Preparation and Structure of Stereoregular Ethyl α-Chloroacrylate Polymers[1a]

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ABSTRACT: Ethyl α-chloroacrylate was polymerized by anionic and free radical initiation under a variety of conditions to yield polymers of differing tacticities ranging from predominantly syndiotactic to slightly isotactic on a triad basis. Only relatively low molecular weight polymers, less than 20,000, were obtained by anionic polymerization. Triad tacticities were estimated quantitatively from the ethoxy methyl nmr peaks; the assignments of these peaks were based in part on their qualitative relation to the backbone methylene peaks. The C–H bending region and the carbonyl band in the infrared spectra were also sensitive to tacticity. The latter may be attributable to the effect of tacticity on the conformation of the pendant carboethoxy groups, and the former could be used as a quantitative measure of tacticity.

Investigations on the polymerization of α-chloroacrylate monomers date back to over 40 years ago, including a large number of patents, and poly(methyl α-chloroacrylate) was available as an industrial plastic at least 30 years ago.[2a] Free radical polymerization reactions have been successfully applied by many investigators to the conversion of α-chloroacrylate monomers to high molecular weight polymers,[2b–4] but comparatively little information has been reported on the stereochemistry of these polymerization reactions.

Polymerization reactions with anionic initiation have also been reported, but, by this route, only low molecular weight polymers have been obtained.[5] Until quite recently little was known about the steric structure of the products when Matsuzaki and coworkers[6] reported an investigation on the stereoregularity of poly(methyl α-chloroacrylates) obtained in polymerization reactions with free-radical as well as anionic initiation. The steric structures of the polymers in this study were elucidated by means of nuclear magnetic resonance.

In the present communication we wish to report the preparation and characterization of poly(ethyl α-chloroacrylates). These polymers were prepared using anionic initiation, and various initiators and solvents were employed in the syntheses.

Results and Discussion

As mentioned earlier, previous attempts to polymerize α-chloroacrylate monomers by anionic initiation have resulted in the formation of relatively low molecular weight polymers, and this problem was encountered in the present investigation. In Table I are presented data on poly(ethyl α-chloroacrylates) obtained with various initiators in different solvents at different temperatures. Very poor yields and low molecular weights were obtained especially with the Grignard initiators, which have been shown to give high yields of high molecular weight polymers when applied to the polymerization of methyl methacrylate.[7] The poor results obtained in the present system might be attributed to an extremely low rate of propagation[7] which cannot compete effectively with termination or transfer in this polymerization. The latter reactions can presumably occur by intramolecular addition of a living end group to an ester carbonyl within the same polymer chain, forming a six-membered cyclic ketone, as observed in the analogous polymerization reaction of methyl methacrylate with Grignard reagents.[7] In the present system termination and chain transfer could also occur by reaction of anionic end groups with chlorine atoms along the polymer backbone, either through elimination or substitution.[8,9] These types of reactions would decrease the chlorine content of the products, and such a decrease was observed in all polymers prepared by anionic initiation in this study (Table I). The lowest chlorine content, 24.2% (expt 3), corresponds to a loss of one chlorine atom per ten repeating units. It may be noted that the sample prepared by free-radical mechanism (expt 11) has the correct, calculated chlorine content.

Polymer Tacticity. Nmr spectra of the polymers were obtained at 100 MHz in *o*-dichlorobenzene solution at 120°. The spectra were rather complex as shown in Figure 1 and also observed for poly(methyl α-chloroacrylates) by Matsuzaki and coworkers,[6] but some features of the spectra are similar to those of poly-

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[1] (a) Presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970; *Polym. Prepr.*, **11**, 105 (1970); work done at the University of Massachusetts; (b) Department of Polymer Chemistry, Royal Institute of Technology, Stockholm, Sweden.

[2] (a) C. E. Schildknecht, "Vinyl and Related Polymers," Wiley, New York, N. Y., 1952, p 234 ff; (b) G. I. M. Bloom, J. E. Duddington, M. F. Vincent, and A. H. Willbourn, U. S. Patent 2,739,615 (Jan 3, 1956).

[3] H. D. Anspon and F. E. Pschorr, U. S. Patent 2,913,441 (Nov 17, 1959).

[4] M. A. Askarov, S. R. Pinkhasov, and A. S. Bauk, *Vysokomol. Soedin., Ser. B*, 9, 601 (1967).

[5] K. Chikanishi, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **80**, 158 (1964).

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[9] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 1046 ff.

