Thermal transitions of ethylene-vinyl chloride copolymers

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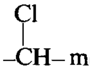
(Received 15 August 1984; revised 2 October 1984)

Differential scanning calorimetry (d.s.c.) measurements were performed on a series of ethylene–vinyl chloride (E–V) copolymers for the purpose of studying the dependence of their thermal transitions upon their microstructure. The method of preparation, via reductive dechlorination of poly(vinyl chloride) with tributyltin hydride, resulted in a series of E–V copolymers differing only in comonomer content, sequence distribution and stereoregularity of adjacent –V– units. Chain length distribution and branching frequencies were identical for each member of the series.

Extrapolation of glass transition temperatures, T_g, measured for our E–V copolymers to pure polyethylene (PE) predicted a $T_g = -85°C \pm 10°C$ for amorphous PE. E–V copolymers with greater than 60 mol% –E– units exhibited melting endotherms characterized by melting temperatures from 20°C to 128°C and degrees of crystallinity from 12 to 63%. Observed melting temperatures were plotted against the composition of the E–V copolymers and compared to Flory's equation for melting point depression of random copolymers containing one crystallizable and one non-crystallizable monomer unit. The melting point depressions observed for our E–V copolymers were in agreement with Flory's theory, if the $-CH_2-CH_2-$ moiety is considered to be the crystallizable unit and the  $-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}-$ moiety is assumed to prevent the $-CH_2-CH_2-$ units attached on either side from being incorporated into the crystal. This implies that among all possible comonomer triad sequences only the EEE triad may crystallize. Therefore only those E–V copolymers with average lengths of consecutive E units greater than 2 exhibit crystallinity.

(Keywords: thermal transitions; ethylene–vinylchloride copolymers; differential scanning calorimetry; comonomer content; sequence distribution; stereoregularity)

INTRODUCTION

In the 40–50 years that polyethylene (PE) and poly(vinyl chloride), (PVC), have been in commercial production, vast quantities of these polymers have been utilized in a myriad of applications. Along with styrene-based polymers, they are the dominant plastics in today's manufacturing processes. However, comparatively few studies of ethylene–vinyl chloride (E–V) copolymers have been reported[1–9]. Such copolymers are of both theoretical and applied interest due to their relatively simple chemical structure and their potentially wide range of physical properties.

The simple chemical structures of ethylene and vinyl chloride monomer units are advantageous for assignment of their spectroscopic resonances (e.g. infra-red and ^{13}C n.m.r. spectra) and thereby for determination of their microstructures which will hopefully lead to establishment of structure–property relationships. For example, the dyad and triad sequence distributions can be used to understand the compositional dependence of thermal, dielectric or mechanical properties[8–13].

In the applied arena, the potential for modification and improvement of homopolymer properties is substantial. For E–V copolymers, the flame retardancy should be enhanced compared to polyethylene, while the smoke produced upon burning may be reduced relative to poly(vinyl chloride). Introduction of ethylene units into a PVC chain will act as internal plasticizers[1]. The prime advantages of internal over external plasticization are permanent plasticization, reduced formulation and compounding requirements, and more simply fabricated products. The range of new materials increases dramatically when variation in the polymer repeat unit is considered as in copolymers, terpolymers, grafted copolymers, etc. The preparation of new materials by modification of inexpensive PE and PVC may be of considerable interest.

Traditional methods of obtaining E–V copolymers suffer from several shortcomings. Chlorination of PE[5] results in head-to-head (vicinal) and multiple (geminal) chlorination leading to structures which are uncharacteristic of E–V copolymers. Direct copolymerization of E and V monomers does not usually lead to random E–V copolymers covering the entire range of comonomer composition. Free radical copolymerization[3,4] at low pressures yields E–V copolymers with V contents from 60 to 100 mol%. Gamma-ray induced copolymerization under high pressures yields E–V copolymers with increased amounts of E, but it appears difficult to achieve degrees of E incorporation greater than 60 mol%. Incomplete reduction of PVC with tributyltin hydride (Bu_3SnH)[14] provides a convenient technique for preparation of E–V copolymers covering the entire compositional range. An analogous series of ethylene–vinyl bromide copolymers has been prepared by Cais and Kometani

0032-3861/85/081195-07$03.00
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Table 1 E–V copolymer characteristics

