8K computer locations. The spectrum represents an accumulation of 26,000 scans.

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References and Notes

(1) (a) Bell Laboratories; (b) University of Massachusetts.
(2) (a) K. B. Abbås, F. A. Bovey, and F. C. Schilling, *Makromol. Chem.*, in press; (b) A. Rigo, G. Palma, and G. Talamini, *ibid.*, **153**, 219 (1972).
(3) C. G. Overberger, private communication during the IUPAC International Symposium on Macromolecules, Rio de Janiero, July 26–31, 1974.
(4) T. Suzuki and M. Nakamura, *Jpn. Plast.*, **4**, 16 (1970).
(5) H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.*, **3**, 63 (1967).
(6) G. E. Maciel, P. D. Ellis, and D. C. Hofer, *J. Phys. Chem.*, **71**, 2160 (1967).
(7) G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).
(8) G. L. Lebel, J. D. Laposa, B. G. Sayer, and R. A. Bell, *Anal. Chem.*, **43**, 1500 (1971).
(9) R. A. Bell, C. L. Chan, and B. G. Sayer, *Chem. Commun.*, 67 (1972).
(10) R. S. Ozubko, G. W. Buchanan, and I. C. P. Smith, *Can. J. Chem.*, **52**, 2493 (1974).

Poly(alkyl α-chloroacrylates). VI. Transitions and Relaxations

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ABSTRACT: Melting points (T_m's) and glass transition temperatures (T_g's) of stereoregular poly(methyl α-chloroacrylates), poly(ethyl α-chloroacrylates), and poly(isopropyl α-chloroacrylates) have been determined by differential scanning calorimetry (DSC). Relaxation processes accompanying these T_g's and secondary relaxation phenomena have been studied by dynamic mechanical and dielectric relaxation. It was found that the extrapolated T_g values for high molecular weight syndiotactic poly(alkyl α-chloroacrylates) and high molecular weight isotactic poly(alkyl α-chloroacrylates) differed by the following amounts: 92° for the methyl esters; 83° for the ethyl esters; and 68° for the isopropyl esters. A secondary relaxation, labeled β, and associated with motions of the ester side chains, occurs in the highly syndiotactic methyl and ethyl polymers and is absent in the isopropyl polymers regardless of their degrees of stereoregularity. Evidence was obtained for the formation of stereocomplexes of isotactic and syndiotactic chains in the case of the poly(methyl α-chloroacrylates).

We have previously reported the synthesis, characterization, and some preliminary physical properties of stereoregular poly(methyl α-chloroacrylates), poly(ethyl α-chloroacrylates), and poly(isopropyl α-chloroacrylates).[1–5] It has been determined by DSC that the T_g differences between the most isotactic and most syndiotactic polymers prepared are 72° for the methyl ester, 57° for the ethyl ester, and 59° for the isopropyl ester. However, when these values are corrected to "infinite" molecular weight and extrapolated to the 100% isotactic and syndiotactic forms the results are 92° for the methyl ester, 80–86° for the ethyl ester, and 68° for the isopropyl ester.[5] In addition to the T_g behavior, crystalline melting points, T_m's, were observed by DSC for isotactic poly(methyl α-chloroacrylate) at 186°, isotactic poly(ethyl α-chloroacrylate) at 109°, and isotactic poly(isobutyl α-chloroacrylate) at 191°. In the present work we examine the T_g results in light of a general theory for the T_g's of stereoregular vinylidene polymers.[6] In addition, the relaxation behavior accompanying these transitions observed by dynamic mechanical relaxation and dielectric relaxation is reported. In general, two relaxation regions are discernible below T_m and these are labeled α and β in order of decreasing temperature. The α relaxation, which is present in all the polymers, arises from microbrownian segmental motion accompanying the glass transition, while the β relaxation, which is present only in the syndiotactic poly(methyl α-chloroacrylates) and poly(ethyl α-chloroacrylates), arises from motions of the ester side group. Activation energies derived from the slopes of plots of the logarithms of the maximum frequencies of the loss peaks versus the reciprocal of the absolute temperature generally correlate well for the various processes for both the dielectric and mechanical techniques, indicating that the underlying motions responsible for these relaxations are the same. Comparisons are made between these polymers and results obtained for the stereoregular poly(alkyl methacrylates).

