Table I, petroleum ether was used instead of methanol). The solids were dissolved in chloroform, reprecipitated from methanol, and dried for several days under vacuum at room temperature.

Polymer Characterization. Ir spectra were run in chloroform solutions on a Perkin-Elmer 257 spectrometer. Nmr spectra were recorded at 120° in *o*-dichlorobenzene solutions using a Varian HA-100 instrument. Number average molecular weights were obtained in benzene solutions with a Hitachi Perkin-Elmer 115 instrument by a vapor pressure depression method.

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Glass Transition Temperatures of Poly(ethyl α-chloroacrylates)

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ABSTRACT: The glass transition temperatures of stereoregular poly(ethyl α-chloroacrylates) have been measured and compared with a previously developed theory. Reasonable consistency was found. A difference of about 300 cal/mol between the Gibbs–DiMarzio flex energies of the syndiotactic and isotactic isomers was calculated.

Despite the impact of the discovery of techniques for the synthesis of stereoregular vinyl and vinylidene polymers, systematic empirical and theoretical correlations between steric configuration and bulk properties in such polymers remain in a rudimentary state. In particular, the influence of stereoregularity on the glass transition temperatures (T_g's) of such polymers is imperfectly understood. As is well known, the T_g of an amorphous polymer is the single most important parameter determining the mechanical properties of the polymer and a knowledge of the molecular structure factors affecting T_g is thus of decisive importance.

Correlation of available data for T_g's of mono(vinyl)- and di(vinylidene)-substituted polymers $(CH_2CXY\text{-})_n$ led to the conclusion that steric configuration affects T_g only in vinylidene polymers (*i.e.*, when neither X nor Y is hydrogen).[2] Conversely, T_g is independent of configuration when hydrogen is one of the substitutents. This empirical observation[3] was then put on a theoretical basis[4] using the Gibbs–DiMarzio[5] theory as a framework. This was accomplished by postulating that (a) the effect of configuration in disubstituted polymers is intramolecular in nature and is brought about by changes in the flex energy of the stereoisomers, and (b) changes in T_g due to other side chain modifications are of strictly intermolecular origin. The results of this treatment may be summarized by the relationship

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 0.59\frac{\Delta\epsilon}{k} \qquad (1)$$

Equation 1 is general for any pair of stereoisomers. T_g(syndiotactic) is the glass transition temperature of the syndiotactic isomer, T_g(isotactic) is the glass transition temperature of the isotactic isomer, $\Delta\epsilon$ is the difference in the Gibbs–DiMarzio flex energy between the syndiotactic isomer and the isotactic, and k is Boltzmann's constant. A knowledge of $\Delta\epsilon$ is thus sufficient to determine the difference in T_g between pairs of stereoisomers. In the original publication,[4] eq 1 was applied to the methacrylates and it was deduced that

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 112° \qquad (2)$$

for any isomeric methacrylate pair. If the foregoing analysis is correct, $\Delta\epsilon$ is simply a function of the α-substituent size. This implies that eq 2 should be applicable to the α-chloroacrylate polymers also inasmuch as the van der Waals radius of the chloride group is about the same as that of the methyl radical.

Recently, Wesslén and Lenz reported the synthesis of stereoregular poly(ethyl α-chloroacrylates)[6] and it is the purpose of this paper to report and discuss the glass transition temperatures of these and use these values to test the theory outlined above.

Experimental Section

The polymers were prepared and characterized according to ref 6. Glass transition temperatures were determined with a Perkin-Elmer differential scanning calorimeter, Model DSC-1B, at a heating rate of 20°/min, and the values reported are averages of three consecutive runs on each sample.

Results and Discussion

In Table I are given glass transition temperatures, T_g, for samples of poly(ethyl α-chloroacrylates) of different molecular weights and tacticities, which were prepared according to ref 6. Tacticities of the polymers were

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TABLE I
GLASS TRANSITION TEMPERATURES FOR POLY(ETHYL α-CHLOROACRYLATES)

Sample no.	Dyad tacticity I	S	$\bar{M}_n$	T_g, °C
1	0.18	0.82	3,500	84
2	0.20	0.80	8,900	100
3	0.21	0.79	16,700	101
4[a]	0.32	0.68	24,500	103
5	0.37	0.63	19,000	99
6	0.38	0.62	9,050	87
7	0.49	0.51	3,400	57
8	0.55	0.45	8,500	58
9	0.62	0.38	14,200	69