Polymer	Mole fraction of vinyl chloride units (X_V)	Density* ρ (g cm^{-3})
PVC	1.0	1.32
E–V-14.7	0.853	1.28
E–V-15.7	0.843	1.28
E–V-29.3	0.707	(1.23)
E–V-37.7	0.623	(1.2)
E–V-38.5	0.615	1.2
E–V-43.0	0.570	(1.18)
E–V-49.9	0.501	1.14
E–V-54.4	0.456	(1.13)
E–V-62.7	0.373	(1.09)
E–V-65.2	0.348	(1.07)
E–V-78.8	0.212	(1.04)
E–V-86.4	0.136	1.024
E–V-97.6	0.024	0.975
PE	0	0.945
PE-1	0	0.97
PE-2	0	(0.98)
PE-3	0	(0.98)
PE-4	0	0.92

* Determined by density gradient column or pycnometry on solution-cast or melt-cast samples. Values in parentheses were interpolated from measured densities.

using this technique[15]. The copolymer microstructure can be well characterized by ^{13}C n.m.r. spectroscopy and the molecular weight distribution is well defined and consistent across the compositional range since all the copolymers come from the same parent PVC homopolymer.

In a previous paper, the ^{13}C n.m.r. analysis of these copolymers was presented[9]. Here we shall report the thermal characteristics of the same E–V copolymers investigated by differential scanning calorimetry.

EXPERIMENTAL

PVC obtained from Aldrich (No. 18958-8) was dissolved in tetrahydrofuran (THF) that had been passed through basic alumina. The PVC was next precipitated in cold methanol, filtered and dried in a vacuum oven overnight at ambient temperature.

Reductions[10,14,15] of the clean PVC by Bu_3SnH (Alfa Products, Ventron Division) were conducted under dry nitrogen atmosphere in THF which had been passed through basic alumina. Overnight reductions at 60°C with refluxing were achieved with about 20% excess Bu_3SnH over the amount calculated for the desired level of dechlorination. Recrystallized azobis(isobutyronitrile) (AIBN) at a concentration of 2 mol% of the PVC charge was used as the initiator. For high levels of reduction, it was necessary to recharge the reaction mixture with AIBN and continue refluxing.

After cooling, the completed reaction mixture was added dropwise to hot n-hexane with stirring. The resultant E–V copolymer was isolated by centrifugation at 50°C from the hot n-hexane and dried overnight in a vacuum oven at ambient temperature.

Whenever a precise level of dechlorination was desired, small aliquots of the reaction mixture were removed periodically and analysed by ^{1}H n.m.r. to obtain comonomer composition. The reaction was stopped as soon as the ^{1}H n.m.r. analysis indicated achievement of the desired level of reduction[9]. The per cent chlorine removed was determined by ^{13}C n.m.r. from the ratio of methine to methylene carbon resonance areas. ^{13}C n.m.r. was also used to determine sequence length information and monomer sequence distributions (e.g., dyad and triad sequences). Densities (ρ) were measured by pycnometry and with a density gradient column for a number of the copolymers. A plot of E–V copolymer density, ρ, against composition, X_V, is nearly linear and can be described by $X_V = 2.63\rho - 2.53$. This relationship provides a simple means for obtaining the composition of E–V copolymers via density measurements. The compositional (X_v) and density (ρ) information for these E–V copolymers are listed in *Table 1*.

Four polyethylenes covering the range of polymers that fall under that generic name were also studied for reference: (1) PE-1, an Aldrich high density polyethylene; (2) PE-2, a NBS standard linear polyethylene with $\bar{M}_n = 1 \times 10^5$ g mol^{-1}, $\bar{M}_w = 1.2 \times 10^5$ g mol^{-1}; (3) PE-3, a linear, high density polyethylene from Phillips, and (4) PE-4, a low-density, branched polyethylene from Aldrich Chem. Co.

Calorimetry was performed using a Perkin-Elmer Model 2B Differential Scanning Calorimeter (d.s.c.). A Freon®two-stage Intracooler II refrigerator was used with a nitrogen purge in the sample chambers to operate down to −60°C. For measurements to −180°C, a liquid nitrogen reservoir, in conjunction with an aluminium heat sink, was used with a helium purge through the sample chambers. Heating and cooling rates of 10°C min^{-1} were employed throughout the study with samples of 10–30 mg. Temperature and heat capacity scales were calibrated using (1) pure metals (indium, lead, tin and zinc) with well known melting transitions and heats of fusion[16], and

