

Side-Chain Crystallinity. III. Influence of Side-Chain Crystallinity on the Glass Transition Temperatures of Selected Copolymers Incorporating *n*-Octadecyl Acrylate or Vinyl Stearate

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Synopsis

The influence of side-chain crystallinity on the glass transition temperatures of selected copolymers was investigated. The copolymers were selected, in part, from those whose crystallinity was treated in the preceding paper. These included the lower amorphous acrylate esters, such as methyl, ethyl, *n*-butyl, and 2-ethylhexyl acrylates, together with methyl methacrylate and acrylonitrile, each copolymerized with *n*-octadecyl acrylate over the range of composition. The decline in the glass transition temperature was linear with increasing weight fraction of *n*-octadecyl acrylate for all systems in the composition range where the copolymers were essentially amorphous. The extrapolated T_g for the amorphous state of poly(*n*-octadecyl acrylate), and for amorphous poly(oleyl acrylate), was close to -111°C . This coincided with a value previously obtained by an extrapolation of data on homologs. Beyond a critical fraction of octadecyl acrylate (0.3 to 0.5), developing side-chain crystallinity in *n*-octadecyl acrylate raised the glass temperature steadily for all systems, up to a value of 17°C , obtained for the crystalline homopolymer. Crystallinity did not develop in stiff copolymers until T_g was about 30°C below the melting point of the most perfect crystals. In compositionally heterogeneous copolymers incorporating vinyl stearate, blocks of crystalline units appeared to be dispersed in a glassy matrix of amorphous co-units. An empirical equation was derived which fitted the experimental data for random copolymers, over all composition ranges, with fair accuracy.

INTRODUCTION

The influence of crystallinity on the glass transition temperature of polymers is not readily predictable.^{1,2} It might be reasonable to expect that the glass transition would always rise as crystallinity increased. In analogy with covalent crosslinking,³ crystallites are thought, by tying certain chains together, to restrict their segmental motion, thus raising T_g . Indeed, for many crystalline homopolymers the glass transition was raised.^{1,2,4-8} Some, however, showed no change,^{9,10} and one system even showed a decrease^{11,12} in T_g . These conflicting observations have not received a uni-

fied explanation, although the behavior of individual systems was rationalized in some of the reports.

The crystallinity present in all of these polymers involved an ordering of main-chain units. No known studies have been made relating a shift of the glass transition in copolymers to crystallinity occurring in side chains. The disrupting influence of side-chain crystallites on the viscoelastic properties of the higher methyl methacrylates has long been known.^{13,14} Some limited observations indicated that developing side-chain crystallinity induced a strongly adverse effect on the mechanical properties of copolymers,^{15,16} without, however, affecting the monotonic decline of their flex temperatures.

In this study the change of the glass temperature with composition was followed for most of the copolymers whose heats of fusion and melting points were determined in the previous paper.¹⁷ Included in the present study were copolymers of *n*-octadecyl acrylate with the lower amorphous acrylate homologs, such as methyl (MA), ethyl (EA), *n*-butyl (BA), 2-ethyl hexyl (EHA) and with stiff comonomers, such as methyl methacrylate (MMA) and acrylonitrile (AN), over the range of composition. Also included were copolymers of vinyl stearate (VS) and oleyl acrylate (OLA) with methyl methacrylate. It was expected that a comprehensive picture of the influence of side-chain crystallinity on T_g would result from the large amount of experimental data collected here. A major consideration centered on detecting any shift in T_g with increasing side-chain crystallinity, conferred by increasing weight fraction of either *n*-octadecyl acrylate or vinyl stearate. Differential scanning calorimetry was used to measure the glass transition temperatures. The conventions and designations of the preceding paper¹⁷ were followed here. A subsequent paper will demonstrate the effect on some mechanical properties of the interrelation of side-chain crystallinity and the glass transition.