Experimental Section

The preparation and characterization of the stereoregular poly(alkyl α-chloroacrylates) used in this study have been previously described in detail.[4,5] Relevant characterization data for the samples used for property studies are collected in Table I. Films were prepared for mechanical and dielectric testing by casting 4–12% (w/v) solutions of the polymers in $CHCl_3$ onto clean plate glass and allowing the solvent to evaporate slowly. This procedure produced films of 4–8 mils thickness which were then dried in a vacuum oven at 60° for 1 to 2 days. After this treatment, it was found that the residual solvent, estimated to be less than 0.5% by weight by pyrolysis gas chromatography, caused a decrease in T_g of up to 50° in the case of the syndiotactic poly(methyl α-chloroacrylates) and about 25 to 30° in the case of the syndiotactic poly(ethyl α-chloroacrylates) and poly(isopropyl α-chloroacrylates). This residual solvent could not be removed by heating in a vacuum oven, and it was found necessary to extract the films with methanol at ambient temperature for several days followed by a similar extraction with water. It is postulated that the large effect on T_g was due to some sort of complex formation between the polymer and the $CHCl_3$. Further studies are necessary to elucidate the nature of this complex.

The mechanical measurements were carried out on a Rheovibron Dynamic Viscoelastometer, Model DDVII. The frequencies employed were 3.5, 11, and 110 Hz and the temperature range was from −100 to +170° depending on the T_g of the polymer under observation. Tan δ, E', and E'' were obtained at the quoted frequencies as functions of temperature by standard techniques.

Dielectric measurements were carried out with a General Radio capacitance bridge, Type 1620-A, in conjunction with a Balbaugh

Table I
Characterization Data for Stereoregular Poly(α-chloroacrylates)

Polymer	Fraction of meso-dyads[a]	$\overline{M}_n$,[b] g/mol
Poly(methyl α-chloroacrylate)	0.70	80,000
	0.29	270,000
	0.25	400,000
Poly(ethyl α-chloroacrylates)	0.73	309,000
	0.29	362,000
	0.20	181,000
Poly(isopropyl α-chloroacrylates)	0.95	50,000
	0.64	50,000
	0.36	77,300

[a] From 300 MHz NMR. [b] From membrane osmometry.

Lab. three-terminal cell, Type LD-3. The dielectric loss tangent and the real and imaginary parts of the dielectric constant, ϵ' and ϵ'', were obtained as functions of temperature at six frequencies: 200 and 500 Hz and 1, 2, 5, and 10 kHz. The temperature range investigated was from room temperature to +190°.

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer instrument, Model DSC-1B. The scanning rate was 20°/min in all cases and calibrations for determining heats of fusion were accomplished using naphthalene, adipic acid, or benzoic acid for the appropriate temperature ranges.

Results and Discussion

Figure 1 presents the dyad tacticity determined from 300 MHz NMR[4] versus the T_g measured by DSC for the poly(alkyl α-chloroacrylates) studied. All values are corrected to "infinite" molecular weight.[5] It may be seen that good straight lines are obtained in all cases making it possible to smoothly extrapolate the observed values to the 100% syndiotactic case on the one hand and to the 100% isotactic case on the other. T_m's are also observable by DSC for the most highly isotactic poly(alkyl α-chloroacrylates), and an intermediate transition labeled T_s is observable for isotactic poly(methyl α-chloroacrylates) at 159°. These data are summarized in Table II.

As suggested in the introduction, the observed T_g differences between syndiotactic and isotactic pairs of vinylidene polymers can be rationalized on the basis of an extension to the Gibbs–DiMarzio theory of the glass transition.[7] This is accomplished by postulating that: (a) the effect of configuration in vinylidene polymers is intramolecular in nature and is brought about by changes in the Gibbs–DiMarzio "flex energy", ϵ, of the stereoisomers; and (b) the 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[6] general for any pair of stereoisomers

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

where 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 flex energy between the syndiotactic isomer and the isotactic, and k is Boltzmann's constant. It was originally deduced that, for the methacrylates

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

Subsequently the relationship was applied to stereoregular poly(ethyl α-chloroacrylates)[2] and was found to be

