Viscosity Index. III. Thermodynamic Parameters for Side Chain Crystallinity in Pour Point-Modified Blends Containing *n*-Octadecyl Acrylate

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Synopsis

The melting transitions and heats of fusion were obtained by differential scanning calorimetry for the crystalline phase of the same mixtures whose rheological properties were reported in the previous two papers. Pour point temperatures were also determined. In addition, the same thermodynamic quantities were also collected for higher polymer concentrations in this work, thus encompassing the entire concentration range. The DSC scans revealed that the distribution of crystallite sizes characteristic of the bulk copolymers was retained in the blends. Phase diagrams indicated isomorphism in all systems studied. An equation was derived to predict the influence of diluent concentration on melting point depression of copolymers, in which one component crystallizes through its side chains but in which the side chains of the other remain amorphous. The difference between the experimental heats of fusion and the value for entirely crystalline poly(*n*-octadecyl acrylate) were used to estimate extent of apparent cocrystallization of the different copolymers with the base oil. While this tended to increase with pour point-depressant ability, concomitant crystallinity of wax and depressant were essential to successful wax crystal modification. A mechanism is proposed in which whole molecules of hexagonally packed copolymers are attached to wax nuclei and accumulate slowly at low diffusion rates. Thus, growth occurs over small crystal areas and is considered responsible for the directing influence of copolymer depressant. The resulting small crystal sizes, accompanied by fast growth of rapidly diffusing paraffins on uncontaminated surfaces, promote more compact habits, like dendrites that postpone network formation to lower temperatures. It was concluded that a melting point difference of less than 25°C between bulk copolymer and base oil is required for successful pour point depression. Consequently, in this base oil, only copolymers with long amorphous side chains in a limited composition range, such as the *n*-octadecyl acrylate–2-ethylhexyl acrylate copolymers, possessed sufficient lattice disorder to meet the specification. The rest produced gelation at higher temperatures.

INTRODUCTION

The previous two papers[1,2] of this series discuss the rheological properties of single-phase blends of acrylate and methacrylate copolymers containing *n*-octadecyl acrylate (OA) as a common comonomer. The first paper[1] deals with viscosity phenomena and the second,[2] with theoretical interpretation. This paper considers thermodynamic aspects of two-phase interactions established in the blends by lowering temperature. The influence of a crystalline phase developing both in the base oil and in the side chains of the modifying copolymers is correlated with the flow properties of the chilled blends.

When many lubricating oils are cooled to about −10° to −30°C, the higher-melting wax components preferentially crystallize.[3–5] These crystals usually take the form of large, thin, convoluted, interlocking platelets,[6] which entrap

oil and thus form a rather tight network. A large discontinuous increase in apparent viscosity results. This leads to an increased power requirement for starting[7,8] and oil circulation[9] in cold motors and serious pumping problems in the transport of lubrication fluids.[3–5] Although this gel is easily broken at the high shearing rates[10] of operating engines,[7,8] yielding considerably lowered viscosities, the initial energy requirement often exceeds available supply, especially since gel modulus increases rapidly with decreased temperature.[11] The crystallites are efficient in their ability to gel the liquids since only 2% wax[12] will prevent gravity flow of 50 ml of an oil in a tube 1.5 in. in diameter (the approximate pour point test). Because crystal habit[6,12–14] has been found responsible for these persistent[10] gel structures, additives to alter the macrocrystalline order have long been[15] and still are[16,17] employed.

Although initially many monomeric materials were employed as pour point depressants,[15] ester-type polymers and copolymers, useful as viscosity index improvers,[1,18–20] were also found to function well in this capacity. Consequently, they are now almost exclusively used, especially those having average side chain lengths of 12–14 carbon atoms.[6,18,21] However, depressant activity is a function of both the average side chain length and the melting point of the wax component of the oil. The required side chain length increases as wax melting point increases.[22] The polymers seem to act by cocrystallization[21,23] of the double-comb side chains[24] with the nucleated wax crystal to suppress growth along the 011 (or XY) crystallographic plane. This encourages dendritic growth at the corners of the nuclei, or it forms small, relatively isotropic rhombic prisms by preferential growth along the Z axis.[12,14] The development of these habits seems to be favored by lattice imperfections[25] resulting from the multiplicity of homologous alkanes found in the oils.[12] However, the varied or contrasting side chain lengths in the depressant copolymers also appear to benefit controlled crystal growth of the alkanes and increased pour point depression.[21] The small compact crystals thus formed fuse to form networks only at higher concentrations (lower temperatures) so that the pour points of wax-bearing oils are depressed.

Recent fundamental studies of the condensed state of double comb-type macromolecules by x-ray diffraction[24,26] and by differential scanning calorimetry[27,30] have revealed information pertinent to pour point-depressant activity. These studies[24–30] and others[31] showed that the rather loose hexagonal crystal modification prevailed in all comb-type homopolymers and copolymers; no other modification was found at any undercooling. The requirement that this form be cocrystallized with the wax lattice would be expected to retard the local planar growth process[32a] and could be responsible for the crystal habits observed. A difference in the critical side chain length of three methylene groups was required to initiate crystallinity in flexible homologs, such as the poly(n-alkyl acrylates), compared with stiff homologs, such as the poly(N-n-alkylacrylamides).[27,30] This was similar to the two-carbon equivalency of average side chain length in pour point depression found for acrylate and methacrylate homologs in a base oil.[21] The thermodynamic properties of copolymers containing side chains of varied length[28,29] are especially relevant to the phase thermodynamics characterizing the blends of this work. The influence of this equilibrium process on the pour points of the blends constitutes the main emphasis of the present investigation.

In this work differential scanning calorimetry (DSC) is used to determine

melting point, freezing point, and apparent heat of fusion of the base oil S105 and the copolymer blends studied. Phase diagrams covering the complete range of blend compositions are constructed for selected copolymer systems. From these, the effects of melting point depression and latent heats of poly(*n*-octadecyl acrylate) in lube oil mixtures containing copolymers having short (C_1) and intermediate (C_8) amorphous side chains, each associated with the long (C_{18}) crystalline side chains, are ascertained. The influence of copolymers having both side chains cocrystallizable (C_{18} and C_{12})[28] is also monitored. All of these data are correlated with the respective pour points and are compared with those of previously studied[1,2] commercial methacrylate esters, whose pour point-depressant activity was found to be good in the experimental base oil.

EXPERIMENTAL

Copolymers

The copolymers used to make the blends of the preceding two papers[1,2] were used for the studies of their bulk properties.

Low-Concentration Blends

The same mixtures that were used for rheological studies[1,2] were used in this work.