EXPERIMENTAL

The preparation, purification, and analysis of the various monomers and copolymers were fully described in the preceding paper.¹⁷ The operation of the differential scanning calorimeter was the same, except that scanning speeds of 40°C/minute (through three separate scans), 20 and 10°C/min (through one scan each) were employed for each sample. Scanning ranges were from -90°C to 20°C above the melting transition. Largest sample weights (14 to 25 mg.) were used for maximum sensitivity. All computations were performed with an IBM 1130 computer by procedures previously described.¹⁶

RESULTS AND DISCUSSION

Glass Transition Temperatures

Most of the copolymer systems investigated and their glass transition temperatures are listed in Table I. In addition, copolymer composition,

TABLE I
Glass Transition Temperatures Found for the Copolymers

Fatty ester in copolymer, mole fraction ^a	Glass transition temperature, °C ^b						
	OA + MA	OA + EA	OA + BA	OA + EHA	OA + MMA	OA + AN	VS + MMA ^c
0	6 ^d	-23.0	-55.0	-77.0	101.6	92.0	101.6
0.050	-10.3	-29.7	-62.0	-78.7	77.0	52.0	109.0
0.075	-20.7	—	-66.0	-80.0	57.8	34.3	89.0
0.100	-31.7	-43.0	-66.4	-80.0	38.0	11.0	88.0
0.125	-39.2	-53.0	-73.0	-82.0	39.0	4.0	86.0
0.150	-48.3	-48.4	-55.0	-83.0	26.0	-13.0	82.0
0.200	-49.3	-55.0	-49.0	-83.0	17.0	-25.0	79.0
0.300	-54.0	-33.0	-48.0	-43.0	22.0	-23.0	77.0
0.400	3.7	-18.0	-33.0	-38.0	20.7	-19.0	—
0.500	10.7	1.0	5.0	-17.0	20.7	-13.0	72.0
0.600	21.0	9.0	—	-13.0	17.0	-2.0	—
0.750	17.0 ^e	6.0	14.0	-13.4	21.0	7.0	75.0
1.00	17.0	17.0	17.0	17.0	17.0	17.0	—

^a Feed composition; compositions found by elemental analysis agreed within experimental error. For the corresponding weight fractions, see Table I of the previous paper.

^b Designations are: OA, n-octadecyl acrylate; MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate; EHA, 2-ethyl hexyl acrylate; MMA, methyl methacrylate; AN, acrylonitrile; VS, vinyl stearate.

^c Mole fractions, of vinyl stearate, calculated from elemental analysis, were 0, 0.024, 0.036, 0.046, 0.076, 0.183, 0.197, 0.377, 0.414, 0.375, 0.744, 0.902.

^d Data from Brandrup and Immergut.²⁵

^e Mole fraction was 0.70.

degree of polymerization and glass transition temperature are listed in Table II for copolymers of oleyl acrylate and methyl methacrylate. *n*-Octadecyl acrylate and vinyl stearate are the crystallizing co-units. Most of the glass transition data that follow are correlated with weight fraction; weight fractions for all of the copolymers, except those in Table II, are listed in Table I of the preceding paper¹⁷ and correspond to the mole fractions listed in Table I of this paper. For convenience, the order in both tables is the same.

The onset temperature was taken in this work to be the glass transition temperature, T_g . This interpretation of T_g is shown as curve 1 in Figure 1B. The choice is somewhat controversial, however. The generally accepted methods of obtaining T_g from DSC traces¹⁸⁻²¹ involve extrapolation of the inflection point, or endotherm maximum,²² of the heat capacity curves for successive finite scanning speeds to zero rate. This method, which recognizes the rate dependency of the transition,²³ is supported on theoretical grounds.^{19,20} However, the alternate method of using the onset temperature apparently gives values independent of scanning speed,²⁴ which are close to accepted literature values. In the present work, values of T_g within about 1-4°C of literature values,^{25a} usually obtained by other

