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Conformational Features of the Carbosilane Polysilapropylene and Comparison with Polypropylene

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ABSTRACT: The first synthesis of the linear polycarbosilane polysilapropylene, $(\text{-CH}_2\text{SiHCH}_3\text{-})_n$, has been reported recently by Bacqué et al. In an effort to correlate the conformational features of polysilane derivatives with their properties, calculations were performed to determine the relative stabilities of the conformational states of the meso and racemic diads of polysilapropylene. Energy maps were constructed in terms of internal rotation angles to calculate the average properties of the chain. In addition, the MM2 molecular mechanics program was used to optimize the geometry in each of the rotational isomeric states to determine the relative stabilities of these states. The calculations show that the difference in energy between the various states of the meso and racemic diads is small. In contrast, it is well-known that the tg state is highly preferred over the tt state in isotactic polypropylene. Hence, polysilapropylene can be considered to be more flexible than the analogous carbon polymer, polypropylene. The characteristic ratios of the unperturbed end-to-end distances for the iso- and syndiotactic polysilapropylene are less than those for the polypropylenes of corresponding tacticity.

Introduction

Understanding the conformational features of polyorganosilanes has been an active area of research in recent years. The thermochromism exhibited by poly(di-*n*-alkylsilanes) and the molecular weight dependence of the UV absorption maximum in the case of oligomers of polysilane derivatives have been attributed to conformational rearrangement of the chain segments.[1-4] The latter was rationalized in our previous work[5] on poly(methylphenylsilane) (PMPS), on the basis of the a priori probabilities p_t and p_g of the trans and gauche conformers which show variation with the number of bonds in the chain until the chain reaches a length of about 40 bonds. On the basis of the conformational analysis, it was suggested that the localized hole transport behavior observed[6] with PMPS can be attributed to the stereoirregularity of the chain.

The difference in the conformational preference of the polysilanes and their carbon polymer analogues has also been examined by various authors. Damewood and West[7] and Welsh et al.[8] calculated the minimum energy conformations of polydimethylsilane and polysilane and compared them with the minimum energy conformations of polyethylene. A brief comparison of PMPS with poly(α-methylstyrene) and the hole-transporting polymer poly(*N*-vinylcarbazole) has been presented before.[5] Ko and Mark[9] measured the unperturbed dimensions of poly(dimethylsilmethylene) and discussed the differences between its conformational features and those of polyisobutylene and polyethylene.

Polycarbosilane, derived from poly(dimethylsilane), has been used as a precursor for silicon carbide fibers.[10-13] Recently, the synthesis of a *linear* carbosilane, polysilapropylene ($(\text{-CH}_2\text{SiHCH}_3\text{-})_n$), was reported by Bacqué et al.[14] In view of its similarity to polypropylene in terms of the chain composition and the current interest in understanding the differences and similarities between the carbon and silicon backbone polymers, we present here the conformational analysis of the meso and racemic diads of polysilapropylene and a comparison of these features with those of polypropylene that were published by Suter and Flory.[15]

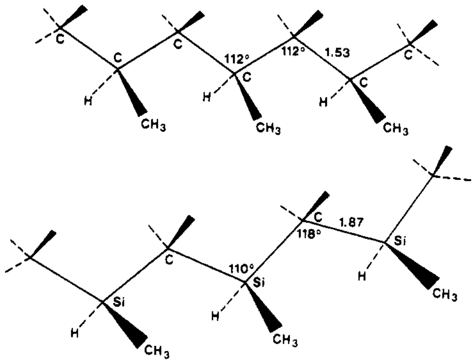

Figure 1. Basic geometric parameters of the segments of polypropylene (top) and polysilapropylene are shown.

Figure 1 compares the differences in the basic geometric features of polypropylene and polysilapropylene chain segments. The Si–C bond length in polysilapropylene is significantly longer than the C–C bond in polypropylene. The skeletal bond angles at the methylene carbon atom and at the α carbon atom are both 112° in the case of polypropylene.[15] However, in the case of polysilapropylene, the skeletal bond angle at the Si atom remains close to tetrahedral, but the angle at the methylene carbon enlarges to about 118°. Such a difference between the bond angles at the successive skeletal atoms along the chain introduces interesting features. Because of the difference of 8° between the skeletal bond angles in polysilapropylene, in the planar all-trans conformation, the chain is not rectilinear but experiences a curvature as shown in Figure 1. This conformation, when perpetuated, would lead to macrocyclization after 45 units. The longer bond length and the larger bond angle, as compared to polypropylene, would no doubt reflect on the overall conformational properties of polysilapropylene.

