3, Table I) show little depression, as would be expected.<sup>1a,3</sup> Here the exceptionally long blocks of vinyl stearate units are retained and the data consequently would follow eq. (9).

As has been discussed, when short a units occur in these systems (Table I), they are largely bridged by developing side-chain crystallinity. As a units increase in length, their effect on reducing the crystallite size of the most perfect crystal increases. Consequently, it is possible to calculate a mole fraction of b units based on the crystallite size at equilibrium melting. Because melting point depression increases as crystal size decreases, use can be made of eq. (10) to calculate  $m_b$ , but using  $\Delta H_{f0} = 6925$  cal/mole, which is the value of  $\Delta H_{f0}$  for poly(*n*-octadecyl acrylate). If these values of  $m_b$ , designated  $m_{bc}$ , fall on theoretical plots for  $\Delta H_{fmax}$  [eq. (6)] of  $x_{cmax}$  [eq. (4)], the condition of equilibrium crystallinity required by eq. (3) will be met. Data are shown in Figure 4 where  $x_{cmax}$  is plotted as a function of  $m_{bc}$  for the systems whose melting points are listed in Table III. For the calculation of  $m_{bc}$  the calculated melting points of Table III were used. An exception was the methyl acrylate system where found values were

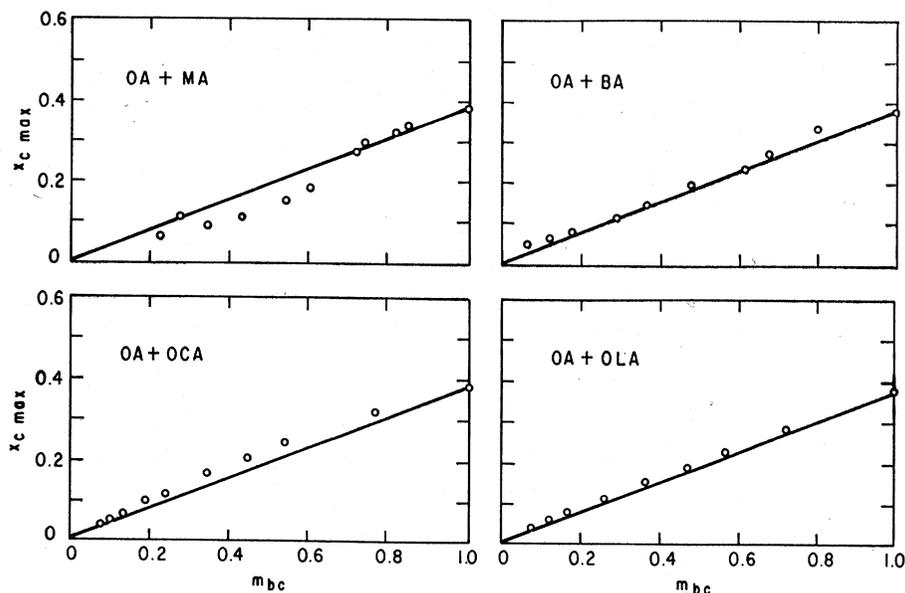


Fig. 4. Plots of  $x_{c \max}$  vs. the mole fraction of crystalline co-unit b: (O) calculated by using eq. (10) (—) theoretical:  $x_{c \max}$  at  $m_{bc} = 1$  is  $x_{co}$ .<sup>19</sup>

employed. As can be seen, the conditions of eq. (3) are generally met. The apparent differences found in this work for copolymers crystallizing through their side chains, compared with other types of crystallizing copolymers,<sup>1a,4,5-13</sup> appear to have a simple coherent explanation.

### SUMMARY AND CONCLUSIONS

The thermodynamics of the crystallinity present in the side chains of selected copolymers has been treated experimentally. Consideration was given to the development of crystallinity in the side chains of b co-units interrupted by randomly dispersed a units of varied lengths. It was concluded that (1) reduction in crystal size was proportional to the amorphous side-chain length; (2) rates of crystallization were high so that equilibrium crystallization was approached at high b-unit concentrations; (3) chain stiffness in the melt had some broadening effect on crystal-size distribution but made a much larger contribution to retarding the attainment of equilibrium; (4) the presence of long blocks of b co-units, as in the heterogenous vinyl stearate copolymers, depressed melting points only slightly, following the accepted theoretical probability sequence function; (5) crystallinity development seemed dependent on stable crystal nuclei forming largely intramolecularly in small volume elements and growing because of the unrestrained cooperative movements of amorphous main-chain and side-chain units.

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Reference to a commercial product does not constitute recommendation by the U. S. Department of Agriculture over any other similar products not mentioned.

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