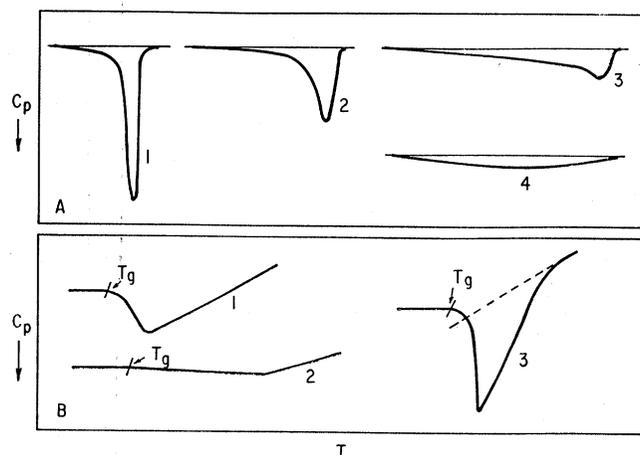


Fig 1. Typical scanning curves for the copolymers. (A) Fusion endotherms of *n*-octadecyl acrylate-ethyl acrylate copolymers, selected as representative with various mole fractions of *n*-octadecyl acrylate, as listed in Table I: (1) 0.75; (2) 0.40; (3) 0.20; curve (4) 0.05. (B) Glass transition curves of systems selected as representative from Table I: (1) ethyl acrylate copolymer system, mole fraction *n*-octadecyl acrylate 0.05; (2) methyl methacrylate copolymer system, mole fraction of *n*-octadecyl acrylate, 0.075; (3) methyl methacrylate copolymer system, mole fraction of *n*-octadecyl acrylate, 0.40.

methods, were obtained by this procedure for polyacrylonitrile, poly(methyl methacrylate), poly(vinyl chloride), poly(ethyl acrylate), and (*n*-butyl acrylate). Glass transitions were obtained at two and sometimes three different scanning speeds and averaged. It would appear that errors inherent in the use of the onset temperature at varied scanning speeds just

TABLE II
Glass Transition Temperatures, and Degree of Polymerization
of Oleyl Acrylate-Methyl Methacrylate Copolymers

Experiment number	Oleyl acrylate in copolymer		DP _n ^a	T _g , °C
	Mole fraction	Weight fraction		
1	0.050	0.145	1631	73.6
2	0.075	0.207	1663	61.3
3	0.100	0.264	1448	50.3
4	0.125	0.315	1016	21.7
5	0.150	0.362	872.8	26.0
6	0.200	0.448	787.7	5.0
7	0.300	0.580	383.9	-14.3
8	0.400	0.682	267.1	-42.3
9	0.500	0.763	193.1	-49.0
10	0.600	0.829	152.6	-57.0
11	0.750	0.906	128.9	-45.0

^a Calculated from osmometric molecular weights by using a weighted average of the molecular weights of the two comonomers. Copolymers were partially crosslinked. The soluble fraction decreased from 94% to 6% from experiments 1 to 11.

manage to compensate for rate effects. In any event, in this work, the onset temperature was the only reproducible temperature. Some scans on amorphous copolymers were obtained indicating very small heat capacity differences between the liquid and glassy states, respectively (curve 2, Figure 1B). In many the inflection point was completely masked by the presence of crystallinity (curve 3, Figure 1B). In the latter cases, the onset of melting (intersection of the dashed line) and the temperature interpreted to be T_g nearly coincided. The trends of the data in passing from the completely amorphous copolymers to the crystalline systems supported the interpretation of T_g . This convergence seems to be a unique characteristic of these systems.

Relation of T_g to Copolymer Composition in the Amorphous Region

The copolymers retained their amorphous character between the limits of 0 and 0.5 maximum for the long side-chain comonomer. This is the region considered in the discussion that follows.

Many theoretical expressions have been derived for the glass transitions of amorphous copolymers²⁶ as a function of composition. Most of these are extensions of treatments obtained from kinetic and thermodynamic theories relating to the vitreous transition in solids.¹ An expression which is empirical but seems to apply to many systems measured is²⁷

$$T_g = T_{ga}w_a + T_{gb}w_b + Kw_aw_b \quad (1)$$

Here T_{ga} and T_{gb} are the glass transitions of the respective homopolymers, w_a and w_b are their weight fractions, and K is an empirical constant. In the special case where $K = 0$, eq. (1) becomes

$$T_g = T_{ga}w_a + T_{gb}w_b \quad (2)$$

Because T_g is linear here with respect to composition

$$T_g = T_{ga} - kw_b \quad (3)$$

where k is the slope [$T_{gb} < T_{ga}$; $k = (T_{ga} - T_{gb})$] and T_{ga} the intercept of plots of experimental T_g against weight fraction of the b comonomer. The glass transition-composition data for all of the copolymer systems in Table I and II, through the composition region where the copolymers are amorphous, followed eq. (3). The parameters for the various copolymer systems are listed in Table III. The magnitude of k steadily decreased as T_{ga} decreased. These data illustrate the monotonic decline in T_g expected with composition^{1,15,16} with no attending complications of curve maxima or minima.^{28,29}