[a] Prepared by free-radical initiation. All other samples prepared with anionic initiation.[6]

determined from the nmr spectra of the ethoxy methyl groups. The polymers range from predominantly syndiotactic to moderately isotactic ones. As can be seen in the table, there is a substantial difference in T_g between polymers of the same molecular weight but of different tacticities, with the more syndiotactic polymers having the higher T_g's. This is analogous to what has been found for polymethacrylates.[3] To obtain an estimate of the T_g values of 100% isotactic and 100% syndiotactic chloroacrylate polymers of high molecular weights, an extrapolation technique was applied.[7] T_g values for polymers of approximately the same tacticity—no. 1, 2, and 3, and 7, 8, and 9, respectively—were plotted *vs.* reciprocal molecular weight, and the limiting values of T_g for these particular mean tacticities were obtained by extrapolation to infinite molecular weight (Figure 1). From these values and the mean dyad tacticities, I_m and S_m, the limiting T_g values, T_g^{i} and T_g^{s}, respectively, for completely isotactic and syndiotactic polymers were estimated by applying an empirical equation relating T_g for a random copolymer to the T_g's of the parent homopolymers[8]

$$\frac{1}{T_g} = \frac{I_m}{T_g^{\text{i}}} + \frac{S_m}{T_g^{\text{s}}} \tag{3}$$

By this treatment the values $T_g^{\text{i}} = 35°$ and $T_g^{\text{s}} = 131°$ were obtained for 100% isotactic and 100% syndiotactic polymer, respectively.

The limiting T_g values were also derived in a slightly different way from the experimental results. Equation 3 was applied to pairs of polymers of similar molecular weights and different tacticities (no. 1 and 7, 2 and 8, 2 and 6, 3 and 9), and the values of T_g thus calculated for completely isotactic and syndiotactic polymers, respectively, were plotted *vs.* the reciprocal of the mean molecular weight for each pair. The results of this treatment are given in Figure 2, from which the values $T_g^{\text{i}} = 45°$ and $T_g^{\text{s}} = 131°$ were obtained. These values differ from the previous ones only for the isotactic polymer, and this difference might be due to some errors in the tacticity determination,[6] and other experimental difficulties. However, by both methods of calculation a difference between T_g's for completely isotactic and syndiotactic polymers of the order of 90° is obtained, close to the 112° predicted for the tactic poly(methyl methacrylates).[4]

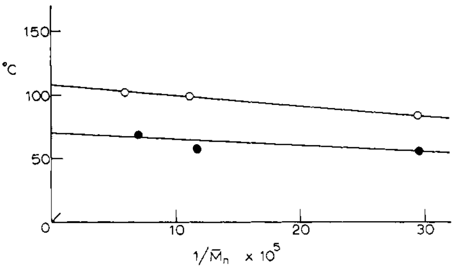

Figure 1. Determination of limiting T_g's from dyad tacticities: ○, $I_m = 0.20$, $S_m = 0.80$; ●, $I_m = 0.56$, $S_m = 0.44$. Infinite molecular weight T_g's for these mean tacticities are 108 and 70°, respectively.

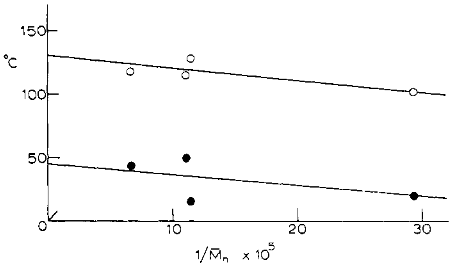

Figure 2. Determination of limiting T_g's: ○, syndiotactic polymer; T_g's are 102, 129, 116, and 118° for mean molecular weights of 3450, 8700, 8975, and 15,450, respectively: ●, isotactic polymer; T_g's are 20, 16, 50, and 46° for corresponding mean molecular weights.

Substituting the value of 90° for the difference in the T_g's of the stereoregular forms of the poly(ethyl α-chloroacrylates) in eq 1, there results a value of $\Delta\epsilon/k$ of 153°. In view of the inherent uncertainties, this is quite comparable to the value of $\Delta\epsilon/k$ of 191° obtained for the polymethacrylates. This result shows that, to a first approximation, the change in flex energy of stereoisomers responsible for the T_g differences observed in vinylidene polymers is a function of the size of the nonester α-substituent and that this can alone account for the observed effect. The effect must therefore largely arise from the steric hindrance to chain rotation introduced by the presence of the α-substituent and this steric hindrance must depend on tacticity, being greater for the syndiotactic form than for the isotactic form. The effect of the ester group is apparently intermolecular. A comparison of the T_g's of the stereoregular poly(ethyl α-chloroacrylates) to those of the corresponding poly(ethyl methacrylates) is given in Table II. It is seen that the former are considerably