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 90° \qquad (3)$$

Table II
Thermal Transitions of Stereoregular Poly(alkyl α-chloroacrylates)

Polymer	Tacticity (meso-dyads)[a]	T_g,[b] °C	T_s, °C	T_m, °C
Poly(methyl α-chloroacrylate)	0.70	90	152	186
	0.29	152		
Poly(ethyl α-chloroacrylate)	0.73	52		109
	0.20	104		
Poly(isopropyl α-chloroacrylate)	0.95	70		191
	0.36	110		

[a] Derived from 300 MHz NMR.[4] [b] Corrected to "infinite" molecular weight.[5]

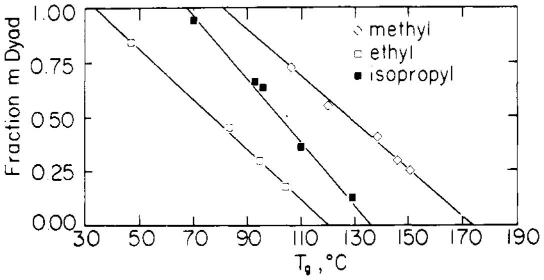

Figure 1. Dependence of glass transition temperatures of poly(alkyl α-chloroacrylates) on tacticity estimated from 300 MHz NMR.

In the present work, the values obtained are based on more complete NMR analyses of tacticity at higher frequencies and a much greater range of stereoregular isomers. These results are for the methyl ester

$$T_g(\text{syndiotactic} - T_g(\text{isotactic}) = 92° \qquad (4)$$

for the ethyl ester

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 80° \qquad (5)$$

for the isopropyl ester

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 68° \qquad (6)$$

The T_g differences decrease with increasing ester side-chain length or bulkiness in apparent violation of the simple theory. Also, the values are all considerably smaller than that originally quoted for the stereoregular poly(methyl methacrylates). The value quoted in eq 2 was based on an extrapolated T_g for the 100% syndiotactic poly(methyl methacrylate) of 160°. More recently, Bywater[8] has shown that the T_g of poly(methyl methacrylate) tends to approach an asymptotically limiting value of 120° at high degrees of syndiotacticity and that the straight line extrapolation on which the 160° value was based is therefore erroneous. If we accept Bywater's value of 120° for the T_g of 100% syndiotactic poly(methyl methacrylate), we obtain an amended figure of 80° for the T_g difference between the stereoregular poly(methyl methacrylates). Bywater's objection to the straight line extrapolation procedure in the case of the poly(methyl methacrylates) may also apply to the poly(alkyl α-chloroacrylates). It can only be said that the data in Figure 1 support the straight line extrapolation procedure for these polymers. It is also worth noting that the highly isotactic poly(alkyl α-chloroacrylates) prepared by the use of the modified Grignard reagent catalyst are extremely "blocky", while the highly syndrotactic polymers prepared by low-temperature free-radical techniques are more or less "random".[4,5] In view of these uncertainties, it

Table III
Activation energies of Relaxation Processes in Poly(alkyl α-chloroacrylates)

Polymer	Mesodyads	Temp range for dielectic (D) and mechanical (M) loss maxima, °C	Activation energy,[a] kcal/mol	Relaxation process
Poly(methyl α-chloroacrylate)	0.70	117–127 (D)	120 ± 5	α
	0.70	103–111 (M)		
	0.70	~180 (D)		α_{sc}
	0.70	~160 (M)		
	0.29	169–174 (D)	150 ± 9	α
	0.29	154–161 (M)		
	0.29	120–150 (D)		β
		100–110 (M)		
	0.25	176–185 (D)	154 ± 16	α
		161–166 (M)		
		125–160 (D)	38 ± 4	β
		100–110 (M)		
Poly(ethyl α-chloroacrylate)	0.73	92–119 (D)	44 ± 1	α
		68–74 (M)		
	0.29	126–142 (D)	85 ± 5	α
		101–111 (M)		
	0.29	~70 (M)		β
	0.20	132–146 (D)	99 ± 5	α
		109–117 (M)		
		~70 (M)		β
Poly(isopropyl α-chloroacrylate)	0.36	128–148 (D)	63 ± 3	α
		106–117 (M)		

[a] From dielectric data only.

is hardly likely that the 20° difference observed between the T_g's for the stereoregular poly(isopropyl α-chloroacrylate) pairs versus the stereoregular poly(methyl α-chloroacrylate) pairs can be significant. Also, the amended value for the stereoregular poly(methyl methacrylate) pair obviously agrees well with those quoted in eq 4, 5, and 6. Pending further elucidation of stereosequence effects and the T_g behavior at high degrees of syndiotacticity, we conclude that the rationalization embodied in eq 1 is adequate to account for T_g effects in both the poly(alkyl methacrylates) and the poly(alkyl α-chloroacrylates).