High-Concentration Blends

Blends covering the concentration range between bulk copolymers and the low-concentration range were made as follows. Two-gram mixtures at a predetermined polymer weight fraction were obtained at regular increments across the concentration range. After being heated on a steam bath under a heat lamp for 5 min, stirred without heating for 3 min, and reheated for 5 min, the samples were equilibrated in an oven at 100°C for 45 min. The cooled mixtures were weighed as liquids (sometimes with warming) in the solvent-type weighing cups provided with the DSC. The density information of the previous paper[2] was used to convert weight fraction to volume fraction by assuming additivity of volumes.

Calorimetry

In general, the procedures described in references 27 and 28 were followed. Sample weights were adjusted to correspond as closely as possible to maximum attenuation or until the maximum sample weight for the cups (18–20 mg) was reached. Only single determinations were made for each blend concentration. Each sample was programmed at 10°C/min from −80°C through three heating cycles to 50°C above the melting temperature and held there for 5 min. Each program was followed by manual return, and one additional run was programmed at a cooling rate of 10°C/min. Peak areas, melting and freezing temperatures, by both techniques were the same. All the other procedures were as reported.[27,28]

Pour Point Determination

The procedure of ASTM D97-57 was followed but was modified by using only 8–10 ml of sample in a redesigned apparatus. The cooling times and other conditions were the same as those of the ASTM proedure. The modified procedure gave the same values for pour points as the conventional one on selected blends. An IBM 1130 computer was used for all correlations.

Subscript Designations

In this work, as in the two preceding papers, w_i, m_i, and v_i are weight, mole, and volume fractions, respectively. The subscript 2 designates copolymer; subscript 1, solvent in the mixtures. Subscript b designates n-octadecyl acrylate in the copolymer; subscript a, the other comonomer. Molar volumes carry the symbol V, with V_u standing for the molar volume of average copolymer unit and V_1, the average molar volume of solvent. Densities used to calculate the molar volumes have been discussed.[2]

RESULTS AND DISCUSSION

General Discussion

All of the heats of fusion and the melting points for all concentrations of the blends prepared in the previous two papers are collected in Table I. The arrangement of this table and that of Table I of the previous papers is the same. However, one new copolymer has been added (experiment 11A), and one copolymer has been omitted (experiment 23 of the previous papers). The reported melting points are probably a few degrees higher than equilibrium values because the relatively high DSC scan speeds (10°C/min) employed do not permit the attainment of true equilibrium between phases.[27] This difference can be as great as 5°C in bulk homopolymers. In this work, as in previous studies, relative differences in T_m are important; consequently, the reported melting points are taken as true values.

Heats of fusion ΔH_f for the polymeric component of the blends and the starting bulk copolymers (ΔH_{f0}, next to the last column) were somewhat similar for most of the experiments at all concentrations. This suggests that the fusion properties characteristic of the bulk copolymers were maintained in the blends. Consequently, it strongly implies that the hexagonal crystal modification persisted unchanged. However, in certain of the blends (experiments 9–11A) observed heats of fusion were greater than those for the respective bulk copolymers. In general, these are the same blends which melt near the T_m of the base oil (experiment 1). This phenomenon is discussed below. The melting points of the blends were displaced about 20°–30°C below those of the starting bulk copolymer (T_{m0}, last column). Trends are not readily apparent. The spread seems to be slightly greater (25°–30°C) for the more flexible copolymers and homopolymers, OA + EHA, OA + DA (experiments 6–13), than for the rest (20°–25°C). The melting point depression (difference between T_m and T_{m0}) is discussed quantitatively below.

It is of special interest[6,21] that incrementally reducing the molecular weight of poly(n-octadecyl acrylate) (POA) homopolymers (experiments 14–21; see

TABLE I

Heats of Fusion and Melting Points of the Polymer Thickened Oils Studied in the Previous Papers

Experimental no.[a]	System[b]	w_b[c]	ΔH_f, cal/g[d]				T_m, °C				Starting copolymer[e]	
			0.005[f]	0.025	0.050	0.075	0.005[f]	0.025	0.050	0.075	ΔH_{f0}, cal/g	T_{m0}, °C
1	S105	0	17.59[g]				−9[g]					
2	OA + MMA	0.636				7.94			26.8	27.8	5.85	51.7
3	OA + MMA	0.798			13.6	16.4	28.0	29.0	30.0	31.0	12.34	53.6
4	OA + MMA	0.883			13.1	17.6	30.0	31.0	32.0	33.0	15.7	55.2
5	OA + MMA	0.948		15.2	16.9	19.5	31.0	34.0	35.0	35.8	19.8	56.6
6	OA + EHA	0.085					−9.2	−10.2	−10.2		0.52	−13.0
7	OA + EHA	0.164					−10.2	−9.2	−10.2		1.72	−9.00
8	OA + EHA	0.237					−10.2	−10.2	−10.2		2.70	10.0
9	OA + EHA	0.306				17.0		−8.2	−8.2	−8.2	4.59	16.0
10	OA + EHA	0.430			20.5	14.5	−4.20	−1.20	−1.20	−2.20	7.95	27.0
11	OA + EHA	0.540		20.5	16.2	15.0	2.80	4.80	6.80	6.80	10.14	31.8
11A	OA + EHA	0.638		12.8	13.6	13.3		13.8	14.8	15.8	11.51	38.0
12	OA + DA	0.252		11.8	18.2	14.7	−10.2	−4.20	−2.20	−1.20	10.30	24.0
13	OA + DA	0.366		14.5	10.5	15.3	−3.20	1.30	2.80	3.80	11.10	27.0
14	POA	1.00		22.8	21.1	21.4	36.0	37.0	40.0	41.0	21.5	57.8
15	POA	1.00		18.0	20.7	19.8	35.8	37.8	38.8	39.8	21.8	56.8

TABLE I (Continued from previous page)

Heats of Fusion and Melting Points of the Polymer Thickened Oils Studied in the Previous Papers

Experimental no.[a]	System[b]	w_b[c]	ΔH_f, cal/g[d] 0.005[f]	0.025	0.050	0.075	T'_m, °C 0.005[f]	0.025	0.050	0.075	Starting copolymer[e] ΔH_{f0}, cal/g	T_{m0}, °C
16	POA	1.00			20.8				39.8		21.6	56.8
17	POA	1.00	24.4	24.3	18.5		37.8	39.8	38.8		21.0	56.8
18	POA	1.00			21.2				38.8		22.5	56.8
19	POA	1.00						21.7	23.9	21.5	22.5	57.3
20	POA	1.00		22.2	21.5	20.9		34.8	36.8	37.8	24.4	56.8
21	POA	1.00		16.6	20.5	22.3		32.8	33.8	34.8	25.2	54.8
22	Acryloid	0.425		none	none	none		none	none	none	none	none
24	Acrvloid	0.425		none	none	none		none	none	none	none	none

[a] Experiment number and description correspond to those of the two previous papers,[1,2] except for experiment 11A. Data for experiment 23 of these papers are not presented here.