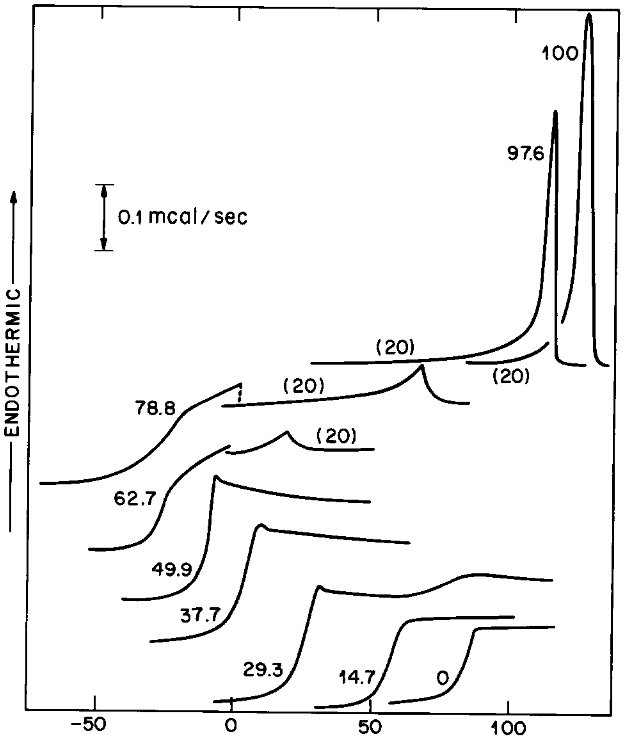

Figure 1 D.s.c. profiles of ethylene–vinyl chloride copolymers. Number adjacent to curves is the mol% of ethylene. (20) means that the heat flow scale is reduced by a factor of 20

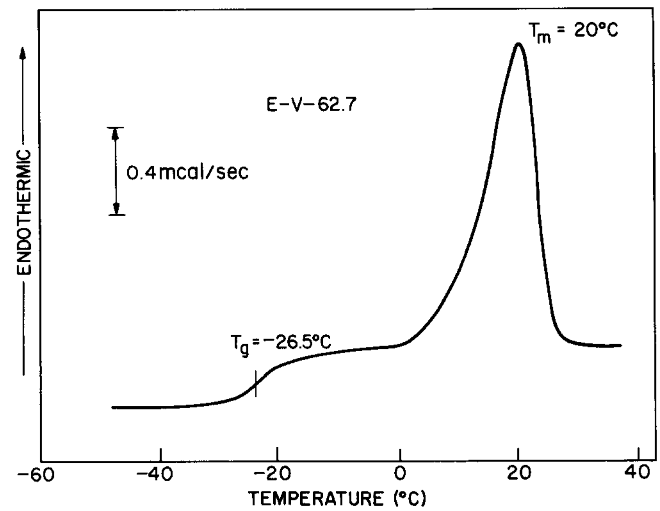

Figure 2 D.s.c. profile of a 10 mg sample of E–V-62.7

Table 2 Thermal parameters

Polymer	T_g (°C) ($\pm$1°C)	T_M (°C) ($\pm$1°C)	ΔH_M (cal g^{-1})	% ethylene units crystallized*
PVC	82.5	–	<0.5	<1
E–V-14.7	54.5	–	<0.5	<1
E–V-15.7	60	–	<0.5	<1
E–V-29.3	23	–	<0.5	<1
E–V-37.7	10	–	<0.5	<1
E–V-38.5	0	–	<0.5	<1
E–V-43.0	4.5	–	<0.5	<1
E–V-49.9	–10	–	<0.5	<1
E–V-54.4	–17	–	<0.5	<1
E–V-62.7	–26.5	20 ($\pm$2)	3.55$\pm$0.1	12
E–V-65.2	–35	19 ($\pm$2)	4.5$\pm$0.2	14
E–V-78.8	–43 ($\pm$2)	54	10.5$\pm$0.2	24.5
E–V-86.4	–	78	18.5$\pm$1	36
E–V-97.6	–	114	34$\pm$0.5	52
PE	–	128	43$\pm$0.5	63
PE-1	–	130	46$\pm$1	67
PE-2	–	134	42$\pm$1	61
PE-3	–	135	54.5$\pm$0.5	79
PE-4	–	111	32$\pm$1	47

* Refs. 18, 19; % crystallinity $= \dfrac{\Delta H_M \text{ (cal g}^{-1})}{W_E \Delta H_M^\circ \text{ (cal g}^{-1})}$

W_E = Weight fraction of ethylene units

ΔH_M° = Fusion enthalpy for polyethylene with 100% crystallinity = 68.6 cal g^{-1}

(2) hydrocarbons of known melting points and crystal–crystal transitions (cyclohexane, cyclopentane, 2-methyl-1-pentene and xylenes)[17].