Description of the Calculations

A schematic of the segment of the polysilapropylene chain is shown in Figure 2, with the relevant geometric variables. In view of the similarity to polypropylene, calculation of the energies of interaction in the various states of the meso and racemic diads of polysilapropylene and

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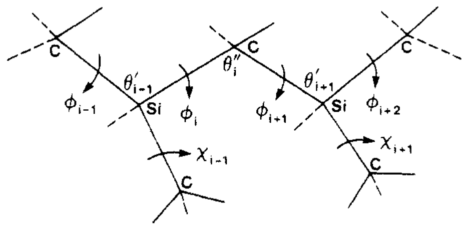

Figure 2. Schematic of the polysilapropylene segment. The relevant geometrical parameters are marked.

the average configurational properties can be treated following the methodologies which have been developed for the corresponding vinyl chains.[16,17]

The Lennard-Jones 6-12 potential functions were used to calculate the nonbonded interaction energies, as a function of the rotations ϕ_i and ϕ_{i+1} at intervals of 10° each. The planar all-trans conformation defines the rotational state $\phi_i = \phi_{i+1} = 0°$. The sense of rotations follows the prescription for the vinyl chains.[16] The parameters for the calculation of the energies were the same as used before.[5] A torsional barrier of 0.4 kcal·mol^{-1} was used for the rotations around the Si–C bonds.[18] The lengths of the Si–C and C–H bonds were taken to be 1.87 and 1.1 Å, respectively.[19] The C–Si–C angle was assigned a value of 109.5°. The angle at the methylene carbon atom was varied in the range 110–120° at each of the states, and the angle which led to the minimum energy for that state was taken into account for the calculations. Similarly, the angles χ_{i-1} and χ_{i+1} were varied in the range 0–120°, for each of the skeletal rotational states to place the methyl hydrogen atoms in their minimum energy conformation.

The positions and energies of the minima were also determined by using the MM2 molecular mechanics program,[20] for each of the rotational isomeric states of the meso and racemic diads. Longer range interactions which arise with the gg and $\bar{g}\bar{g}$ states of the bonds $i-1$ and i were analyzed in terms of the tetrads, using the MM2 program. One of the fundamental tenets of the rotational isomeric state theory is not to identify the conformational states exclusively with the minima. The shapes of the energy surfaces surrounding the minima should be considered. It was for this reason that in a number of studies in the past the statistical weights were determined with Boltzmann-averaged energies surrounding each of the minima.[21] The positions of the rotational states for the treatment of the average properties were not identified with the positions of the minima but again Boltzmann-averaged with the domain surrounding the minima. The influence of the differences in the shapes of the energy surfaces between the various domains was taken into account by introducing preexponential factors for the statistical weights.

The use of a helix parameters map in understanding the influence of the shape of the local segment on the average dimension of the chain has been pointed out before.[5,22,23] The values of n, the number of units per turn of the helix, and h, the advance per monomer along the helix axis (pitch = nh), were calculated as a function of ϕ_i and ϕ_{i+1}, as described before.[5,22,23] The repeat unit for the calculations was taken to be the part of the chain from Si$_{i-1}$ to Si$_{i+1}$. This comprises two skeletal bonds. Hence, for a given n, the number of skeletal bonds per turn of the helix is $2n$.

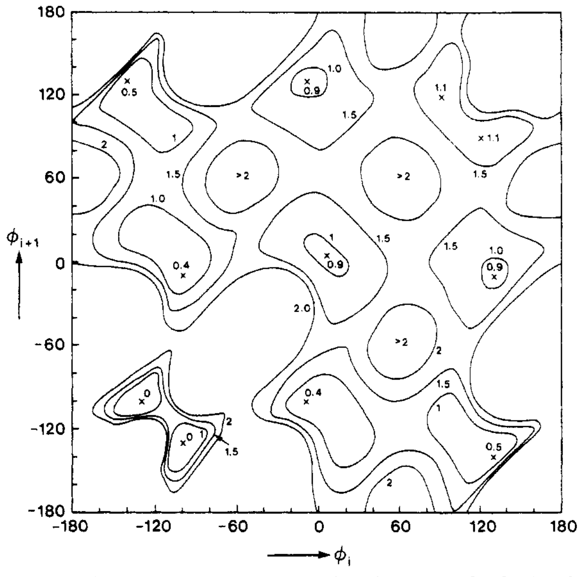

Figure 3. Isoenergy contour map for the meso diad of polysilapropylene in terms of the skeletal rotation angles. The contours are drawn relative to the minimum in the $\bar{g}\bar{g}$ state, the energy of which is −5.67 kcal·mol^{-1}.