[b] Designations are: S105, Arco base oil S105; OA, *n*-octadecyl acrylate; MMA, methyl methacrylate; EHA, 2-ethylhexyl acrylate; DA, *n*-dodecyl acrylate; POA, poly(*n*-octadecyl acrylate). Acryloid Rohm and Haas numbers are: experiment 22, 732; experiment 24, 772.

[c] Weight fraction of *n*-octadecyl acrylate in the copolymers, except for experiments 22–24, where w_b is thought to be *n*-dodecyl methacrylate (see previous paper[1]).

[d] The heat of fusion ΔH_f was calculated using the relation $\Delta H_f = f[A_2/(w_2 W_s)]$, where A_2 is the scan area contributed by the copolymer, W_s is the total weight of sample, w_2 is the weight fraction of copolymer in the thickened oil, and $f = (W_I/A_I)/\Delta H_{fI}$; the subscript I designating pure indium. The reported ΔH_f, therefore, is that of the copolymer only.

[e] The thermodynamic constants for the pure copolymers. See also reference 28.

[f] Weight fraction of copolymer S105.

[g] The apparent heat of fusion and T_m of the unthickened base oil.

Table I of reference 1 for molecular weights) had no appreciable effect on either ΔH_f or T_m of either the bulk polymer or blend. Finally, no crystallinity was found in either bulk copolymers or in lube oil blends containing commercial methacrylate copolymers (experiments 22–24). This suggests that their observed average side chain length ($n_c \sim 8$) is composed of two essentially amorphous comonomer units (n-dodecyl and n-hexyl methacrylate, reference 1). The seeming absence of crystallinity is surprising in view of the discussion in the introduction, because these were effective pour point depressants for the base oil.

Fusion Endotherms

Typical DSC scans for pure base oil S105 (experiment 1) and blends of POA (experiment 14) are shown in Figure 1. The figure includes incremental blends for compositions between bulk POA ($w_2 = 1.0$) and the VI improving range of interest, where w_2 lies between 0.075 and 0.005. Note the effect on peak broadening, as well as the T_m depression, as the polymer was diluted by the base oil. The melting point was taken as the end of the fusion curve (vertical slashes) following the interpretation discussed in references 27–30. The sample weight used for bulk POA ($w_2 = 1$) was about one half that of the blends, giving rise to the relatively smaller peak area observed. Melting of the components of the base

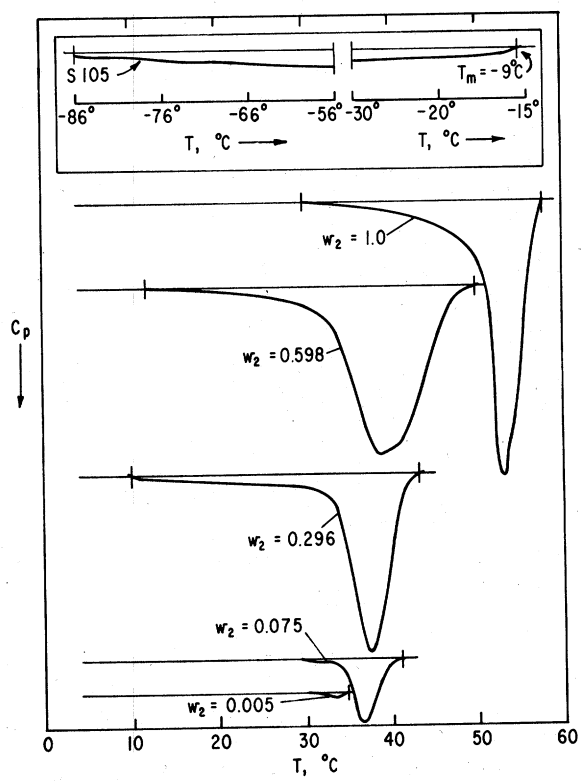

Fig. 1. Typical scans using differential scanning calorimetry (DSC) for poly(n-octadecyl acrylate) (experiment 14), in base oil S105. A partial scan of the base oil is shown in the box. The total weight of the samples used was about 18 mg, except for $w_2 = 1.0$, where it was 7 mg. Vertical slashes denote the melting point T_m (or T_{m0} for $w_2 = 1.0$).

oil was very broad, as can be seen in the box. This suggests a very wide spectrum of components having a broad molecular weight distribution. A reproducible T_m of −9°C was taken as the temperature of melting for the oil. However, this value is really only the approximate T_m of the highest melting component, depressed by the presence of the other components. The reported heat of fusion of the oil, 17.6 cal/g (experiment 1, Table I), may be low because some components remained uncrystallized even at −86°C.

Typical scans (experiment 4) for the blends using relatively stiff copolymers of n-octadecyl acrylate and methyl methacrylate,[28] over all w_2, are shown in Figure 2. The melting point depression beyond that due to POA, introduced by the small methyl side chain, was small (2.6°C). The rather broad distribution of crystallite sizes of the bulk copolymer ($w_2 = 1.0$) is preserved and also extended in the blend, even at high dilution (bottom two scans). Melting points (vertical slashes) were again depressed by the oil as shown. The copolymer endotherm occurred at relatively high temperatures compared with that for the base oil. The terminus of the base oil endotherm is barely seen at the left in all figures. However, no eutectic peaks[27,33] can be observed for these systems unless they are associated with the fusion endotherm of the base oil (far left) and are not visible.

In contrast, the fusion endotherm of oil and copolymer tended to merge (Fig.

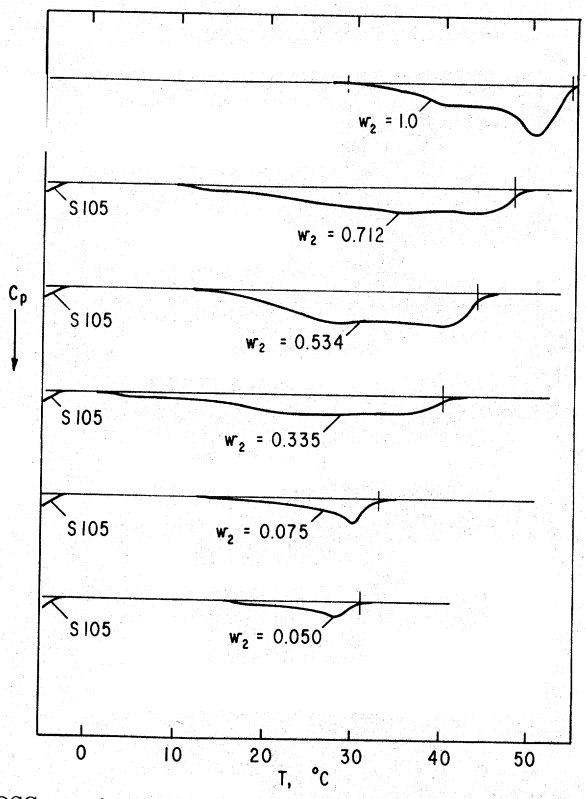

Fig. 2. Selected DSC scans for typical copolymers of n-octadecyl acrylate and methyl methacrylate (experiment 4, illustrated) over all w_2. The total weight of sample was about 16 mg, except for $w_2 = 0.335$, where it was 9.32 mg. The end of the base oil melting transition can be seen at the extreme left of the figure.