Typical data are shown in Figure 2 for copolymers of *n*-octadecyl acrylate or oleyl acrylate with methyl methacrylate. The data for the *n*-octadecyl system, shown as the solid line, at the left side of the plot, up to a weight fraction of 0.365, represent the decline in T_g in the absence of appreciable crystallinity. Above this weight fraction the T_g -composition curve is

TABLE III
Curve Fitting Parameters for Various Equations

System	Equation (3) ^a		Equations (9) and (10)		
	T_{ga}	k	$(x_c/x_{c \max})_0$	α	β
OA + MA	280.1	126.0			
OA + EA	250.9	77.59			
OA + BA	218.3	63.10			
OA + EHA	195.9	21.66			
OA + MMA	375.8	213.4			
OLA + MMA	374.5	210.0			
OA + AN	368.8	200.6			
VS + MMA	369.9	30.86			
Set 1			0.3250	1.639	-1.023
Set 2			0.1030	-0.3567	1.290

^a From Table I the glass transition temperatures correlated corresponded to these mole fractions of the C₁₈ component: MA, 0.050 to 0.20; EA, 0 to 0.20; BA, 0 to 0.125; EHA, 0 to 0.20; MMA, 0 to 0.150; AN, 0 to 0.20; VS + MMA, all mole fractions.

affected by developing crystallinity. In contrast, T_g for the entirely amorphous oleyl acrylate-methyl methacrylate copolymers, shown as the line, declined linearly to a weight fraction of about 0.73. Appreciable crosslinking through the oleyl side chain is thought to distort the curve beyond this point.³ Poly(oleyl acrylate), like poly-*N*-oleylacrylamide,¹⁶ is entirely amorphous, as revealed by differential scanning calorimetry. Both amorphous curves extrapolate to values for the respective homopolymers near 162°K (-111°C). This is the value marked with a star in the figure. A T_g of 162°K was the value assigned as the glass transition of a variety of structurally varied homopolymers having 18 carbon linear side chains when in their amorphous state.¹⁵ It had been obtained by extrapolating the glass transition temperature of several systems of amorphous

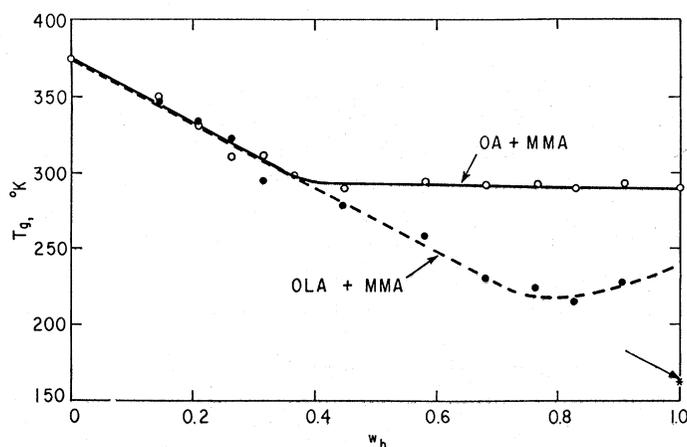


Fig. 2. Plot of glass transition temperature vs. weight fraction of fatty ester for copolymers of, respectively, *n*-octadecyl acrylate or oleyl acrylate with methyl methacrylate.

lower homologs to a side-chain length of 18 carbon atoms by using the relation¹⁵

$$T_g = T_{g0} - \beta(\ln \alpha) \quad (4)$$

where α is the number of flexible bonds in the unit, β is the rate of change of T_g with $\ln \alpha$, and T_{g0} is a constant characteristic of a homologous series. Thus these data on copolymers, in particular the data on the amorphous oleyl system, confirm the reported T_g for the amorphous state of poly(*n*-octadecyl acrylate) and for poly(oleyl acrylate). Further confirmation is found in the amorphous regions of the T_g -composition curves for several other systems. These are shown as the linear portions of the curves in Figure 3. Again all of the data follow eq. (3), and extrapolation leads to T_{gb} near 162°K (−111°C).