TABLE I
PREPARATION OF POLY(ETHYL α-CHLOROACRYLATE)

Expt no.	Initiator	Solvent	Temp, °C	Time, hr	Yield, %	M_n	Chlorine,[e] %
1	*n*-BuMgBr[a]	Toluene	−78	22	Trace		
2	*n*-BuMgBr[a]	THF	−78	48	0		
3	PhMgBr[b]	Toluene	0	48	8[f]	3,400	24.2
4	PhMgBr[c]	THF	−78	48	6[f]	3,500	24.5
5	*n*-BuLi[d]	THF	−78	22	43	16,700	25.7
6	Fluorenyllithium[d]	Toluene	0	29	39[g]	8,500	24.6
7	Fluorenyllithium[d]	Toluene	−78	49	14	14,200	25.6
8	Fluorenyllithium[d]	THF	−78	17	59	19,000	25.4
9	Fluorenyllithium[d]	THF–DEDE (1:2)	−78	47	25	8,900	25.6
10	Fluorenyllithium[d]	DEDE[h]	0	3.5	80	9,050	25.3
11	None	None	25–30	49	23.5	24,500	26.4

[a] Monomer, 16.5 mmol; initiator, 0.37 mmol; solvent, 15 ml. [b] Monomer, 58.0 mmol; initiator, 20 mmol; solvent, 20 ml. [c] Monomer, 62.0 mmol; initiator, 3.0 mmol; solvent, 50 ml. [d] Monomer, 33.0 mmol; initiator, 0.45 mmol; solvent, 30 ml. [e] Calcd for $C_5H_7ClO_2$, 26.40%. [f] Soluble in methanol. [g] Yellow color. [h] DEDE–diethylene glycol diethyl ether.

(methyl methacrylate). The pattern of resonance signals from the backbone methylene groups (2.75–3.6 ppm, downfield from tetramethylsilane) was found to be quite different for polymers prepared in solvents of different polarity. The strong peak at 3.07 ppm in spectra from polymers prepared with anionic initiators in nonpolar solvents (Figure 1B), as well as from the polymer prepared by free-radical mechanism (Figure 1A), can be assigned to racemic methylene groups, that is, to syndiotactic enchainments. This assignment is strictly analogous to assignments made for poly(methyl methacrylate)[10] and poly(methyl α-chloroacrylate).[6] In addition to this strong peak, a number of smaller peaks are observed in the backbone methylene region of the spectrum. For polymers prepared in toluene, the relative order of intensity between the singlet at 3.07 ppm and the downfield peaks was opposite to that for the polymers prepared in polar solvents, presumably due to the presence of a larger number of meso dyads (that is, isotactic enchainments) in these polymers. The meso dyad would be expected to give rise to an AB quartet, as observed for poly(methyl methacrylate),[10] and the complex spectra obtained in the present case can be attributed to the presence of different types of tetrad structures each generating a quartet with slightly different chemical shifts. Unfortunately, the resolution of these quartets at 100 MHz is not good enough for making tetrad assignments, as seen in Figure 2, and further work on tetrad assignments from 220 MHz spectra of poly(ethyl α-chloroacrylates) is under progress and will be reported on shortly.

Matsuzaki and coworkers reported that the methoxy methyl group resonance in nmr spectra of poly(methyl α-chloroacrylates) at 100 MHz is sensitive to the steric configuration of the polymers, and that three different chemical shifts were observed for these methyl groups.[6] The three signals were assigned to isotactic, heterotactic, and syndiotactic triads (designated *mm*, *mr*, and *rr*, respectively) in the order of increasing field strength. These assignments were based on a qualitative correlation within the spectra between the methyl group peaks and those for the backbone methylene groups. In contrast for poly(methyl methacrylate), it has been shown that the proton resonance of the ester methyl group is rather insensitive to differences in tacticity as compared to that of the α-methyl group, although the former is subject to solvent effects.[11] That is, in aromatic solvents three peaks can be observed for the methoxy methyl groups in poly(methyl methacrylate), and their relative intensities correlate qualitatively with those of the α-methyl groups.

In the present polymers, which contain ethyl ester groups, complex splitting patterns were observed in

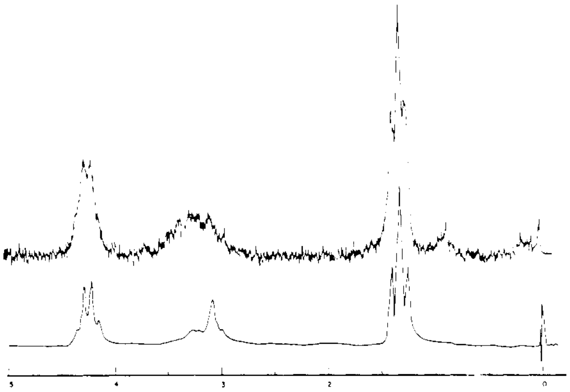

Figure 1. 100-MHz nmr spectra of poly(ethyl α-chloroacrylate) prepared by (A) free-radical initiation (lower line) and (B) anionic initiation in toluene (upper line).