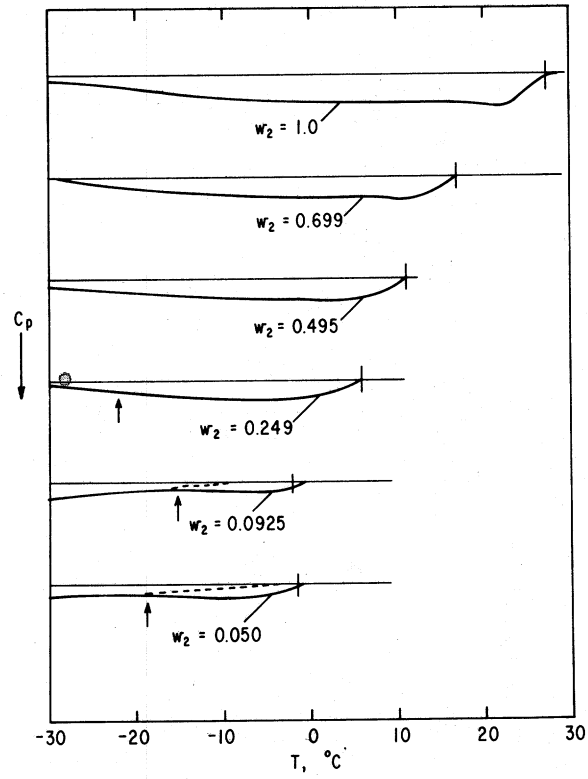

Fig. 3. Selected DSC scans for typical copolymers of n-octadecyl acrylate and di-2-ethylhexyl acrylate (experiment 10) over all w_2. The total weight of sample was about 20 mg. The transition of the base oil and copolymer merge, especially at low w_2; arrows mark the approximate separation region.

3) when the melting range of the bulk copolymers was considerably reduced compared with that of the OA + MMA bulk copolymers of Table I by incorporating a longer amorphous side chain into the copolymer (OA + EHA copolymers).[28] The approximate demarcation between polymer and oil was taken as indicated by the vertical arrow. The fusion of the bulk copolymer (w_2 = 1.0) was much broader than OA + MMA of Figure 2 and POA of Figure 1, illustrating the disturbing influence of long amorphous side chains on the lattice order.

The coalescence of the two endotherms (base oil and copolymer) in Figure 3 coincided with the apparent increase in ΔH_f reported above for experiments 9–13. This casts some doubt on the reported values. However, the increase in peak area for w_2 = 0.050 compared with that for w_2 = 0.0925 indicates that fusion of paraffinic material incorporated with the polymer increases as actual polymer concentration diminishes. This can be taken as evidence for a real increase in ΔH_f suggesting isomorphic replacement. Pour point depression was observed only for this experiment (experiment 10) and other similar experiments (9–13) of Table I. All showed coalesced scans in both melting and freezing DSC programs. Wax and additive must crystallize at about the same temperature span to achieve pour point depression.[22]

Heat of fusion data for all of the blends prepared for this paper between w_1 = 0 to w_1 = 0.975 are shown for selected experiments in Table II. As the bulk copolymers were incrementally diluted (increase in w_1), the apparent heat of

TABLE II

Heats of Fusion of Selected Copolymers with Increasing Dilution by Base Oil S105

9[a]		10		11		11A		14	
w_1	ΔH_f, cal/g	w_1	ΔH_f, cal/g	w_1	ΔH_f, cal/g	w_1	ΔH_f, cal/g	w_1	ΔH_f, cal/g
0	4.59	0	7.95	0	8.19	0	11.5	0	21.5
0.097	4.56	0.103	8.12	0.099	9.84	0.105	12.7	0.100	19.1
0.202	4.06	0.194	7.88	0.206	7.85	0.209	11.1	0.204	20.7
0.306	5.12	0.301	7.40	0.303	9.93	0.305	11.3	0.307	21.4
0.401	4.78	0.400	8.73	0.399	9.16	0.407	11.8	0.402	21.4
0.503	6.06	0.505	8.27	0.502	9.16	0.500	10.8	0.502	21.1
0.603	6.01	0.598	9.26	0.703	10.9	0.703	11.9	0.705	22.0
0.702	6.32	0.751	12.4	0.801	12.6	0.801	12.4	0.925	21.4
0.801	11.2	0.802	12.5	0.900	14.4	0.929	13.3	0.950	21.1
0.925	17.0	0.900	17.8	0.925	15.0	0.951	13.6	0.975	22.8
0.950	—	0.925	14.5	0.950	16.2	0.975	12.8		
0.975	—	0.950	20.5	0.975	20.5				

[a] Experiment number from Table I. Theoretical values of the heats of fusion ΔH_f, in cal/g, for the 100% crystalline copolymers were as follows: experiment 9, 6.58; experiment 10, 9.25; experiment 11, 11.61; experiment 11A, 13.72; experiment 14, 21.50. These were calculated as $w_b\ \Delta H_{f0}$, where ΔH_{f0} is the heat of fusion of poly(*n*-octadecyl acrylate) (21.50 cal/g) estimated using eq. (2) of reference 27.

fusion of the copolymers increased steadily, especially at high dilution, in experiments 9–11A but not in experiment 14. Blends containing less n-octadecyl acrylate (experiments 9 and 10) showed greater increase in the rate of change of the heat of fusion and lowest melting points of those of the bulk polymers, and were the best pour point depressants of the series in the table. The simultaneous crystallization of both oil and copolymer, leading to higher apparent ΔH_f in the latter, coupled with no observed eutectic peak, strongly suggests isomorphic replacement. This supports the principle[12,21,22] that cocrystallization produces depression in the pour point since only those additives showing coalesced T_m endotherms (experiments 6–11, Table I) acted as depressants.