The glass transition temperature (T_g), was defined as the midpoint of the transition in the d.s.c. scan, while the melting temperature (T_M) was taken to be the maximum of the fusion endotherm after correction for the thermal lag of the instrument.

RESULTS AND DISCUSSION

Figure 1 shows a selection of the d.s.c. profiles obtained for the E–V copolymers. The melting transitions are shown at 1/20th of the true heat capacity scale for convenience (note the 20 in parentheses adjacent to those segments of the profile plotted on the reduced scale). A single glass transition was normally observed for the copolymers until high conversion was reached ($X_E \sim 0.8$), thereafter the transition was no longer distinguishable from the baseline. Three E–V copolymers showed a second glass transition suggesting a two-phase amorphous morphology.

After 60% of the chlorines had been replaced by hydrogens, a fusion or melting transition was observed, which increased in magnitude and temperature as more chlorines were replaced. *Figure 2* shows the d.s.c. profile of E–V-62.7 to illustrate the relative magnitudes of the two transitions for a representative E–V copolymer.

Table 2 lists the glass transition temperatures (T_g), melting temperatures (T_M), melt transition enthalpies (ΔH_M) and per cent crystallinity found for our polymers. *Figures 3* and *4* show the position (T_g) and magnitude (ΔC_p) respectively of the glass transition as a function of composition. The glass transition temperature decreased as the mole fraction of ethylene units increased, extrapolating to an intercept of –93°C for polyethylene using a linear extrapolation. The magnitude of the transition,

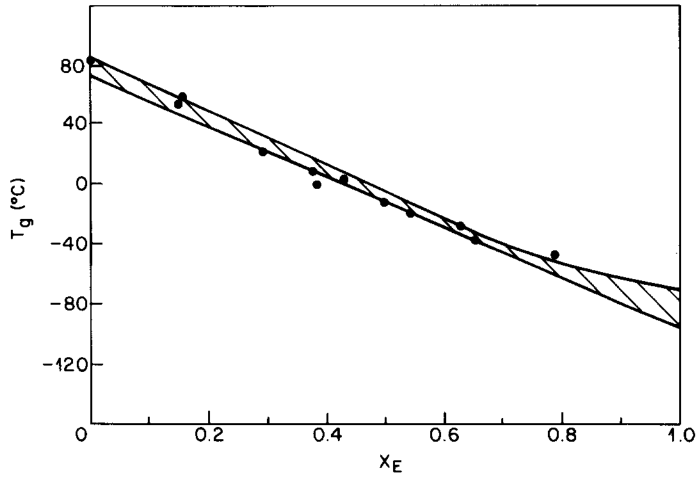

Figure 3 Glass transition temperature (T_g) *versus* mole fraction of ethylene (X_E). All theoretical fits to data points fall within shaded area

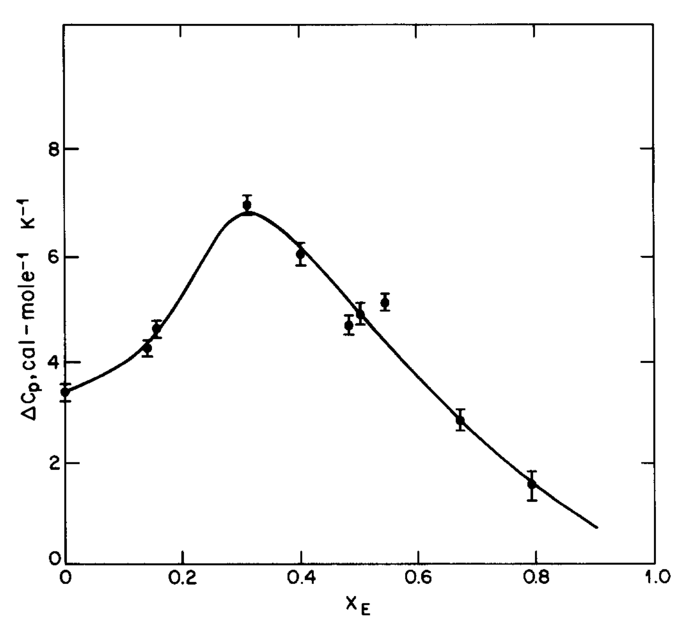

Figure 4 Magnitude of glass transition (ΔC_p) in cal mol^{-1} K^{-1} *versus* mole fraction of ethylene (X_E)