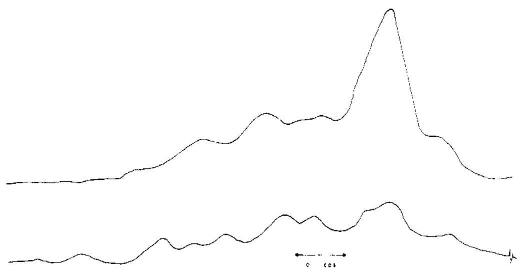

Figure 2. 100-MHz nmr spectra of backbone methylene groups in poly(ethyl α-chloroacrylate) prepared by anionic initiation in (A) toluene (lower line and (B) THF (upper line).

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(10) F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).

(11) K. C. Ramey and J. Messick, *ibid.*, *Part A-2*, **4**, 155 (1966); M. Nagai and A. Nishioka, *ibid.*, *Part A-1*, **6**, 1655 (1968).

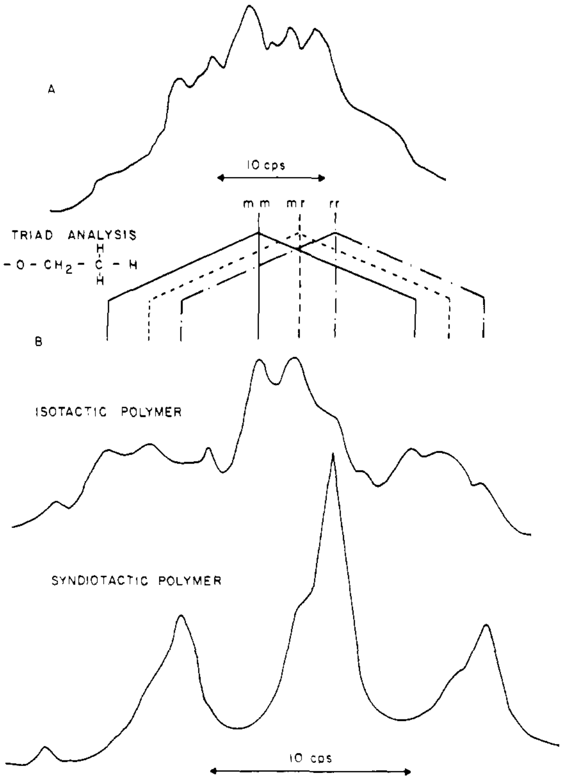

Figure 3. 100-MHz nmr spectra of (A) ethoxy methylene groups and (B) ethoxy methyl groups in poly(ethyl α-chloroacrylate).

both the methylene and methyl groups of the ethoxy function and these are shown in Figure 3. The chemical shift differences for the different methylene quartets were found to be of the same order of magnitude as the coupling constants so that severe overlapping of the signals resulted as shown in Figure 3A. For the methyl groups, however, the three different triplets were sufficiently well resolved, Figure 3B, that assignments attributable to *mm*, *mr*, and *rr* triads were made in that order with increasing field strength. This assignment correlated qualitatively with the assignments made from the peaks for the backbone methylene groups. It is interesting to note that the hydrogen atoms of the ethoxy methyl group are separated from the dissymmetric center by as many as four atoms. A similar sensitivity to stereochemistry has been reported for the methoxy groups of poly(*o*-methoxystyrene).[12]

Because of the small difference in chemical shifts between methyl groups in *mm*, *mr*, and *rr* triads a completely unambiguous triad analysis is difficult to make. However, in Table II is given a triad analysis based on the assignments mentioned above. As seen in this table, formation of predominantly syndiotactic polymers occurred when the monomer was polymerized either by a free radical mechanism or by anionic mechanism in a polar solvent. This result is analogous to that for the polymerization of methyl methacrylate[13] and to the recent results reported for methyl α-chloroacrylate[6] under similar conditions. However, the samples prepared with anionic initiation in toluene were found to be almost atactic with only slight predominance of *mm* triads over the *rr* triads. This result is in contrast with the polymerization of methyl methacrylate by initiation with Grignard reagents in toluene, which has been shown to give almost completely isotactic polymers.[14] Matsuzaki and coworkers observed that phenylmagnesium bromide generated a predominantly isotactic poly(methyl α-chloroacrylate) at 0° but an atactic polymer at lower temperatures.[6]