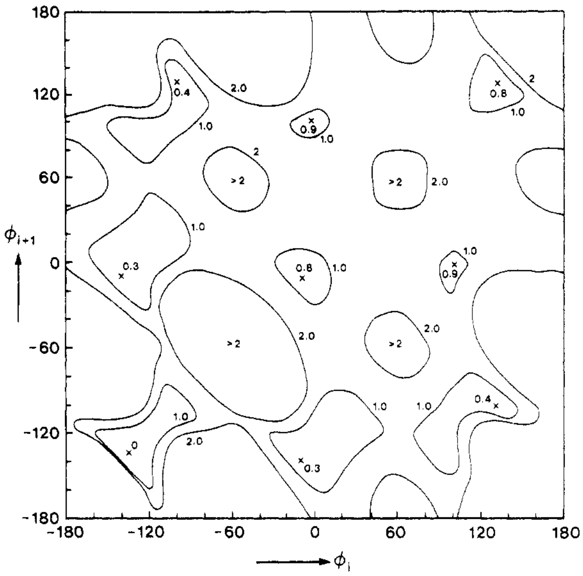

Figure 4. Isoenergy contour map for the racemic diad of polysilapropylene in terms of the skeletal rotation angles. The contours are drawn relative to the minimum in the $\bar{g}\bar{g}$ state, the energy of which is −5.6 kcal·mol^{-1}.

Results and Discussion

The conformational maps for the meso and racemic diads are shown in Figures 3 and 4, respectively. For the meso diad, the lowest minimum occurs in the $\bar{g}\bar{g}$ state. The minimum corresponding to the tt state occurs at $(\phi_i, \phi_{i+1}) = (5°,5°)$ and is 0.9 kcal·mol^{-1} higher in energy than the $\bar{g}\bar{g}$ minimum. The minima corresponding to the other states are shifted from perfect staggering by 10–20°. The bond angle at the methylene carbon for the various regions varied from 116° to 119°. For the racemic diad also, the lowest minimum occurs in the $\bar{g}\bar{g}$ state and the tt minimum is about 0.8 kcal·mol^{-1} higher in energy, occurring at $(\phi_i, \phi_{i+1}) = (-5°,-5°)$. A notable feature of the conformational maps for the meso and racemic diads is that the energy difference between the various minima is small. Except for the $\bar{g}\bar{g}$ state, the minima corresponding to all the other states differ in energy by not more than 0.5 kcal·mol^{-1}. For the meso diad, except for the $\bar{g}\bar{g}$ state, the barrier between all the other states is less than 2 kcal·mol^{-1}. Similarly, for the racemic diad, the barrier between all the rotational isomeric states is less than 2 kcal·mol^{-1}. This leads to the conclusion that polysilapro-

Table I
Results of the MM2 Calculations for the Polysilapropylene Diads[a]

state	θ'_{i-1}	θ'_{i+1}	θ''_i	ϕ_i	ϕ_{i+1}	E, kcal·mol^{-1}
$(\mathrm{tt})_\mathrm{m}$	109.2	109.2	118.2	9.8	9.0	−4.71
$(\mathrm{tg})_\mathrm{m}$	109.8	110.7	116.4	−2.5	123.5	−5.33
$(\mathrm{t\bar{g}})_\mathrm{m}$	109.4	111.7	118.2	1.8	−104.7	−5.14
$(\mathrm{gg})_\mathrm{m}$	111.7	111.8	118.0	107.9	112.1	−4.72
$(\mathrm{g\bar{g}})_\mathrm{m}$	111.8	111.1	118.2	120.3	−131.3	−5.14
$(\mathrm{\bar{g}\bar{g}})_\mathrm{m}$	111.5	112.2	119.7	−105.8	−129.7	−5.12
$(\mathrm{tt})_\mathrm{r}$	109.8	109.8	116.5	−1.6	−1.7	−5.33
$(\mathrm{tg})_\mathrm{r}$	109.3	111.9	118.1	14.1	116.2	−4.72
$(\mathrm{t\bar{g}})_\mathrm{r}$	109.4	111.1	118.2	1.8	−131.3	−5.14
$(\mathrm{gg})_\mathrm{r}$	110.7	110.7	116.5	124.0	124.1	−5.33
$(\mathrm{g\bar{g}})_\mathrm{r}$	111.8	111.5	118.1	121.6	−102.6	−5.15
$(\mathrm{\bar{g}\bar{g}})_\mathrm{r}$	111.5	111.5	119.7	−105.7	−105.7	−5.12