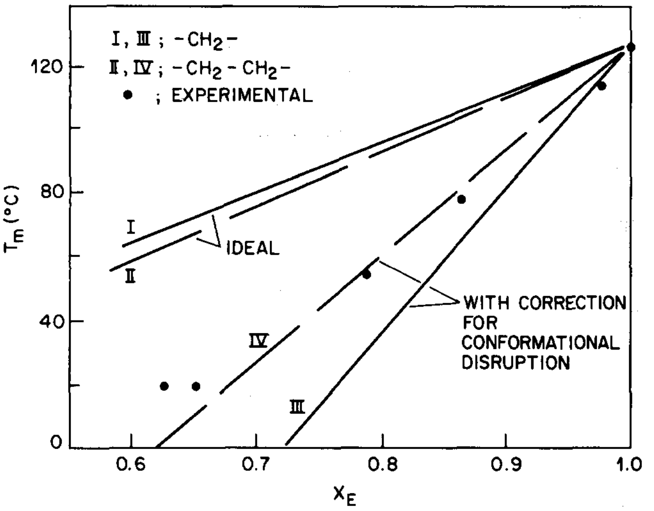

Figure 5 Melting temperature (T_M) of ethylene–vinyl chloride copolymers *versus* mole fraction of ethylene. Curves I–IV are theoretical curves from Flory's equation (equation (5)) with different criteria for crystallizable units. See text for details

ΔC_p, increased initially as chlorines were replaced, reached a maximum at $X_V \sim 0.7$ and then decreased towards zero as X_V approached zero.

A number of equations have been used to describe and/or predict the glass transition of copolymers as a function of their composition[20–28]:

$$(T_g)^{-1} = (A_E/T_{gE})^{-1} + (A_V/T_{gV})^{-1} \quad (1)$$

$$T_g = T_{gE} + \frac{K(T_g - T_{gV})W_V}{1 - W_V} \quad (2)$$

$$\log(T_g) = b\sum_i X_iE_i + \sum_i X_iE_i^* + \log(T_{gE}) \quad (3)$$

$$\ln(T_g) = \frac{W_E\Delta C_E \ln T_{gE} + W_V\Delta C_V \ln T_{gV}}{W_E\Delta C_E + W_V\Delta C_V} \quad (4)$$

where $T_g = T_g$ of E–V copolymer
$T_{gE} = T_g$ of polyethylene
$T_{gV} = T_g$ of poly(vinyl chloride)
$A_E = X_E$, W_E or Φ_E
$A_V = X_V$, W_V or Φ_V
X = mole fraction
W = weight fraction
Φ = volume fraction
E_i = intermolecular interaction parameter, equal to the molar cohesive energy[20,24,29]
E_i^* = intramolecular interaction parameter (steric)
k,b = constants (empirical)
$\Delta C_E, \Delta C_V$ = heat capacity changes at the glass transition for polyethylene and poly(vinyl chloride), respectively.

(1) is the Fox equation ($A = W$) and variations on the Fox equation[22]. Equation (2) was suggested by Gordon and Taylor[21] while equation (3) was derived by Wyman[24] using cohesive energies determined from solution properties of the homopolymers[29]. Equation (4) was derived by Couchman[26,27] from basic thermodynamic considerations.

Each of these equations was fitted to our data for the ethylene–vinyl chloride copolymers. From the best fit a value for the glass transition temperature of polyethylene can be determined, see *Table 3*. Each of the curves can be equally well fitted to our data and no particular preference for one theory over another was observed based on this comparison.

The melting transitions found for E–V copolymers with high ethylene content ($X_E > 0.6$) are shown in *Figure 5 versus* molar composition. For a random copolymer, Flory's equation for melting point depression predicts[30–32]:

$$(T_M)^{-1} = (T_M^\circ)^{-1} - \frac{R}{\Delta H_B}\ln X_B \quad (5)$$

with T_M = melting temperature
$T_M^\circ = T_M$ for fully reduced PVC
$= 128°\mathrm{C}$
R = gas constant
X_B = mole fraction of crystallizable units (B)
ΔH_B = enthalpy of fusion for unit B

Assuming B is a methylene unit, $\left(\mathrm{CH_2}\right)$, then $\Delta H_B = 960\ \mathrm{cal\ mol^{-1}}$ and curve I is predicted. Assuming B is an ethylene unit, $\left(\mathrm{CH_2{-}CH_2}\right)$, with $\Delta H_B = 1920\ \mathrm{cal\ mol^{-1}}$ gave curve II shown in *Figure 5*[19].