Table II

Triad Analysis of Poly(ethyl α-chloroacrylates)

Polymer from expt no.	Triad contents *mm*	*mr*	*rr*
3	0.33	0.32	0.35
4	0.07	0.22	0.71
5	0.08	0.25	0.67
6	0.36	0.39	0.25
7	0.44	0.36	0.20
8	0.15	0.45	0.40
9	0.08	0.24	0.68
10	0.19	0.38	0.43
11	0.15	0.35	0.50

Infrared Spectra. Furukawa and coworkers[5] noted some differences in the infrared spectra of poly-α-chloroacrylates prepared with different initiators, and they suggested that these differences were due to different tacticities of the polymers. This suggestion is substantiated by results obtained in the present study. In Figure 4 are shown ir spectra in the region 1300–1800 cm^{-1} for one moderately isotactic and one syn-

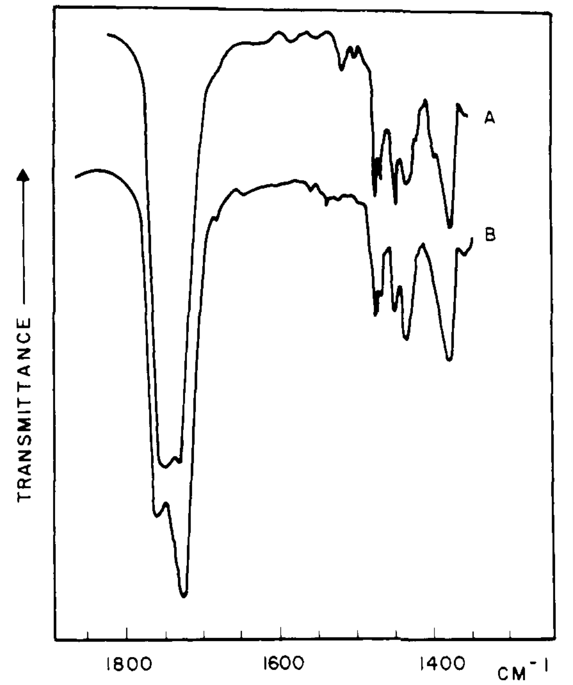

Figure 4. Infrared spectra of (A) moderately isotactic and (B) syndiotactic poly(ethyl α-chloroacrylate).

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[12] H. Yuki, Y. Okamoto, Y. Kuwae, and K. Hatada, *J. Polym. Sci., Part A-1*, 7, 1933 (1969).

[13] M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968, p 466 ff.

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diotactic poly(ethyl α-chloroacrylate). Two major differences between the two spectra are apparent. The syndiotactic polymer (Figure 4B) shows two resolved carbonyl bands of unequal intensity, the major one at 1732 cm^{-1} and the minor one at 1761 cm^{-1}. The more isotactic polymer, however, exhibits a broad carbonyl band, which shows a tendency of splitting into two maxima of equal intensity, at 1735 cm^{-1} and 1755 cm^{-1}. According to Bellamy and Williams,[15] the double carbonyl absorption for α-halo esters is indicative of rotational isomerism, with conformations in which the rotational angle between the ester carbonyl group and the α-halo atom is close to 0° giving rise to the absorption at the higher frequency (Figure 5A). Conformations with the rotational angles greater than 90° (Figure 5B) leave the position of the absorption maximum unaffected, that is, the peak appears at the frequency normal for saturated aliphatic esters (1730 cm^{-1}). It might thus be concluded that there exists a difference in conformation of the pendent carboethoxy group between isotactic and syndiotactic sequences in the polymers, which in turn may be due to different conformations of the chain backbones within the sequences.

There also exists a difference between polymers of different tacticities in the C–H bending region of the infrared spectrum, as can be seen in Figure 4. The relative intensities of the bands at 1452 and 1438 cm^{-1} are reversed in the syndiotactic polymer in relation to the more isotactic one. Furthermore, it was found that the intensities of these bands varied in a regular manner with the tacticities of the polymers, as determined from nmr spectra. A parameter J was defined as the ratio between the absorbance at 1452 and 1438 cm^{-1}, respectively, and this parameter was found to correlate with diad tacticity in a linear manner, as shown in Figure 6. Tacticities of poly(methyl methacrylates) have been determined from ir data by a similar treatment.[16,17]

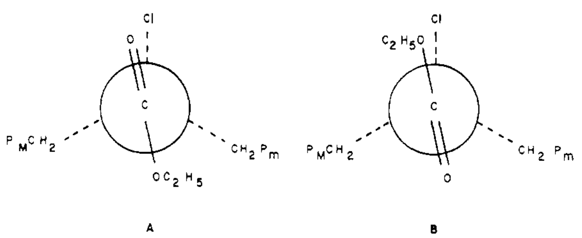

Figure 5. Rotational isomers of pendant ester groups in poly(ethyl α-chloroacrylate).