Turning to the crystallization behavior, it is perhaps surprising that any crystallization occurs at all in the isotactic poly(methyl α-chloroacrylates) and poly(ethyl α-chloroacrylates) which have only about 0.7 fractions of mesodyads. The effect, however, is traceable to the blocky nature of those polymers prepared using the modified Grignard reagent catalyst and to the fact that there is considerable stereo inhomogeneity in these polymers as demonstrated by fractionation which results in portions of greatly enhanced stereoregularity.[5] It should be pointed out that the observed enthalpies of fusion are small, of the order of 2 cal/g for both the methyl and ethyl polymers and of the order of 8 cal/g for the more highly isotactic isopropyl polymer. The enthalpies of fusion for the 100% crystalline poly(alkyl α-chloroacrylates) are unknown, but if the reported value for isotactic poly(methyl methacrylate) of 22 cal/g[9] is used as a rough basis of comparison, it is apparent that the degrees of crystallinity are low. Wide angle X-ray diffraction patterns of the unoriented materials reveal a very low degree of crystalline order, although it has been possible to obtain lattice parameters from such measurements on specimens oriented above their T_g's.[10] A frequently quoted empirical observation is that the ratio (T_g/T_m) lies in the range of 0.50 to 0.75 for many polymers. If we evaluate this ratio for the isotactic poly(alkyl α-chloroacrylates) studied we find values of 0.79, 0.85, and 0.74 for the methyl, ethyl, and isopropyl polymers, respectively. Using literature values for isotactic poly(methyl methacrylate), a value of 0.74 is obtained.[11] Thus, only poly(isopropyl α-chloroacrylate) behaves in a "normal" fashion. It is well known that many exceptions to the empirical generalization exist.[12] In the present case the rather low degrees of stereoregularity of the methyl and ethyl polymers may lead to the formation of small crystals with depressed melting points.

The presence of a third transition intermediate between the T_g and T_m in the case of the isotactic poly(methyl α-chloroacrylate) has been commented on previously and evidence has been presented for the assignment of this phenomenon to the glass transition of a stereocomplex of isotactic and syndiotactic polymer molecules.[5] It is not possible to confirm or reject this hypothesis on the basis of available evidence.

The results of the mechanical and dielectric relaxation studies are embodied in Table III and Figures 2, 3, and 4. An inspection of Figures 2–4 reveals that all of the polymers show a prominent relaxation associated with the glass transition and labeled α in Table II. As expected, the temperatures and activation energies of these relaxations are strong functions of the steric structures of the polymers. The activation energies listed in Table III are obtained from the slopes of plots of the logarithm of the maximum frequency of the dielectric loss constant versus $1/T$. Inasmuch as only three frequencies are available mechanically (3.5, 11 and 110 Hz), it is difficult to derive reliable values from the mechanical results. It can be said, however, that the dielectric and mechanical α relaxations correlate well with one another and are consequences of the same molecular motions (i.e., microbrownian segmental motions accompanying T_g). A secondary relaxation occurring in the glassy state had previously been reported for "conventional" poly(methyl α-chloroacrylates) prepared by free-radical techniques.[13] This β relaxation occurs also in the poly(alkyl