Phase Diagrams

Phase diagrams are presented for eight copolymers in base oil S105 in Figure 4. Melting point–composition curves are presented in insert A; the corresponding data for freezing points are shown in insert B. Dashed lines in both inserts are the melting and pour point temperatures, respectively, for the base oil. The curves in insert A were calculated using a relation to be derived below; those in insert B were the best lines drawn through the experimental points. Undercooling of 10°C was a common requirement for fast crystallization of the blends. Data obtained over the range of weight fraction increments from $w_1 = 0$ to $w_1 = 1.0$, as in Table II, were used to fit the lines. The most important feature to be noted in the diagrams in insert A is that no eutectic melting point can be observed; the lines are essentially linear over w_1. Consequently, isomorphic

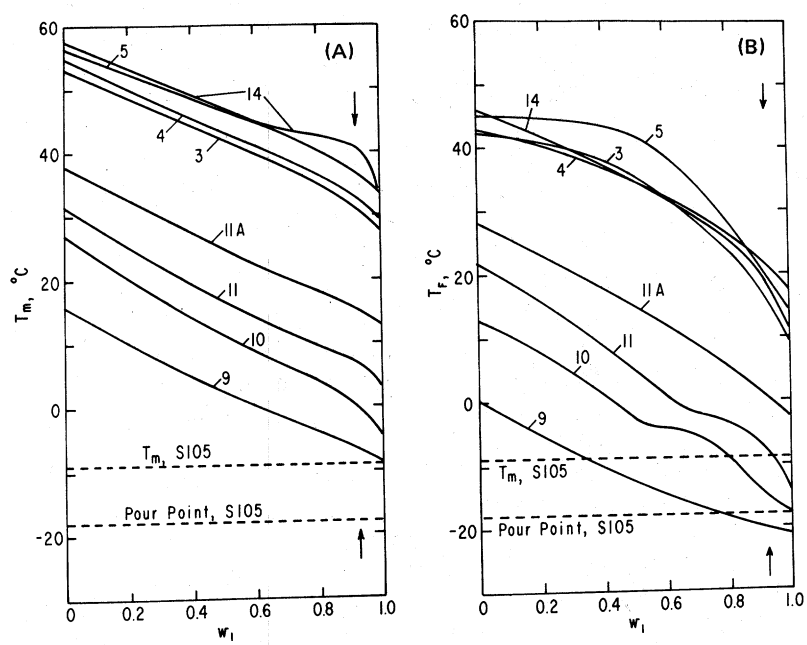

Fig. 4. Plot of melting temperature T_m (insert A) and freezing point T_F (insert B) vs weight fraction of base oil S105, w_1, for selected copolymers, numbered as in Table I. The T_m and pour point of the base oil are indicated. Data to the right of the arrows are in the concentration range of viscosity index improvers. Curves in insert A were calculated using eq. (4) and the heats of fusion of Table III.

replacement[27,28,32c,33] characterizes the fusion curves of all of the blends, even those of the higher-melting homopolymers and copolymers (experiments 3–5, 14), whose blend melting points were greater than that of the base oil in the viscosity index range. However, the occurrence of cocrystallization did not produce pour point depression here; only those systems, such as experiments 9, 10, and 11 of insert B, where both base oil and copolymer in the viscosity index range w_1 of 0.925–0.995 crystallized together below the dashed lines produced pour depression. The higher-melting systems in the figure had high pour points, closer to the illustrated freezing points (insert B) and to the melting points of their blends given in Table I. These lie close to the right of the arrows in inserts A and B. Obviously, preferential crystallization of the copolymer in a diluent leads to a crystal habit that also creates a network of high modulus in the blend. Although evidence for cocrystallization was found for these systems, too (insert A), initial nucleation and growth of wax crystals are required before crystal habits of the blends can be altered in the direction of greater isotropy. These diagrams offer an explanation in thermodynamic terms for the specificity of side chain length required, according to Ruehrwein[22] and Lorensen,[21] for pour point depression.

A possible mechanism for the directive[21,23] influences of the cocrystallization might be cast in terms of the low segmental diffusion rate[34] of polymer chains compared to simple monomeric materials. The crystal growth front of the transition state of many crystallizing systems, such as metals and simple organic compounds, is specified by the characteristic diffusion distance given[35] by $\sigma = D/G$. Here, D is the diffusion constant and G is the crystal growth rate. Since G is the same for many polymers and metals, crystal size is governed largely by the magnitude of D. Because D is small for polymers, small crystals grow into spherulites instead of dendrites and into the larger, regular habits of simple compounds unless they are highly diluted. When segments of long side-chain polymer chains are deposited on the 011 plane of a nucleated wax crystal, continued deposition of polymer would be restricted to a small front by the small magnitude of D. Deposition of the whole polymer should be required by the hexagonal packing characteristic of these comb-type polymers, as discussed in the introduction.[24,26,27,30] At the same time, the more rapidly diffusing wax alkanes would deposit on uncontaminated nuclei corners and grow rapidly with branching to form dendrites, as was discussed by Holder.[12,14] Modification of this process to other crystal habits is straightforward. In this scheme whole polymer chains and whole alkanes would deposit completely on an exposed front before segments of the next molecule become attached. The lower translational energy comprising the total latent heat is expended in depositing initial segments of the polymer chain. This leaves the components having higher vibrational and rotational energy components to direct attachment of the remaining segments. Therefore, total polymer deposition should be energetically favored over the partial deposition of many species.[35] When the polymers crystallize in the presence of diluent (experiments 11A, 3–5, and 14, Fig. 4), this small D should lead first to spherulites built from laminar crystals, growing from screw dislocations, and then to spiral growths,[32d,36] which could deposit in networks and lead to the observed gels in the blends. Tertiary nucleation[35] is apparently rate controlling for at least the polymer crystallization process because of the observed 5°–10°C undercoolings.[30] In this type of nucleation, rapid entropy loss, ac-

companying initial chain attachment, then requires lower temperatures to re-establish equilibrium.[37] Although speculative, this extension of proposed mechanisms is not at variance with experimental facts.[6,12,14,18,21,22,24,26,30]

Factors Governing the Melting Point Depression

Further analysis of the phase diagrams of Figure 4, insert A, can lead to a quantitative description of factors governing the melting point depression. This section considers this aspect in considerable detail.

The relation between the melting point depression of a crystalline copolymer in the presence of a monomeric diluent in which only one component of the copolymer can crystallize is given by[38]

$$1/T_m = 1/T_{m0} + [R/\Delta H_f(p + 1)V_u/V_1]v_1 + \chi_1 v_1^2 \tag{1}$$

where χ_1 is the solvent polymer interaction parameter[39a]; V_u and V_1 are the molar volumes of polymer units and solvent molecules, respectively; v_1 is the volume fraction of diluent; and $p = m_x/m_b$, where m_x is the mole fraction of copolymer components and m_b is the mole fraction capable of crystallization. The quantity T_{m0} is the equilibrium melting point of the bulk copolymer. In the previous use of eq. (1),[38] χ_1 was assumed to be zero, thus eliminating the last term. When eq. (1) was applied to the melting points of this work, it failed to describe T_m depression. This is not surprising. There are well-known differences in the thermodynamics of fusion for homopolymers and copolymers crystallizing through their side chains[27–30] rather than along main chains, as in the classical copolymer treatment.[40] Equation (1) was derived from the latter treatment but modified for the case of a copolymer melting in a diluent.