If we assume that the units adjacent to the $-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}-$ moiety cannot be incorporated into the crystal and subtract them from X_B, then curves III and IV were calculated from curves I and II, respectively. The mole fractions of such structures were obtained from dyad and triad sequence information determined by analysis of the ^{13}C n.m.r. spectra measured for these copolymers by Schilling *et al.*[9].

To a first approximation, it appears the $-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}-$ moiety causes conformational disruption up to the β-methylene groups in the main chain.

If each $-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}-$ moiety prevents the $-\mathrm{CH_2{-}CH_2}-$ units on either side from crystallizing, then the -EEE- triad is the shortest consecutive sequence of E units which can be incorporated into the crystal. This is consistent with the observation that only those E–V copolymers with average lengths of consecutive E units greater than 2 exhibit crystallinity (see *Table 2* and ref. 9).

The melting point depression curve of Flory[32] (equation (5) above) is not expected to be precise as X_V increases

Table 3 T_g of polyethylene

Theoretical equation used	Extrapolated T_g for PE (°C)
$T_g = X_E T_{gE} + X_V T_{gV}$	-93 ± 4
equation (1) (see text) using X_E	-69 ± 4
equation (1) (see text) using W_E	-92 ± 4
equation (1) (see text) using Φ_E	-80 ± 4
equation (2) (see text)	-75 ± 8
equation (3) (see text)	-80 ± 6
equation (4) (see text)	-82 ± 6

Table 4 Compositional dependence of copolymer parameters

Parameter	Dependence
ΔH_M	$\Delta H_M = 0.98 \Delta H_M^{\circ} e^{-6.5X_V}$
$X_C = \%$ crystallinity	$X_C = 0.97\, X_C^{\circ} e^{-4.3X_V}$
$X_{EEE} =$ mole fraction of –EEE– triads	$X_{EEE} = 1.05\, e^{-4.6X_V}$

$\Delta H_M =$ heat of fusion, $\Delta H_M^{\circ} = \Delta H_M$ for fully reduced PVC
$X_C = \%$ crystallinity, $X_C^{\circ} = X_C$ for fully reduced PVC
$X_{EEE} =$ mole fraction of –EEE– triads; from ref. 9
$X_V =$ mole fraction of vinyl chloride units in copolymer

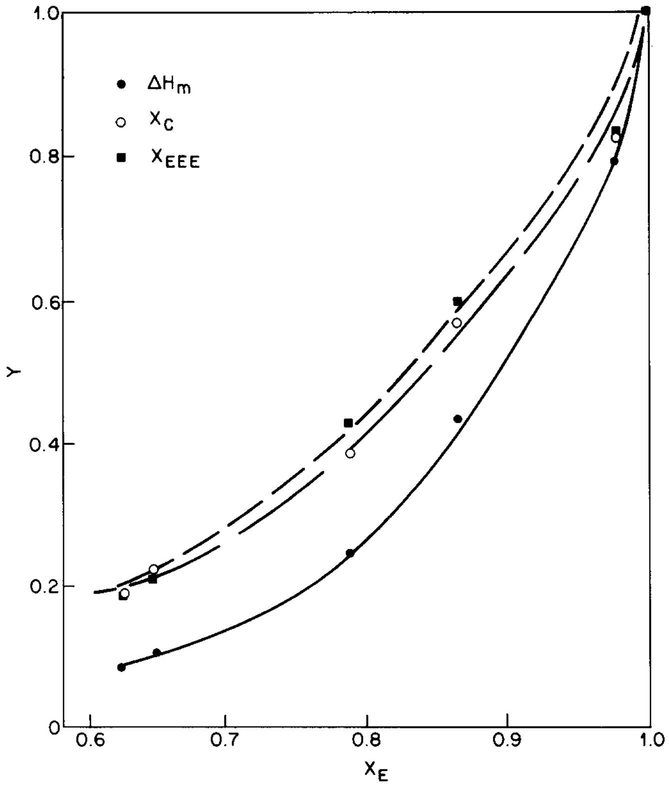

Figure 6 Structure and property parameters *versus* composition of copolymer (X_V). $Y = \Delta H_M / \Delta H_M^{\circ}$ (●); X_C / X_C° (○); or X_{EEE} (■). See *Tables 2* and *4* for details

and long sequences of methylene units become rare. It is the long methylene sequences that determine the crystallinity. The exponential decrease in ΔH_M and per cent crystallinity is analogous to the exponential decrease in number of long methylene sequences (e.g. -EEE- triads); see *Table 4* and *Figure 6*. As X_V increases, the number of long methylene sequences decreases exponentially, the amount of crystallizable material decreases exponentially and ΔH_M was also seen to decrease exponentially. As the number of long sequences diminishes, the maximum crystallite thickness will diminish and therefore the magnitude of T_M will decrease, see *Figure 5*.