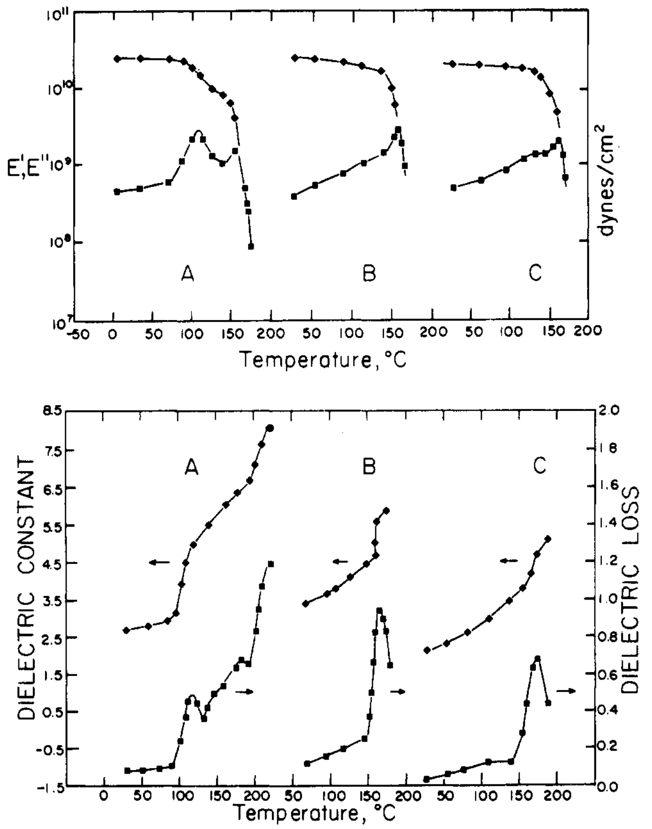

Figure 2. Upper: temperature dependence of E' and E'' at 200 Hz for (A) isotactic poly(methyl α-chloroacrylate), (B) atactic poly(methyl α-chloroacrylate), and (C) syndiotactic poly(methyl α-chloroacrylate). Lower: temperature dependence of the dielectric constant and loss at 200 Hz for (A) isotactic poly(methyl α-chloroacrylate), (B) atactic poly(methyl α-chloroacrylate), and (C) syndiotactic poly(methyl α-chloroacrylate).

methacrylates) and is assigned to motions of the ester side group about the carbon–carbon bond joining it to the main chain. This β relaxation is discernible only in the highly syndiotactic methyl and ethyl polymers and is absent in the syndiotactic isopropyl polymers. It is a minor feature throughout and is not observable dielectrically for the syndiotactic ethyl polymer. The dielectric behavior of the β relaxation in the poly(alkyl α-chloroacrylates) is in marked contrast to its behavior in the poly(alkyl methacrylates). In the latter case, "conventional" or syndiotactic poly(methyl methacrylate) has a dielectric β relaxation considerably greater in magnitude than the α relaxation in the same polymer, while the situation is reversed in isotactic poly(methyl methacrylate).[14] This observation is interpretable on the basis that the side-chain relaxation occurs independently of the main-chain relaxation in the syndiotactic poly(methyl methacrylates) but is correlated with the main-chain relaxation in the isotactic poly(methyl methacrylates). The greater dipole moment of the ester side chain compared to the α-methyl group then accounts for the observed dielectric magnitudes. In the poly(alkyl α-chloroacrylates), the polar α-Cl group introduces a main-chain dipole moment of much greater magnitude than that of the ester side chain, and so the α relaxation is the predominant dielectric feature regardless of the tacticity of the polymer. The absence of the β relaxation in the isotactic poly(alkyl α-chloroacrylates) does suggest that the ester side-chain motion may merge with that of the main chain in these polymers in a similar manner to what is postulated to occur in the isotactic poly(methyl methacrylates).

The relaxation labeled α_{8c} for the isotactic poly(methyl α-chloroacrylate) in Table II is thought to correlate with