The classical expression for the melting point depression of a crystalline homopolymer in a diluent[32b] is

$$1/T_m = 1/T_{m0} + (R/\Delta H_{f0})(V_u/V_1)v_1 + \chi_1 v_1^2 \tag{2}$$

where ΔH_{f0} is the heat of fusion of the entirely crystalline material. This equation was shown to apply to poly(vinyl stearate) and poly(n-octadecyl acrylate) in earlier work.[27] In a previous discussion[28] it was further shown that the proper value of ΔH_{f0} for side chain crystallization occurring in the bulk state in copolymers was the maximum heat of fusion, $\Delta H_{f\,\max}$. This quantity is proportional to the maximum extent of crystallinity, $x_{c\,\max}$, wherein all units capable of crystallizing are present in crystallites. It was defined as

$$\Delta H_{f\,\max} = \Delta H_{f0} w_b \tag{3}$$

where ΔH_{f0} is the heat of fusion for the respective entirely crystalline homopolymer and w_b is its weight fraction in the copolymer. Provided that $x_{c\,\max}$ is approached by the copolymer in the diluent, eq. (3) can be substituted into eq. (2) to yield an expression equivalent to eq. (1) in describing the melting point depression contributed by a monomeric diluent to copolymers having a single crystallizable side chain. Thus modified, eq. (2) becomes

$$1/T_m = 1/T_{m0} + (R/\Delta H_{f0})(V_u/V_1)(1/w_b)v_1 + \chi_1 v_1^2 \tag{4}$$

If the maximum extent of crystallinity does not develop, eq. (4) can be further modified to allow for the decreased extent by substituting for w_b the corrected value for the weight fraction w_c of entirely crystalline material using[29]

$$w_c = w_b(x_c/x_{c\ \max}) = w_b(\Delta H_f/\Delta H_{f\ \max}) \quad (5)$$

where x_c and ΔH_f are the experimental extent of crystallinity and heat of fusion, respectively. Expressions have been developed for estimating w_c even when ΔH_f is unknown.[29]

Equations (2) and (4) may be recast in a form yielding the interaction energy density B instead of the solvent polymer interaction parameter χ_1. Thus,

$$(1/T_m - 1/T_{m0})/v_1 = (R/\Delta H_{f0})(V_u/V_1)(1/w_b)[(1 - BV_1/R)(v_1/T_m)] \quad (6)$$

where $\chi_1 = BV_1/RT$. Equation (6) is often more convenient for evaluating ΔH_{f0} than eq. (4), especially when the interaction parameter χ_1 is relatively large. In this work both equations were used. The results are found in Table III and Figure 5.

In Figure 5, insert A, are shown representative data from the experimental results of Table I correlated by eq. (6). Data for $v_1 > 0.90$ were omitted, following usual practice.[32b,c] Values of ΔH_f and χ_1 for all of the systems evaluated are given in Table III. The relatively small magnitude of χ_1 and the anomalous variation of slopes in the insert for these chemically similar systems suggest that χ_1 can be taken as approximately zero for all of them. This value was also found statistically when eq. (4) was used for the evaluation of the same data (inserts B and C, and Table III). This shows that the base oil was thermodynamically a good solvent. However, the lack of variation in χ_1 as structure changed (Table III) suggests that the alkane side chains are dominant in determining interaction with this largely paraffinic solvent. Anomalous independent interactions of long side chains of comb-type molecules have been observed in a variety of experimental studies.[24] Behavior such as this could also be responsible for the isomorphism found in the phase diagrams in Figure 4.

The near-zero values for χ_1 for all systems in Table III seem at variance with their differences in efficiency discussed in the previous papers.[1,2] Solvent power of the base oil for experiments 3 and 4 should have been expected to be relatively small, thus raising χ_1 to positive values. Again the relatively independent interaction of side and main chain units may be involved; in single-phase dilute mixtures, naked dipoles probably exert the major influence in regulating solvent interactions.

According to theory,[32b,c,40] the heats of fusion calculated using eqs. (4) and (6) should represent the latent heat of the entirely crystalline phase. Because only n-octadecyl acrylate can crystallize in these copolymers,[27,28] ΔH_f should

TABLE III

Thermodynamic Quantities Characterizing the Fusion of Selected Copolymers in Diluent S105

Experiment no.	System	Equation (6)		Equation (4)	
		ΔH_f, cal/mole	χ_1	ΔH_f, cal/mole	χ_1
2	OA + MMA	3310	−0.34	5,150	0
3	OA + MMA	7870	−0.44	6,520	0
4	OA + MMA	7440	−0.26	6,890	0
5	OA + MMA	8490	−0.13	9,110	0
9	OA + EHA	8760	0.28	11,300	0
10	OA + EHA	7540	0.08	7,880	0
11	OA + EHA	8510	−0.19	7,330	0
11A	OA + EHA	7980	0.02	7,620	0
14	POA	8720	0.03	8,390	0