In this connection the glass temperature of polymethylene deserves consideration. It now appears that the true glass transition for linear polyethylene is −130°C (143°K).^{9,30} This coincides with the γ transition² for the hydrocarbon. This value is very close to a temperature of −135°C found³¹ by extrapolation of the T_g of a series of poly(alkylene oxide)s, of varying methylene length, $-(\text{CH}_2)_n\text{O}-$ to the limit of polymethylene by using the method of Grieverson.³² The value of T_g at $n = 18$ is about −125°C by this method. Thus the glass transition temperatures for poly(oleyl acrylate), and for the amorphous state of poly(*n*-octadecyl acrylate) and probably of other flexible linear 18-carbon homopolymers such as poly(vinyl stearate), poly(*n*-octadecyl vinyl ether), and poly(*n*-octadecyl methacrylate),³³ lie close to −111°C. At very long extensions of the side chains the glass transition for amorphous polymethylene (−130°C) would be approached for all systems.

Relation of T_g to Composition in the Crystalline Region

The solid or dashed lines extending to the right on the curves in Figures 2 and 3 continue the experimental values of the glass transition-composition curve (Tables I and II). It is obvious that the regular decline of T_g beyond a weight fraction of *n*-octadecyl acrylate of about 0.4 is reversed by developing crystallinity. In Figure 3, as the temperature rises for such a composition, the lower part of the dotted line marks the onset of crystallite melting; the upper part of the line is where the last trace of crystallinity disappears. The latter was taken as T_m in the preceding paper. In the numbered regions, scanning curves had the appearance of the corresponding curves of insert A, Figure 1. The spread of the curves is taken as an indication of the distribution of crystallite sizes³⁴ found as composition changed. Temperature intervals were from 22 to about 45°C. The position of each number in Figure 3 marks the approximate beginning of the melting range indicated. Of course, the regions to the left of the dotted area are the completely amorphous regions discussed above.

The curves show (Fig. 3) that main-chain stiffness has an appreciable effect on the development of crystallinity in the copolymers. In the