[a] θ and ϕ values in degrees.

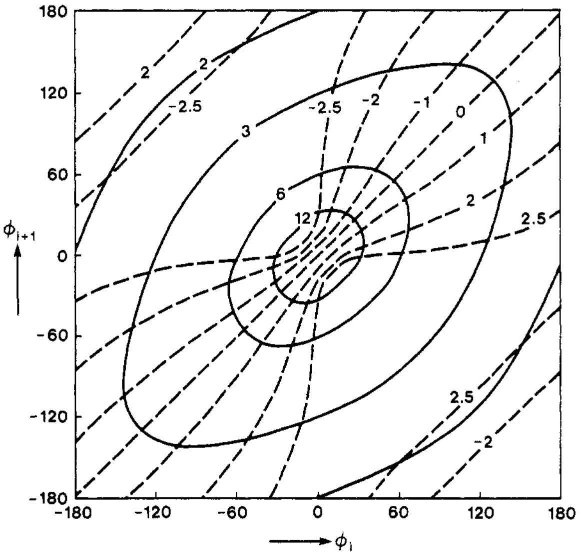

Figure 5. Contour map of the helix parameters *n* (solid curves) and *h* (dashed curves) for polysilapropylene in terms of the skeletal rotation angles. The negative values of *h* correspond to left-handed helices.

pylene is a highly flexible chain.

In the case of the analogous carbon chain, polypropylene, the analysis of Suter and Flory[15] showed that for the meso diad the tg state is highly preferred. The energy of the tt state is very high. For the racemic diad, the tt state is lower in energy but about 2 kcal·mol^{-1} than the tg state. In addition, the treatment of the chain was based on two g and two $\bar{\mathrm{g}}$ states, i.e., a five-state rotational isomeric model. Such a high preference for the tg state for the meso diad or the tt state for the racemic diad is not indicated in the case of polysilapropylene.

The results of the MM2 calculations, corresponding to the various rotational isomeric states of the meso and racemic diads, are given in Table I. The skeletal bond angle θ'' at the methylene carbon varies from 116.4° to 118.2° for the different states of the diads, except that in the $\bar{\mathrm{g}}\bar{\mathrm{g}}$ state, it enlarges to 119.7°. This range of bond angles is similar to the results cited above with regard to Figures 3 and 4. The skeletal bond angle θ'_{i-1} or θ'_{i+1} at the Si atom is close to the tetrahedral value in the trans conformation of the neighboring bond and increases to 111° or more if one or both of the bonds i and $i+1$ are in the gauche state. For example, in the tt states of the meso and the racemic diads, θ'_{i-1} and θ'_{i+1} are 109.2° and 109.8°, respectively. In the $(\mathrm{t\bar{g}})_\mathrm{m}$ state, the value of θ'_{i-1} is 109.4°, whereas θ'_{i+1} increases to 111.7°. For the $(\mathrm{gg})_\mathrm{m}$ state, these angles are 111.7° and 111.8°, respectively. Table I shows that the energy difference between the various states of the meso and racemic diads is small, which agrees with the results presented in Figures 3 and 4. The shifts of the minima from perfect staggering are also similar to those in the above figures. It should be noted that for the construction of Figures 3 and 4 all the torsional angles and the bond angle at the methylene carbon were varied to minimize the energy in each of the (ϕ_i,ϕ_{i+1}) states. Although the bond lengths and the bond angles at the Si atoms were not treated as variables, the results shown in Figures 3 and 4 are not drastically different from those obtained by using the MM2 method.