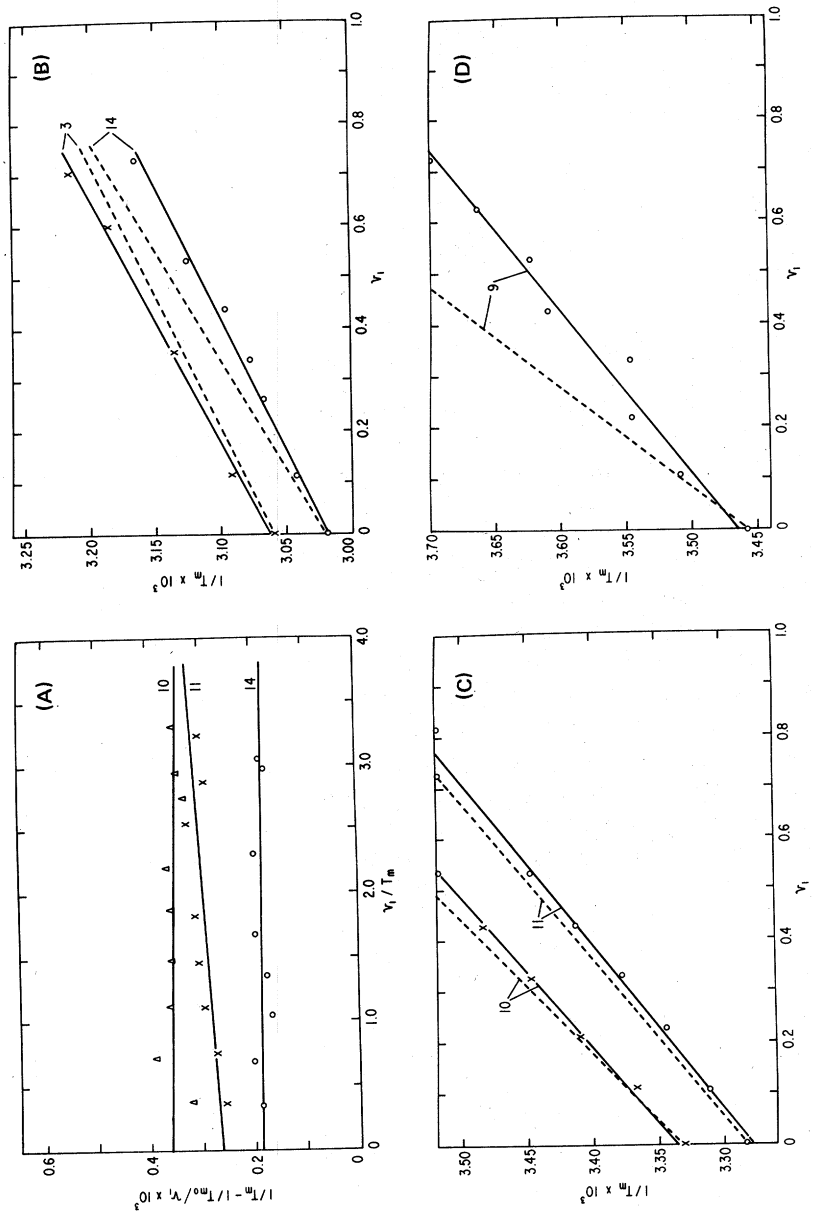

Fig. 5. Melting point depression as a function of the volume fraction v_1 of the base oil for selected copolymers. Numbering follows Table I. Equation (6) was used in insert A; eq. (4) was used in the other inserts. Dashed lines are the theoretical curves for eq. (4) using the heat of fusion of 100% crystalline poly(n-octadecyl acrylate), 6977 cal/mole.

have the same value as 100% crystalline poly(n-octadecyl acrylate), namely, 6977 cal/mole, obtained as an average value using a diluent. While some values in Table III agree with this, others do not. The dashed lines in Figure 5, inserts B, C, and D, were obtained using eq. (4) with ΔH_f of 6977 cal/mole. The generally high values of ΔH_f indicate lower depression than theory specifies and suggest that cocrystallization effectively removes some of the solvent volume fraction v_1. This is creditable because the multicomponent nature of the solvent

and the character of the phase diagram both indicate isomorphism. Substitution of w_c for w_b using eq. (5) only increased the differences. Consequently, it was possible to estimate the amount of solvent that cocrystallized in individual experiments with the various copolymers.

Estimation of the Isomorphic Volume Fraction of Solvent

An estimation may be made of the volume fraction of base oil S105 cocrystallized with the copolymers in Table III by rearrangement of eq. (4) with $\chi_1 = 0$, yielding

$$v_e = (1/T_m - 1/T_{m0})/[(R/\Delta H_{f0})(V_u/V_1)(1/w_b)]v_1 \tag{7}$$

where v_e is the effective volume fraction of S105 involved in depressing the copolymer melting point. The difference between this volume and unity, $1 - v_e$, is the volume fraction presumably lost in depressant ability by being removed as part of the crystallizing component. The quantity v_e could be found for individual systems by inserting the experimental slope of eq. (4), namely, $(R/\Delta H_f)(V_u/V_1)(1/w_b)$, into eq. (7) with ΔH_{f0} taken as the heat of fusion of POA (6977 cal/mole) and T_{m0} is taken from Table I. A plot of $1 - v_e$ over all experimental v_1 is presented in Figure 6 for selected systems. The magnitude of $1 - v_e$ reflects extent of isomorphism. The rate of change of $1 - v_e$ with respect to v_1 was zero for most v_1; only when pure solvent concentration was approached, so that v_2 vanished, did isomorphism rapidly decline.

With higher melting copolymers whose T_m is greater than T_m of the oil, the plots (experiments 4, 5, and 14) showed no regular pattern. The lower-melting copolymers (experiments 9–11) showed a steady increase in isomorphism as T_m declined with decreasing n-octadecyl acrylate content. This was the direction

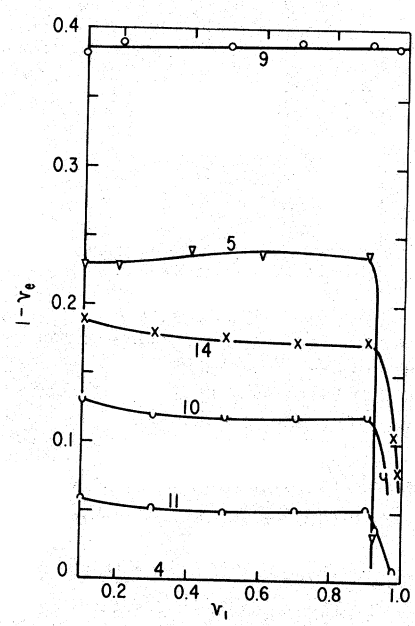

Fig. 6. Relation between calculated volume fraction, eq. (7), of cocrystallizing diluent, $1 - v_e$, and volume fraction of diluent, v_1, for selected systems from Table I.

for increasing pour point-depressant activity. Isomorphic replacement apparently involves a considerable portion of the oil. For example, about 1 mole of oil was associated with 2 moles of copolymer units (assuming equal molar volumes[2]) for the extreme case of experiment 9 in Figure 6. In the concentration range of interest for these blends as viscosity index improvers, although cocrystallization extent declined with v_2 (Fig. 6), isomorphism was still present. The heat of fusion data, then, provide additional support for a cocrystallization mechanism in regulating crystal habit.

Pour Point Depression

In Table IV are listed the blend compositions of the copolymers of this work (Table I) that exhibit pour point depression. In Table V are listed those experiments from Table I that did not. Experimental pour points T_p, freezing temperatures T_F, and melting points T_m are given in both tables. In general, as has been discussed at various places in the above sections, only those blends whose freezing temperatures coincide with the freezing temperatures of the base oil exhibited pour point depression (Table IV). These include only those copolymers having long amorphous side chains (OA + EHA) or shorter cocrystallizing side chains (OA + DA). Sufficient disorder was introduced by the amorphous side chain diluents to depress the bulk melting points enough that the freezing temperatures of blend and oil coincided. However, even in these systems w_b had to be below 0.40 (Table I) for effective depression because experiments 10 and 11 were borderline (Table IV).