TABLE II
T_g'S (°C) AND $\Delta\alpha$'S (°C^{-1}) FOR STEREOREGULAR POLY(ETHYL METHACRYLATES) AND POLY(ETHYL α-CHLOROACRYLATES)

Polymer	T_g (syndio)	T_g (iso)	$10^4\Delta\alpha$ (syndio)	$10^4\Delta\alpha$ (iso)	$10^4\Delta\alpha$ (conventional)
Ethyl methacrylate	120	8	2.8	4.0	2.65, 3.0
Ethyl α-chloroacrylate	131	35	2.8	3.7	

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higher. Such a result has also been obtained for conventional poly(alkyl α-chloroacrylates) and the corresponding poly(alkyl methacrylates). This is probably due to the strong intermolecular forces introduced by the presence of the polar chloride groups.

An assumption inherent in the theoretical treatment is the applicability of the Simha–Boyer relationship[9] to the polymers, regardless of tacticity

$$T_g\Delta\alpha = 0.113 \qquad (4)$$

where $\Delta\alpha$ is the difference in the volume expansion coefficient above and below T_g. Values of $\Delta\alpha$ derived from eq 4 are given in Table II for the stereoregular poly(ethyl α-chloroacrylates) and the stereoregular poly(ethyl methacrylates). These values have not been experimentally verified and work is in progress to accomplish this.

Conclusions

The predictions of the simple model proposed earlier regarding the effect of stereoregularity on the glass transitions of disubstituted vinylidene polymers appear to have been confirmed in a test case. The reasonably satisfactory quantitative agreement lends some support to the basic assumptions of the theory.

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The Prediction of Surface Tensions of Liquid Polymers

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ABSTRACT: Values of the surface tension of polymers as a function of temperature and molecular weight have been predicted and compared with experimental values from the literature. The following methods of prediction were used: a corresponding states correlation, a modified solubility parameter approach, a relation of Schonhorn,[7] and the parachor. The corresponding states correlation and the parachor are more successful than the other two approaches. They give similar, and good results predicting the LeGrand–Gaines $M^{-2/3}$ dependence of γ. The parachor is preferred on grounds of simplicity.

Recent work has yielded a considerable amount of data on the surface tension of liquid polymers, and its variation with temperature[1,2] and the molecular weight of the polymer.[2,3] The decrease of γ with T is less rapid than for a low molecular weight substance, implying a lower surface entropy, while LeGrand and Gaines[3] have shown that a linear dependence of γ on $M^{-2/3}$ holds with remarkable generality

$$\gamma = \gamma_\infty - kM^{-2/3} \qquad (1)$$

We propose using these data to test three approaches which allow polymer surface tensions to be predicted from the bulk properties, as follows.

(1) Correlation with Solubility Parameters. Hildebrand and Scott[4a] found a correlation of γ with the solubility parameter (δ) of a low molecular weight substance. Their relation can be expressed[4b] as

$$\gamma = 0.039\delta^{2.30}V^{1/3} \qquad (2)$$

where V is the molar volume in cm^3 of the molecules which are assumed to be spherical, and the units of γ and δ are ergs cm^{-2} and cal$^{1/2}$ cm$^{-3/2}$, respectively. The solubility parameter is related to the cohesive energy density (CED), energy of vaporization (ΔE^{V}) and internal pressure (P_{i}) through

$$\delta^2 = (\mathrm{CED}) = \Delta E^{\mathrm{V}}/V \simeq \mathrm{P_i}/1.1 \qquad (3)$$

The factor 1.1 is generally applicable for nonpolar liquids.[5] Hildebrand and Scott point out[4a] that a linear relation between γ and the CED would yield almost as good a correlation of the data as eq 2. A least mean squares analysis of the data[4a] shows the relation to be

$$\gamma = 0.075\delta^2V^{1/3} \qquad (4)$$

$$\gamma = 0.075\Delta E^{\mathrm{V}}/V^{2/3} \qquad (5)$$

It is clear that the rationale of the form of this expression lies in $\Delta E^{\mathrm{V}}/V^{2/3}$ being a contact energy between molecules expressed per unit area of the molecule, which is necessarily spherical. However, Lee[6] has calculated γ for many polymers using eq 2 with V replaced by the volume per mole of a chain element which is taken to be the polymer repeat unit. Theoretical work by Schonhorn[7] gives a result similar to eq 4 but with a different numerical factor and a slightly different choice of chain element

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