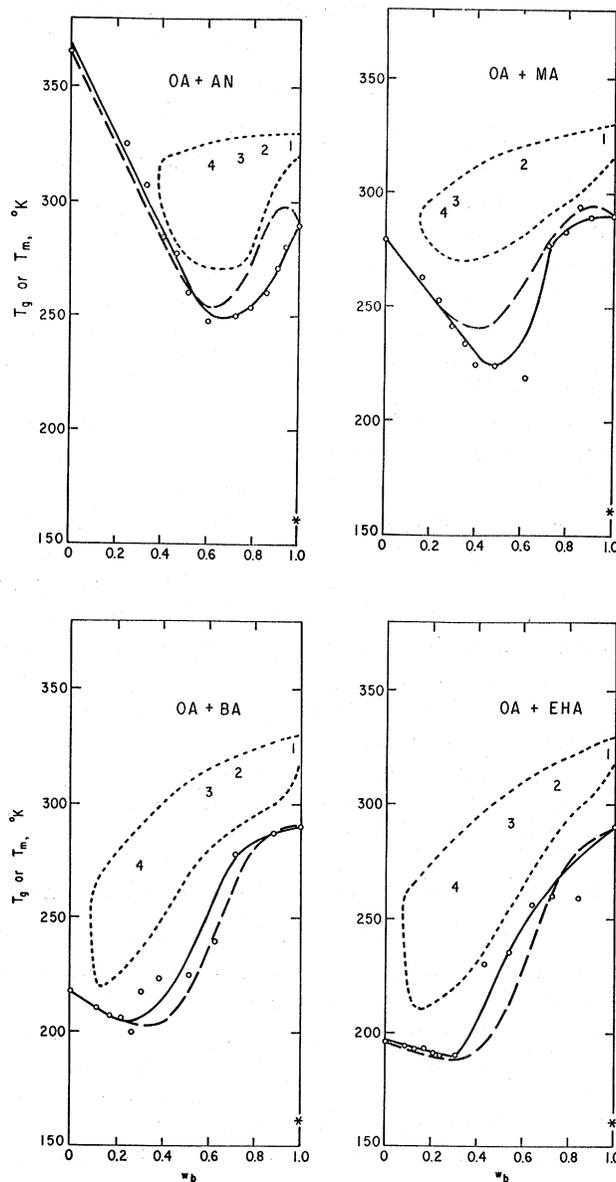


Fig. 3. Effect of side-chain crystallinity on the glass transition temperatures of copolymers of *n*-octadecyl acrylate with various comonomers: (—) experimental data for T_g ; (---) T_g calculated by using eq. (8); (···) crystallinity range. Abscissa, weight fraction *n*-octadecyl acrylate.

n-octadecyl acrylate-acrylonitrile (OA + AN) system, measurable crystallinity, as indicated by the dotted line, was not present till the glass transition temperatures had been reduced to about 290°K (17°C). This occurred at a weight fraction of about 0.4 *n*-octadecyl acrylate. Somewhat

similar results were found for the *n*-octadecyl acrylate-methyl methacrylate copolymers (Table I). In contrast, as T_g progressively decreased with change to more flexible comonomers (MA, BA, EHA), crystallinity first appeared at smaller weight fractions of the long-chain ester. In the latter systems equilibrium crystallinity was approached over a much wider composition range than was found in the former. This phenomenon has been discussed in the preceding paper.¹⁷ It may be concluded that before appreciable crystal formation began in these copolymers, glass transitions were reduced some 20 to 30°C below the equilibrium melting point. The composition range at which this occurs will be determined by the difference between T_{gb} and T_{ga} for the respective homopolymers, that is, by the magnitude of k in Table III. At a composition somewhat higher in component b, characteristic of each system, T_g begins to rise. It is possible that this rise corresponds to the region where crystal impingement becomes important.²

While the amorphous region has been adequately described by eq. (3), it might be helpful to develop a relation governing the extent of change of T_g with composition that will include the region where side-chain crystallinity developed. The simplest expression to be considered is an additive one, such that

$$T_g = w_a T_{ga} + w_b' T_{gb} + w_c' T_{gc} \quad (5)$$

In this expression T_{ga} is the glass transition temperature of amorphous homopolymer a, T_{gb} is that of the hypothetical amorphous state of crystalline homopolymer b, and T_{gc} its observed glass transition (Fig. 3). For poly(*n*-octadecyl acrylate) T_{gc} was 290°K (17°C). In eq. (5) w_a is the weight fraction of homopolymer a and $w_b = w_b' + w_c'$. The weight fraction of crystallizable comonomer is w_b , and w_b' and w_c' are the portions of w_b that are amorphous and crystalline, respectively. These quantities may be computed as

$$w_b' = (1 - x_c/x_{c \max})w_b \quad (6)$$

$$w_c' = (x_c/x_{c \max})w_b \quad (7)$$

The ratio $x_c/x_{c \max}$ relates experimental crystallinity for the copolymer, x_c , to the maximum crystallinity possible at equilibrium. These ratios were discussed in the preceding paper¹⁷ and are found there in Table I.

Equation (5), however, did not fit the experimental data. Apparently at low w_b the contribution of crystallinity to rendering the main chain rigid is reduced, and the amorphous contributions predominate, so that the proposed partition is not adequate. Similarly, at high w_b the effect of crystalline impingements would intensify. Consequently eq. (5) can be modified by introducing a parameter as an exponent which will be sensitive to the initially small and later intense influence of developing crystallinity with increasing *n*-octadecyl acrylate. If the exponent is assumed to be linear with composition of *n*-octadecyl acrylate, eq. (5) becomes

$$T_g = w_a T_{ga} + [w_b' + (w_c' - w_c'^{C+k_s w_b})] T_{gb} + (w_c'^{C+k_s w_b}) T_{gc} \quad (8)$$

with

$$w_c' = [(x_c/x_{c \max})_0 + \alpha w_b + \beta w_b^2]w_b \quad (9)$$

and

$$w_b' = 1 - w_c' \quad (10)$$

By an iterative procedure, C and k_s were assigned the values of 4.0 and -4.0 . To obtain w_c' and w_b' through eqs. (9) and (10), values of $x_c/x_{c \max}$ were correlated against w_b (Table I in the preceding paper), the curve fitting being carried through a fifth degree polynomial and analyzed for significance by an F test in the computer. The significant constants are shown in Table III. Two sets of constants were required. Parameters for systems of high main-chain mobility (the entirely n -alkyl acrylate copolymers) are listed in set 1. When main chains were stiff (methyl methacrylate, acrylonitrile), the constants of set 2 applied.