Although no crystallinity has been found by DSC for the acryloids (experiment 24), they are very effective depressants. This is not completely understood. It may be that a small portion of C_{18} methacrylate ester is present together with crystallizable n-dodecyl methacrylate in these copolymers, enough to fulfill the mechanistic requirement of cocrystallization. Such complex multicomponent

TABLE IV
Copolymer Systems Which Exhibit Pour-Point Depression in Base Oil S105

Transitions, °C[a]	w_2	Experiment Number: S105	OA + EHA						OA + DA		Acryloid
		1	6	7	8	9	10	11	12	13	24
T_m	0	−9	−13	−9	10	16	27	31	24	27	None
	0.005		−9	−10	−10	−8	−4	3	−10	−3	−9[b]
	0.025		−10	−9	−10	−8	−1	5	−4	1	−10[b]
	0.050		−10	−10	−10	−8	−1	7	−2	3	−10[b]
	0.075					−4	−2	7	−1	4	
T_F	0	−18	−23	−19	0	6	14	22	2		
	0.005		−19	−19	−20	−21	−20	−14	−20	−20	−19
	0.025		−18	−18	−20	−20	−17	−11	−17	−12	−20
	0.050		−21	−20	0	−20	−16	−9	−15	−10	−21
	0.075					−17	−15	−8	−14	−8	
T_p	0	−18.0									
	0.005		−17	−17	−30	−25		−17	−18	−15	−30
	0,025		−14	−31	−20	−21		−7	−15	−12	−30
	0.050		−17	−23	−20	−15	−15	−8	−15	−9	−27
	0.075		−14	−17	−17	−15		−5	−15	−9	−27

[a] T_m and T_F melting point and freezing temperature using DSC; T_p is the pour point.
[b] T_m of base oil.

TABLE V
Copolymer Systems Which Do Not Exhibit Pour Point Depression in Base Oil S105

Transitions[a]	w_2	S105 1[b]	OA + MMA 2	3	4	5	POA 14
T_m	0	−9	52	54	55	57	58
	0.005			28	30	31	36
	0.025			29	31	34	37
	0.050		27	30	32	35	40
	0.075		28	31	33	36	41
T_F	0	−18	23	43	43	45	46
	0.005				16	12	18
	0.025			14	17	19	17
	0.050		14	15	17	19	30
	0.075		14	14	7	19	22
T_p	0	−18					
	0.005		−21	−16	−16	−15	−19
	0.025		−2	10	16	15	−16
	0.050		10	15	19	22	−10
	0.075		13	18		21	23

[a] T_m and T_F, melting point and freezing temperatures, respectively, using DSC; T_p is the pour point.
[b] Experiment number.

polymers are often used in industrial practice.[16,17] Because it is known that stiff polar comb-type homopolymers, such as poly(N-*n*-octadecyl acrylamide) and poly(N-*n*-dodecyl acrylamide),[27] exhibit very broad DSC scans, the scans for the methacrylates could easily be interpreted as baseline. This would be especially true for copolymers because they exhibit much smaller exotherms than do homopolymers.[28] Unfortunately, the bulk properties of the higher methacrylate copolymers have not been obtained using DSC, although limited thermal analyses of their homopolymers are available.[41,42]

It follows that the much higher-melting *n*-octadecyl acrylate–methyl methacrylate copolymers are not depressants for S105 (Table V). However, as discussed above, these preferentially crystallizing copolymers are able to gel their solutions and produce the high pour temperatures shown in the table. The close correspondence of T_F and T_p suggests that only small amounts of crystallizing copolymer are necessary for pour point depression because the crystallinity concentration present at T_F is small. This analogy does not account for the lower cooling rates used to determine T_p, however. More significantly, concentrations of only slightly less than 0.025 weight fraction of copolymer were required to produce the minimum modulus required to pass the pour point test. This can be seen for experiments 2–5 in the table. This minimum correlates well with a minimum of 2% paraffin needed to gel a lube oil.[12] Thus, although the expected crystal habits produced in solution are different—spherulites for the former[32d,35,36] and large platelets for the latter[6,12,14]—the critical concentrations for incipient gelation were similar.

Based on the observations of Tables IV and V, an empirical expression was developed for estimating, qualitatively, the critical fusion temperature T_{mc} for an undiluted copolymer, below which temperature pour point depression can be expected at high dilution. This relation is

$$T_{mc} = [1/(1/T_{m0})] + [(R/\Delta H_{f0})(V_u/V_1)(1/w_b)]0.95 \quad (8)$$

where ΔH_{f0} is the value of the heat of fusion for pure poly(n-octadecyl acrylate), 6977 cal/mole, and v_1 was taken arbitrarily as 0.95. Consequently, this approximate equation avoids the problem of possible cocrystallization. Computed values of T_{mc} for selected copolymer blend systems are shown in Table VI. The ability of eq. (8) to predict whether a given copolymer at any assigned composition will produce pour point depression is compared with actual behavior in the last two columns. In general, the equation was qualitatively successful. Its use leads to the present generalization (Table I) that the difference between the melting point of the base oil and bulk copolymer containing n-octadecyl acrylate must be less than 25°C for successful pour point depression. Consequently, eq. (8) would appear to be useful for predictive purposes if ΔH_{f0} for the crystallizing homopolymer and T_{m0} and composition of the pour point depressing copolymer are all known.

SUMMARY AND CONCLUSIONS

Some thermodynamic quantities for fusion of the blends whose rheological properties were treated previously[1,2] are obtained in this work. The DSC scans reflect the crystallite distribution of the starting bulk copolymers perturbed by the modifying influence of the base oil diluent. Monotonic melting point depression with increasing weight fraction of diluent is always observed. An equation is derived for predicting the melting point depression of a diluent for copolymers like these, in which one component crystallizes through side chains and the side chains of the other remain amorphous. The relation between latent heat and extent of cocrystallization is estimated. Anomalously constant polymer–solvent interaction seemingly insensitive to structure is discussed in terms of independent interaction of main and side chain units. Finally, the thermodynamic parameters for all of the experiments are related to their pour point values. It is concluded that for successful pour point depression, the modifying copolymer and the highest melting paraffins of the base oil must crystallize concurrently. The growth of hexagonally packed side chains in discrete areas on the faces of the wax crystal nuclei, aided by small polymer diffusion rates, is in support of observations of others that smaller, more isotropic wax crystals produce pour point depression. Consequently, only the lower-melting copoly-

TABLE VI
Use of T_{mc} to Predict the Possibility of Depressing the Pour Point for Selected Systems

Experiment no.[a]	System	Transitions in S105, °C		T_{mc}, °C	Prediction of T_p	
		T_m	T_p		Possible	Observed
3	OA + MMA	−9	−18	35	no	no
6	OA + EHA			−90	yes	yes
7	OA + EHA			−59	yes	yes
8	OA + EHA			−33	yes	yes
9	OA + EHA			−20	yes	yes
10	OA + EHA			−3	no	no
11	OA + EHA			5	no	no
12	OA + DA			−29	yes	no
13	OA + DA			−13	no	no

[a] Numbered as in Table I.

mers were found to be effective; the higher-melting copolymers crystallize from their own nuclei at higher temperatures and gel the blends. Unfortunately, these were the same copolymers whose rheological properties showed the greatest efficiency as viscosity index improvers in previous work. In the selection of flexible acrylate copolymers containing *n*-octadecyl acrylate as viscosity index improvers, a balance must be struck between control of single-phase and two-phase effects in solution properties; of these, the latter are more important rheologically.

Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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