Table II
Results of the Energy Calculations[a]

state	$\langle E \rangle$, kcal·mol^{-1}	$\langle \phi_i,\phi_{i+1} \rangle$	$\langle \theta''_i \rangle$	Z
$(\mathrm{tt})_\mathrm{m}$	0.28	5,5	115.6	142.3
$(\mathrm{tg})_\mathrm{m}$	0.39	−0.5,117.1	115.4	140.7
$(\mathrm{t\bar{g}})_\mathrm{m}$	0.0	8.8,−111.1	116.1	212.6
$(\mathrm{gg})_\mathrm{m}$	0.47	107.9,107.9	115.7	109.4
$(\mathrm{g\bar{g}})_\mathrm{m}$	−0.01	110.9,−124.5	116.3	189.7
$(\mathrm{\bar{g}\bar{g}})_\mathrm{m}$	−0.29	−115.0,−115.0	118.55	183.1
$(\mathrm{tt})_\mathrm{r}$	0.36	−0.9,−0.9	115.3	139.7
$(\mathrm{tg})_\mathrm{r}$	0.32	5.9, 107.8	115.6	103.5
$(\mathrm{t\bar{g}})_\mathrm{r}$	−0.01	11.5,−125.2	116.0	263.2
$(\mathrm{gg})_\mathrm{r}$	0.36	119,119	115.4	124.7
$(\mathrm{g\bar{g}})_\mathrm{r}$	0.11	104.5,−109.6	116.2	167.9
$(\mathrm{\bar{g}\bar{g}})_\mathrm{r}$	−0.32	−121.9,−121.9	118.5	207.3

[a] θ and ϕ values in degrees.

Table III
Statistical Weight Parameters Derived from Energy Calculations

statistical weight	energy kcal·mol^{-1}	prefactor
η	−0.004	0.983
τ	−0.325	0.879
ω''	−0.074	0.887
ω'	−0.031	0.782
ω	0.075	0.786

The map of the helix parameters n and h, in terms of ϕ_i and ϕ_{i+1}, is shown in Figure 5. A value of 118° was used for θ''. For all the conformations in which $\phi_i = \phi_{i+1}$, the value of h is zero, which would generate macrocyclic structures. Due to the inequality of the skeletal bond angles at the Si and C atoms, the all-trans planar conformation, with $\phi_i = \phi_{i+1} = 0°$ corresponds to $n = 42.35$ and $h = 0$. For the minimum energy position with $\phi_i = \phi_{i+1} = (5°,5°)$ for the meso diad, $n = 35.65$ and $h = 0$. In addition, it is seen that the curve for $h = 0$ traverses regions of low energy in Figures 3 and 4. It should not obviously be construed that the same values of ϕ_i and ϕ_{i+1} would perpetuate along the chain so as to generate regular cyclic structures with a large number of units. However, the results show that formation of macrocyclic species is stereochemically favorable. This accords with the proposal of the presence of cyclic species in the synthesis of polysilapropylene.[10-13] The minimum in the tg state of the meso diad, with $(\phi_i,\phi_{i+1}) = (-10°,130°)$, corresponds to a helix with $n = 2.68$ and $h = -2.67$ Å (or a pitch of 7.15 Å). With $(\phi_i,\phi_{i+1}) = (0°,120°)$, the chain adopts a threefold helical form with $h = -2.62$ Å or a pitch of 7.86 Å. With a value of 116° for θ'', the pitch reduces to 7.77 Å. These repeat distances are longer than that of the corresponding threefold helix of isotactic polypropylene (6.5 Å), due to the longer length of the Si–C bond and the larger skeletal bond angle at the methylene carbon atom.

Statistical Weights and Characteristic Ratios

The statistical weight matrices for the treatment of the polysilapropylene can be adapted from those for the monosubstituted vinyl chains.[16,17] Accordingly, the matrix $\mathbf{U}'$ for the pair of bonds $i - 1$ and i, $\mathbf{U}''_{\mathrm{m}}$ for the bond pair i and $i + 1$ in a meso diad, and $\mathbf{U}''$ for such a bond pair in a racemic diad are given by