Glass transition temperatures calculated by using eq. (8) are shown in Figure 3 as the dashed lines. The empirical equation appears to describe the main features of the experimental data fairly well. It is versatile enough (providing the correct constants of Table III are employed) to apply to the usual range of T_g (100 to -80°C) encountered in copolymers. Consequently the changing glass-transition temperature, introduced by side-chain crystallinity, appears to be adequately described by this simple relationship.

When copolymer compositions are highly heterogeneous, both the crystalline and amorphous co-units polymerize in blocks and usually aggregate into separate domains. Consequently, developing side-chain crystallinity should little influence the apparent glass transition. This was found for

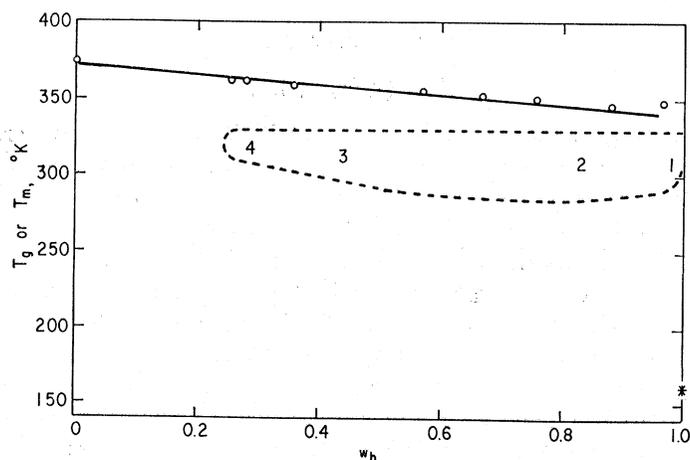


Fig. 4. Effect of side-chain crystallinity on the glass transition temperature of copolymers of vinyl stearate and methyl methacrylate: (—) glass transition temperature; (---) melting transition temperature. Abscissa, weight fraction vinyl stearate.

copolymers of vinyl stearate and methyl methacrylate (Table I), in which compositional heterogeneity is marked.^{25b} Data are shown in Figure 4. Apparently, domains rich in methyl methacrylate suffered little decrease in T_g with increase in the overall weight fraction of vinyl stearate. Consequently the value of k in Table III was low. The value of T_{gb} for amorphous poly(vinyl stearate), shown as the star in the figure, was never approached. This contrasts with the curves in Figure 2 for random copolymers. On the other hand, chains rich in vinyl stearate, crystallizing in the region marked by the dotted line, showed little melting point depression. This behavior is different from that found for random copolymers in Figure 3. The plots in Figure 4, consequently, reflect the aggregation of the crystalline and amorphous domains. The limit of this behavior would be incompatible mixtures of the two homopolymers.

SUMMARY AND CONCLUSIONS

The effect of crystallinity developing in side chains on the glass transition temperature of selected copolymers was investigated. The decline in the glass transition for all of these copolymer systems was linear with respect to n -octadecyl acrylate in the composition range where the copolymers were essentially amorphous. The extrapolated T_g of poly(n -octadecyl acrylate) in the amorphous state, as well as for amorphous poly(oleyl acrylate), was close to -111°C . This coincided with the value previously obtained by an extrapolation of data on series of homologs. Beyond a critical composition, developing side-chain crystallinity raised the glass temperature steadily, up to a value of 17°C , obtained for the crystalline homopolymer. Crystallinity did not develop in any random system until the glass transition temperature had been reduced to about 30°C below the melting point of the most perfect crystals. Compositionally heterogeneous copolymers acted as if chains containing blocks of crystalline units were dispersed in a glassy matrix of largely amorphous co-units. An empirical equation was derived which fitted the experimental data for random copolymers over the composition range with fair accuracy.

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