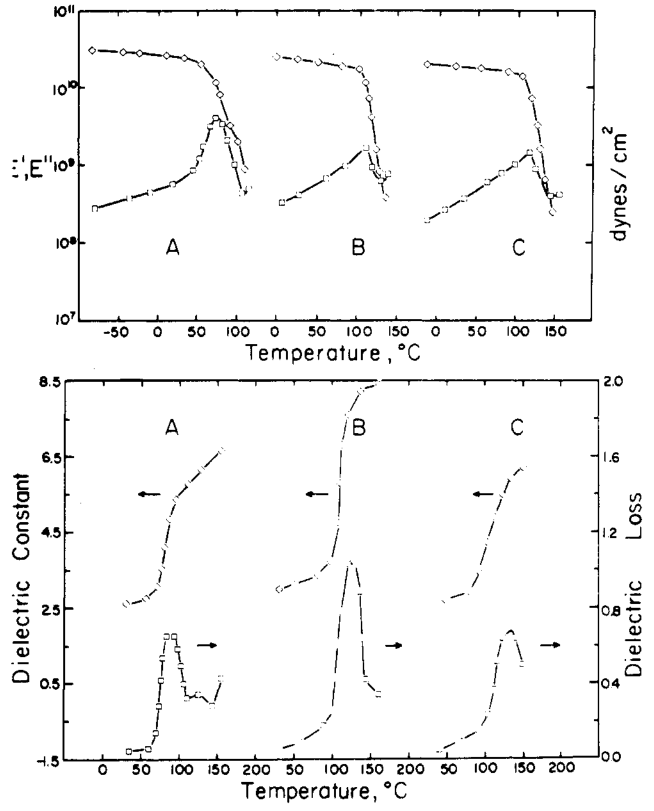

Figure 3. Upper: temperature dependence of E' and E'' at 200 Hz for (A) isotactic poly(ethyl α-chloroacrylate), (B) atactic poly(ethyl α-chloroacrylate), and (C) syndiotactic poly(ethyl α-chloroacrylate). Lower: temperature dependence of the dielectric constant and loss at 200 Hz for (A) isotactic poly(ethyl α-chloroacrylate), (B) atactic poly(ethyl α-chloroacrylate), and (C) syndiotactic poly(ethyl α-chloroacrylate).

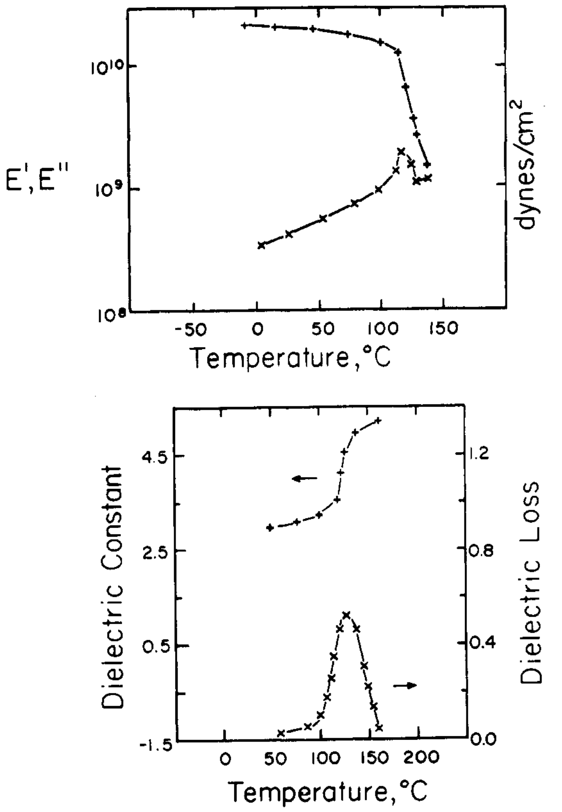

Figure 4. Upper: temperature dependence of E' and E'' at 200 Hz for syndiotactic poly(isopropyl α-chloroacrylate). Lower: temperature dependence of the dielectric constant and loss at 200 Hz for syndiotactic poly(isopropyl α-chloroacrylate).

the transition observed by DSC at 150° and is tentatively assigned to motions accompanying the glass transition of the "stereocomplex" postulated to occur in these polymers, composed of isotactic and syndiotactic chains.

The only previous report of activation energies for poly(methyl α-chloroacrylates) is for the "conventional" free-radical polymer which can be assumed to be reasonably syndiotactic.[13] The values quoted are 130 kcal/mol for the α relaxation and 26 kcal/mol for the β relaxation. The present results (Table II) are in qualitative agreement with these values. In general the activation energies for the α relaxations decrease with increasing ester side-chain length or bulkiness and the isotactic isomers have α relaxation activation energies about 35–50 kcal/mol lower than the comparable syndiotactic isomers.

Conclusions

(1) The T_g's of stereoregular poly(alkyl α-chloroacrylates) are strong functions of tacticity and can be rationalized, to a first approximation, on the basis of the previously proposed theory.[6]

(2) Evidence exists for the presence of a stereocomplex composed of a combination of isotactic and syndiotactic poly(methyl α-chloroacrylate).