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \tag{1}$$

$$\mathbf{U}''_{\mathrm{m}} = \begin{bmatrix} \omega'' & 1/\eta & \tau\omega'/\eta \\ 1/\eta & \omega/\eta^2 & \tau\omega'/\eta^2 \\ \tau\omega'/\eta & \tau\omega'/\eta^2 & \tau^2\omega''\omega/\eta^2 \end{bmatrix} \tag{2}$$

$$\mathbf{U}''_{\mathrm{r}} = \begin{bmatrix} 1 & \omega'/\eta & \tau\omega''/\eta \\ \omega'/\eta & 1/\eta^2 & \tau\omega/\eta^2 \\ \tau\omega''/\eta & \tau\omega/\eta^2 & \tau^2\omega'^2/\eta^2 \end{bmatrix} \tag{3}$$

The first-order interactions in the t and ḡ conformations of the skeletal bonds are taken into account by the statistical weights η and τ, respectively. The statistical weights ω, ω', ω'' correspond to $CH_2\cdots CH_2$, $CH_2\cdots CH_3$, and $CH_3\cdots CH_3$ interactions, respectively, which are of second order. The three second-order statistical weights could perhaps be reduced to one by approximating the interactions involving CH_2 and CH_3 groups to be equivalent. However, the above assignment is maintained here so as to be applicable for the treatment of other chains of similar constitution. The gg and ḡḡ states of the bond pair $i - 1$ and i in the $\mathbf{U}'$ matrix have been assigned a weight of zero, as for the vinyl chains. Calculations using the MM2 program and tetrads showed the energy of these states to be very high. The average energies $\langle E \rangle$ of the states and the values of $\langle \phi_i,\phi_{i+1} \rangle$ and $\langle \theta \rangle$ were calculated by Boltzmann averaging over the domains corresponding to the various states in Figures 3 and 4 and are given in Table II. These calculations were performed by using energies relative to that of the minimum in the racemic tt state. A statistical weight ξ is expressed as

$$\xi = \xi_0 \exp(-E_\xi/RT) \tag{4}$$

The prefactor ξ_0 takes into account the differences in the shapes of the energy domains in the various states. The statistical weights and their prefactors were evaluated by using an overdetermined set of equations as described before[15] and are given in Table III. The small energy difference between the various states of the diads is reflected in the energies corresponding to the statistical weights given in this table.

The characteristic ratio $C_x = \langle r^2 \rangle_0 / x l^2$, calculated by using the parameters in Table III is shown in Figure 6 as a function of the degree of polymerization for isotactic and syndiotactic chains. As in the case of the analogous vinyl chains, the value of C_x reaches the asymptotic value in about 50 units. The values of C_∞ for the isotactic and syndiotactic chains are 4.28 and 3.8, respectively. This is in contrast to the case of polypropylene for which $C_\infty = 13$ for the syndiotactic chain, which is significantly greater than the value of 5.7 for the isotactic chain.[15] The characteristic ratios for the isotactic and syndiotactic polysilapropylene are smaller than those of polypropylene. This can be attributed to the small energy difference between the various rotational isomeric states and the contributions from the conformations which promote macrocyclization.

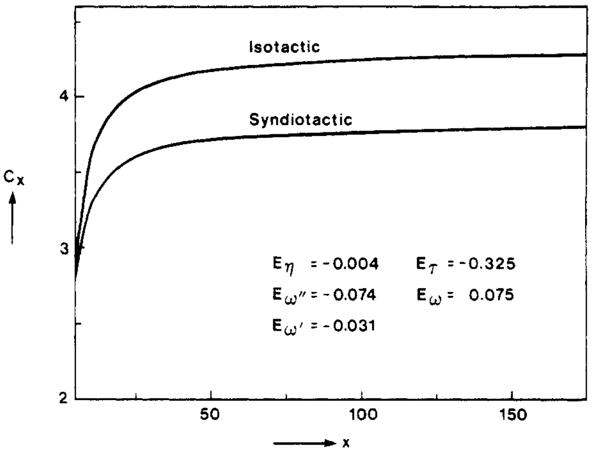

Figure 6. Plot of the characteristic ratio as a function of degree of polymerization x for iso- and syndiotactic polysilapropylene.