Three of the E–V copolymers exhibited two glass transition temperatures, see *Table 5*. No corresponding structural variation could be found from ^{13}C n.m.r. studies or infra-red spectroscopic studies[9,33]. For example, the sequence distributions, as determined by ^{13}C n.m.r. and infra-red spectra[33], of E–V-14.7 and E–V-15.7 are almost identical as one would expect for copolymers with similar composition. However, E–V-15.7 has two T_g values and E–V-14.7 has only a single T_g. The reason for such behaviour is unclear at the present time.

The glass transition of polyethylene has been discussed widely in the literature. Mechanical relaxation, torsional braid analysis and other dynamic mechanical tests on numerous ethylene copolymers have been reported for many years[28,34–39]. Two transitions have been observed[34,36,37,40], one at $-20 \pm 10°C$, usually labelled the β-transition, and one at approximately $-120°C$. Recently Popli and Mandelkern[37] summarized much of this copolymer data from n.m.r. and mechanical relaxation studies, and deduced that the β-transition is a reflection of segmental motions within the crystalline-amorphous interfacial region and does not relate to the glass transition. An alternative explanation is contained in the report on volume relaxation studies by Davis and Eby[41]. Studies by Illers[34] on ethylene–vinyl acetate, ethylene–propylene and ethylene–vinyl propionate copolymers using various techniques found the T_g of polyethylene to be $-77°C$. A value of $-55°C$ was found from d.s.c. measurements performed on ethylene–hexafluoropropylene copolymers[38]. Lam and Geil[39] studied crystallization growth rates and annealing effects of polyethylene by electron microscopy and torsion braid analysis from which they deduced a $T_g(\text{PE}) = -80°C$ to $-90°C$.

Our copolymer studies lead to an extrapolated glass transition temperature for polyethylene of $-85°C \pm 10°C$. The principal advantage of our E–V copolymers is that the only variable across their compositional range is chlorine content and sequence. All the copolymers have the same degree of polymerization and the same branching structure, which may vary considerably for copolymers formed from the individual monomers by free radical and/or Ziegler–Natta polymerizations. Transitions at $-20°C$ and $-125°C$ were found from mechanical studies[34,40] of chlorinated polyethylenes. However, such polymers will contain vicinal and geminal chlorine moieties[5]. Our E–V copolymer system has been well characterized by ^{13}C n.m.r. and shown to be nearly random in sequence distribution[9]. Therefore one can with confidence observe the effects of chlorine substituents in the absence of other structural variation.

The increase in ΔC_p values, see *Figure 4*, upon removal of the first 30% of chlorine atoms is not fully understood. The ethylene units may be acting as internal plasticizers, thereby enhancing the extent of possible segmental motion. Therefore the glass-to-rubber transition will be increased in magnitude; i.e. ΔC_p will increase. As more ethylene units are introduced into the chain the magnitude of the transition decreases until no transition can be observed at high X_E ($X_E > 0.80$). Although ~40% of the fully reduced polymer (PE) is amorphous no glass transition was detected ($\Delta C_p \approx 0$). The observed ΔC_p at T_g is

Table 5 T_g behaviour of two-phase copolymers

Polymer	T_g (°C)	ΔC_p (cal g^{-1} K^{-1})	ΔC_p (cal mol^{-1} K^{-1})
E–V-15.7	60	0.053	3.0
	24	0.024	1.37
E–V-29.3	23	0.11	5.8
	72	0.033	1.7
E–V-38.5	0	0.12	5.9
	57	0.014	0.69

not proportional to the per cent amorphicity as would be expected on the basis of a two phase (crystalline–amorphous) system. This was first reported many years ago for polyethylene terephthalate[42] and polycarbonate[43]. It is unclear why a small amount of crystallinity in some polymers restricts the amorphous polymer chains from attaining their liquid-like motions and the corresponding heat capacity above T_g. The segments adjacent to crystalline units in the fold regions will be restricted, since their ends are both securely anchored in the crystallite. Such considerations would explain part of the ΔC_p reduction but a full understanding of the effect is not available at present.