(3) Crystallinity can be observed for the highly isotactic poly(alkyl α-chloroacrylates) and appears to be analogous to the behavior of isotactic poly(alkyl methacrylates).

(4) The relaxation behavior accompanying the glass transitions in stereoregular poly(alkyl α-chloroacrylates) is generally in accord with previous results on atactic polymers.

(5) The secondary or β relaxation, assigned to motions of the ester side group, is a minor feature dielectrically in contrast to the behavior of the poly(alkyl methacrylates).

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References and Notes

(1) B. Wesslen and R. W. Lenz, *Macromolecules*, **4**, 20 (1971).
(2) B. Wesslen, R. W. Lenz, W. J. MacKnight, and F. E. Karasz, *Macromolecules*, **4**, 24 (1971).
(3) B. Wesslen, R. W. Lenz, and F. A. Bovey, *Macromolecules*, **4**, 709 (1971).
(4) G. Dever, R. W. Lenz, W. J. MacKnight, and F. E. Karasz, *Macromolecules*, submitted for publication.
(5) G. Dever, R. W. Lenz, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, submitted for publication.
(6) F. E. Karasz and W. J. MacKnight, *Macromolecules*, **1**, 537 (1968).
(7) J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
(8) S. Bywater and P. M. Toporowski, *Polymer*, **13**, 94 (1972).
(9) J. M. O'Reilly, F. E. Karasz, and H. E. Bair, *Bull. Am. Phys. Soc.*, **9**, 285 (1964).
(10) R. H. Marchessault, H. V. Hein, and G. P. Dever, in press.
(11) O. G. Lewis, "Physical Constants of Linear Homopolymers", Springer-Verlag, New York, N.Y., 1968, p 106.
(12) W. A. Lee, *Br. Polym. J.*, **5**, 3762 (1971).
(13) K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polym. Sci.*, **13**, 565 (1954).
(14) H. Shindo, I. Murakami, and H. Yamamura, *J. Polym. Sci., Polym. Chem. Ed.*, **1**, 297 (1969).

Depolarized Rayleigh Spectroscopy Studies of Relaxation Processes of Polystyrenes in Solution

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ABSTRACT: Depolarized Rayleigh spectra and integrated intensities of atactic polystyrenes in solution have been measured as a function of molecular weight. All spectra (except at the lowest molecular weights) consisted of two components of roughly equal intensity. The relaxation time of the narrow component increased rapidly with molecular weight. This time is approximately equal to one-half the relaxation time of the longest wavelength mode of a Rouse–Zimm chain. The relaxation time of the broad component is roughly independent of molecular weight and can be related to the internal relaxation time of the individual phenyl groups on the chain. The total integrated depolarized intensities agree fairly well with those calculated by rotational isomeric state models (except for an excess intensity at high molecular weight).

I. Introduction

The study of the dynamics of macromolecules has long been an important branch of polymer science. Measurements of the translational and rotational motion of macromolecules have been important, for instance, in elucidating the structure of macromolecules in solution. The study of the intramolecular dynamics is not only important in studying macromolecular structure but is also of importance in determining viscoelastic and macroscopic mechanical properties of macromolecules. A knowledge of the intrachain dynamics at the molecular level would be invaluable in designing polymer systems with specific desired macroscopic properties. Unfortunately, however, there are few methods which may be used to probe these dynamic processes for macromolecules in solution, especially at high frequencies. Techniques such as dynamic viscosity and flow and electric birefringence are valuable at lower frequencies. Dielectric dispersion is currently the method most widely used over a wide frequency range, while NMR and EPR promise to be of great use. Clearly, complementary techniques for probing these motions are needed. In this article, we describe a new probe, depolarized Rayleigh scattering spectroscopy.

Rayleigh scattering total intensity measurements are routinely used to study equilibrium properties of polymers in solution. For instance, the isotropic Rayleigh component intensity is often measured to obtain molecular weights, radii of gyration, and solution virial coefficients of macromolecules.[1] More recently, the much weaker depolarized intensities have been used to study the local conformation of polymer chains.[2,3] Modern light beating and interferom-