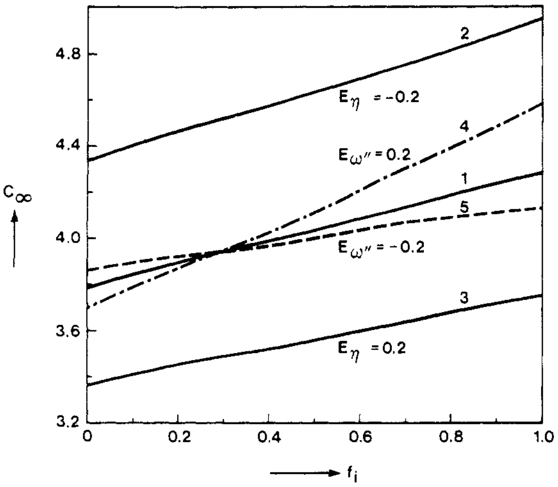

Figure 7. Plots of C_∞ as a function of the isotactic content of the polysilapropylene chain. The parameters in Table III were used, except as noted on the curves.

The value of C_∞ as a function of the isotactic content of the chain is shown in Figure 7. Monte Carlo chains of 200 units each were generated, and the average over 10 such chains was used for the values shown in Figure 7. The standard deviation in all cases was less than 0.02 and hence is not marked on the curves. The curves 1, 2, and 3 in this figure show the effect of small variations in the value of E_η. Although the value of C_∞ remains small, increasing the value of E_η decreases the value of C_∞ for all compositions. This is due to the fact that the populations of all the gauche states depend inversely on η. Curves 4 and 5 in Figure 7 show the effect of increasing the value of $E_{\omega''}$. An increase of 400 cal·mol^{-1} in $E_{\omega''}$ increases C_∞ by 0.4 for the isotactic chain. The effect is insignificant for the atactic and syndiotactic chains. The curves in Figure 7 show that the value of C_∞ increases with the isotactic content of the chain. This behavior is again different from that of polypropylene, for which the

C_∞ decreases with isotacticity.

The value of the temperature coefficient $d(\ln C_\infty)/dT$ calculated at 300 K by using the parameters given in Table III is 2.2×10^{-4} deg^{-1} for the isotactic chain and 2.4×10^{-5} for the syndiotactic polymer. Such small values of the temperature coefficient can be rationalized on the basis of the small energy difference between the various conformers.

At present, there are no experimental data on either the characteristic ratio or its temperature coefficient for this polymer. As noted above, the first synthesis of the linear polymer was reported just recently.[14] However, in view of the reasonable success of these types of calculations to date in accounting for the experimental observations, and the emerging efforts in the direction of predicting material properties in advance of their synthesis, we consider that the difference in the calculated behavior of polysilapropylene and polypropylene would be of interest. Revisions to the calculations or methodology may be required when the experimental data are derived, but such revisions enhance our ability to treat such chains in a more effective manner.

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Small-Angle X-ray Scattering Study for Structural Changes of the Ion Cluster in a Zinc Salt of an Ethylene–Methacrylic Acid Ionomer on Water Absorption

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ABSTRACT: The dimensional change of the ion cluster in a zinc salt of poly(ethylene-*co*-methacrylic acid) ionomer during moisture absorption was investigated by small-angle X-ray scattering (SAXS). Unlike the cases of previously investigated hygroscopic ionomers, the apparent peak position shifted toward the high-angle side with an increase in water content. The desmeared SAXS curves were analyzed in terms of the Percus–Yevick equation, and the structure parameters were derived by curve fitting. The observed change in SAXS with the absorbed water content was interpreted as follows. Although the intercluster distance increased a little with water content as expected, the interparticle interference and minor change in other structural parameters perturbed the scattering profile in an unexpected manner, since the scattering intensity was so weak.

Introduction

A series of copolymers of ethylene (E) and methacrylic acid (MA), where the MA units are partially or fully neutralized with metal hydroxides, is known as an ionomer under the trade name Surlyn (E. I. du Pont de Nemours and Co., Inc.). Introduction of small amounts of ionized groups into the nonionic polyethylene chains causes profound changes in mechanical properties of the copolymers: a remarkable increase in elastic modulus as well as in melt viscosity. Such characteristic changes are thought to be ascribed to the formation of aggregates of the ionized groups called "ionic clusters" in the nonionic polymer matrix.

Since the ion cluster is more or less hydrophilic, their mechanical properties are influenced by moisture absorption. In order to elucidate the change in intracluster structure during the absorption–desorption process, we have examined the change in the infrared bands due to the carboxylate antisymmetric stretch mode (1500–1650 cm^{-1})

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