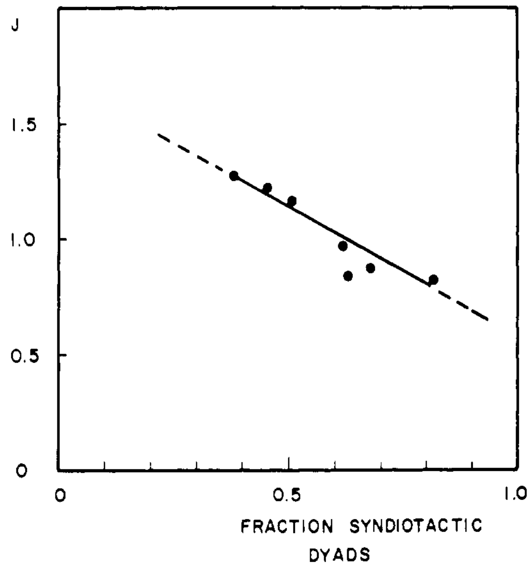

Figure 6. J values (A_{1452}/A_{1438}) *vs.* dyad tacticity for poly(ethyl α-chloroacrylate).

Experimental Section

Purification of Reagents. Prepurified nitrogen was further purified by passing through molecular sieve (Linde Type 5A, Union Carbide Corp.). Reagent grade toluene and tetrahydrofuran (THF) were refluxed over sodium for 24 hr and distilled under nitrogen. Diethylene glycol diethyl ether (DEDE) was stirred with sodium under nitrogen for 24 hr at 120° and distilled under nitrogen at reduced pressure. Ethyl α-chloroacrylate (Monomer–Polymer Laboratories) was distilled under nitrogen at reduced pressure through a 25-in. column packed with glass rings. After a forerun of approximately 10%, a center cut amounting to about 40% of the total volume of the crude monomer was collected. This fraction was kept over calcium hydride under nitrogen for 48 hr in the refrigerator. After separation of the hydride and addition of hydroquinone the fraction was distilled in the same manner as before. The center cut was kept refrigerated under nitrogen.

Initiators. *n*-Butyllithium (2.25 *M* in heptane, Alfa Inorganics, Inc.) and *n*-butylmagnesium bromide (2.5 *M* in diethyl ether, Columbia Organic Chemicals Co., Inc.) were used directly as purchased. Phenylmagnesium bromide was prepared in diethyl ether in the usual manner.[18] After filtration under nitrogen, the concentration of the Grignard reagent (2.0 *M*) was determined by titration. Fluorenyllithium was prepared *in situ* by metalation of fluorene with *n*-butyllithium.[19] A slight excess of fluorene was used.

Polymerization Procedures. Ethyl α-chloroacrylate was polymerized in bulk by allowing the monomer to stand in light for 48 hr in the presence of air. The viscous solution obtained was diluted with chloroform, and the polymer was precipitated in methanol. The solid was collected and dried under vacuum for several days at room temperature. Anionic polymerization reactions were carried out in a two-necked, pear-shaped flask, equipped with rubber septums. The flask was thoroughly flamed out under nitrogen. Solvents and initiators were added by the use of predried hypodermic syringes. After cooling the solution to the appropriate temperature, previously cooled monomer was added slowly with a syringe, the contents of the flask being stirred during the addition. In case of fluorenyllithium as initiator, the bright orange color of the fluorenyl anion disappeared almost instantaneously. Polymers were generally collected by precipitation from methanol (in expt 1–4 of

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(15) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957).

(16) T. G Fox, W. E. Goode, S. Gratch, C. M. Huggett, J. F. Kinkaid, A. Spell, and J. D. Stroupe, *J. Polym. Sci.*, **31**, 173 (1958); W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *ibid.*, **46**, 317 (1960).

(17) E. L. McCaffery, "Laboratory Preparation for Macromolecular Chemistry," McGraw-Hill, New York, N. Y., 1970, pp 237–238.

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(19) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," 2nd ed, Interscience, New York, N. Y., 1968, p 286.

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 $(CH_2CXY-)_n$ 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

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

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

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

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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[1] Department of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden.

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