If we focus solely on the ΔC_p values measured for the completely amorphous E–V copolymers (i.e., $X_E \leq 0.6$), it is possible to correlate the heat capacity changes at T_g with the comonomer sequence distributions. That is, a plot of the –VEV– triad fractions[9] *versus* comonomer composition (X_E) also peaks at $X_E = 0.3$ and decreases sharply as $X_E \rightarrow 0$ (PVC) and $X_E \rightarrow 1.0$ (PE). This comparison argues for the suggestion that E units act as internal plasticizers when they separate V units along the E–V chain. The fact that ΔC_p correlates with VEV triads and not with the overall E content implies an intramolecular component for the internal plasticization of PVC by E units.

Figure 7 shows the melting point depression curves for our E–V copolymers and data reported for ethylene–propylene copolymers[44]. The methyl substituent in the ethylene–propylene copolymers is approximately the same size as a chlorine substituent, but their polarities are significantly different. Most ethylene–copolymer studies[44–48] show larger melting point depressions than predicted by Flory's equation. The differences between the data sets arise from different polymerization conditions. The ethylene–propylene copolymers were formed via a $VOCl_3/Al(C_2H_5)_2Cl$ catalyst system which minimizes long and short chain branching[2,3]. The parent PVC homopolymer from which all of our E–V copolymers were made is known to have 1–3 branches per 1000 chain carbon atoms[14]. This results in the lower T_M value for PE (128°C cf. 136°C), see *Figure 7*. Our copolymers were quenched at 10°C min^{-1} from the melt. A slower cooling rate or slow crystallization from solution would enhance crystallite size and total per cent crystallinity which in turn would increase T_M and ΔH_M respectively. This may also contribute to the difference in initial T_M values seen in *Figure 7*. The larger-than-predicted melting point depressions found for the copolymers is attributed to the theory's assumption that small sequences are able to form crystallites. For example the 5 consecutive methylene groups in the –VEEV– sequence are considered as crystallizable units in the theory, equation (5). Such a short segment may not form a part of any measurable crystallite, since the disruption of the crystal lattice produced by two CH–Cl units will likely dominate. It is the long sequences of methylene units that determine the magnitude of T_M and ΔH_M. These long sequences decrease exponentially with decreasing mole fraction of ethylene, see *Table 4* and *Figure 6*. There are no large differences between the E–V copolymer and ethylene–propylene data in *Figure 7*. Since a chlorine-substituent is approximately the same size as a methyl-substituent, the melting point reduction is probably determined primarily by size not polarity.

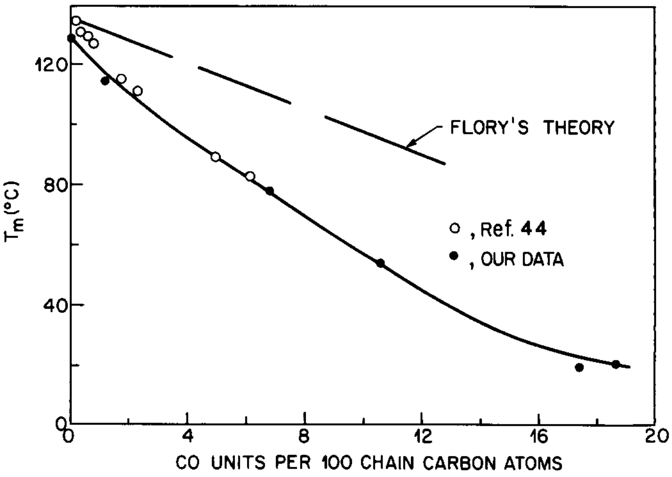

Figure 7 Melting temperatures (T_M) *versus* co-units per 100 chain carbon atoms for our E–V copolymers and for ethylene–propylene copolymers reported in ref. 44. A co-unit represents a vinyl chloride or a propylene unit. The dashed line equals the predicted melting point depression from equation (5) with a methylene unit as the crystallizable unit

CONCLUSION

We have investigated the thermal characteristics of a set of well characterized ethylene–vinyl chloride copolymers. Correlations between their molecular structure, as determined by ^{13}C n.m.r. spectroscopy, and their thermal transitions (T_g and T_M) were determined and discussed in terms of current theoretical models. The extrapolated glass transition for polyethylene was found to be −85°C and the $-\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{H}-$ moiety was found to cause conformational disruption up to β-methylenes in the crystal.

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