

# Monte Carlo Simulations on the Stereoregularity, Crystallinity, and Related Physical Properties of Poly[methyl(3,3,3-trifluoropropyl)siloxane]

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**ABSTRACT:** Recent experiments have demonstrated the first preparations of stereochemically-variable polysiloxanes that have sufficient regularity to undergo large amounts of chain crystallization. The specific polymer, poly[methyl(3,3,3-trifluoropropyl)siloxane], had been prepared from various proportions of *cis* and *trans* cyclic trimers using special catalysts, and a number of its properties documented. The present computational investigation was carried out to interpret these results, using Monte Carlo methods to generate representative sequences and to study the possible packing of such sequences into crystalline regions in multichain systems. The quantities of particular interest were the nature of the stereochemical sequence distributions, degrees of crystallinity, melting points, interfacial free energies, and moduli (calculated on the basis of the crystallites acting as cross-links in an elastomeric structure).

## Introduction

It is now well-known that the physical properties of a stereochemically-variable polymer depend to a great extent on its stereoregularity and its distribution of stereoregular sequences.<sup>1–3</sup> However, very little is known regarding stereoregularity–property relationships in polysiloxanes since the monomers and catalysts generally employed in the ring-opening polymerizations used to prepare such chains lead to very irregular (atactic) structures.<sup>3</sup> These stereochemical irregularities are of great importance since they prevent crystallization and thereby limit the utilization of these polymeric materials. Recently, however, there has been a report of the preparation of stereochemically-variable polysiloxanes that do have sufficiently regularity to undergo large amounts of chain crystallization.<sup>4</sup> The specific polymer, poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS), had been prepared in anionic ring-opening polymerizations of various proportions of *cis* and *trans* cyclic trimers using special catalysts that suppress randomization. More specifically, the trimer is 1,3,5-trimethyl-1,3,5-tris(3',3',3'-trifluoropropyl)cyclo-trisiloxane, and the structures of the *cis* and *trans* forms (*cis*-F<sub>3</sub> and *trans*-F<sub>3</sub>) are shown in Figure 1. PMTFPS polymers, in general, are inherently interesting and of considerable commercial interest, being members of the siloxane family of high-performance elastomers.<sup>5</sup> The possibility of obtaining some forms of this polymer that can crystallize can make them even more important. For example, large amounts of stereoregularity could give sufficient crystallinity to put them into the category of thermoplastics, whereas smaller amounts could enable the chains to undergo strain-induced crystallization, with the highly desirable reinforcement this provides.<sup>5</sup>

A number of the properties of the new structural forms of this polymer have now been documented, typically as a function of composition.<sup>4</sup> The major techniques employed were nuclear magnetic resonance



**Figure 1.** Sketches of the cyclic trimers, where R represents the (CH<sub>2</sub>)<sub>2</sub>CF<sub>3</sub> group. The molecule to the left of the *cis* form, and that to the right is the *trans* form.

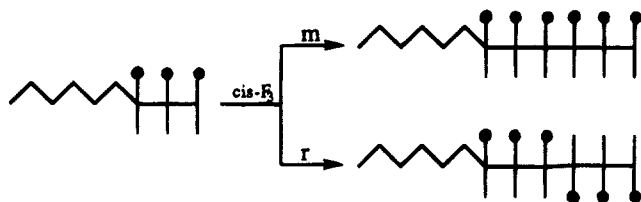
(NMR), X-ray diffraction, and differential scanning calorimetry, and the properties of interest included overall stereoregularity, distribution of stereosequences, and degrees of crystallinity. Of particular interest was the observation that polymers prepared from the *cis*-F<sub>3</sub> cyclic trimer were solid and crystalline at room temperature, while the more typical polymers from mixtures of isomers containing less than 50% *cis*-F<sub>3</sub> were liquid and amorphous.<sup>4</sup>

The present investigation attempts to interpret some of the properties reported for PMTFPS and even to predict some properties not yet measured. Monte Carlo simulations were first used to simulate single chains of the polymer in order to study triad and pentad distributions, for comparisons with those determined experimentally from NMR measurements.<sup>4</sup> Next, a model for the packing of copolymeric chains based on that developed by Windle and co-workers<sup>6,7</sup> was used to interpret some of the other properties reported, with extensions to related properties also of considerable interest.<sup>8–10</sup>

## Simulation Methods and Related Theory

**Simulations on Single Chains.** The calculations were carried out using the following basic assumptions:<sup>11</sup> (i) steady-state copolymerization, (ii) constant monomer feed, and (iii) only “terminal” chain effects (only the prior unit on the growing chain influences the type of unit being added). Three major assumptions based on

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**Figure 2.** Sketch of the two ways, meso and racemic, that a *cis* trimer can add to a growing chain.

the conclusions of Saam and co-workers<sup>4</sup> were also taken into consideration: (i) similar reactivity of *cis*-F<sub>3</sub> and *trans*-F<sub>3</sub> "monomeric" units, (ii) equal probability that any of the three silicon atoms of a monomeric unit is attacked by the growing chain, and (iii) probability of meso insertion (*m*) (pendant groups of the attacked silicon atom pointing in the same direction as those of the prior unit on the growing chain in the planar form) equal to that of racemic insertion (*r*) (pendant groups pointing in the opposite direction). In the older terminology employing arbitrary atomic configurations, meso would correspond to *dd* or *ll* and racemic to *dl* or *ld*.

Various stereoregular sequences on a polymeric chain will be generated for different compositions, in accordance with these assumptions. Two stereoregular sequences are expected in the case of *cis*-F<sub>3</sub>, specifically *ddd* and *lll*. As is illustrated in Figure 2, two triad configurations are possible from the opening of a single *cis*-F<sub>3</sub> ring and four pentad configurations from the opening of two *cis*-F<sub>3</sub> rings. *trans*-F<sub>3</sub> arrangements, on the other hand, are inherently less regular and could presumably be *ddl*, *lld*, *ldl*, *ldd*, and *dll*. Consequently, the longest stereoregular sequence in the case of *trans*-F<sub>3</sub> polymers must be of four units or fewer. Ring opening of *trans*-F<sub>3</sub> will thus lead, as described, to six possible nonequivalent sequences at the chain ends. This would lead to three possible triad and nine pentad configurations. Since *cis*- and *trans*-F<sub>3</sub> rings are assumed to have the same reactivity with equal consumptions during the polymerization process,<sup>4</sup> the conditional probabilities that a chain end will add a unit of either type will depend solely on the mole fraction of the material being added. The simulations of the stereochemical structures were carried out for chains having degrees of polymerization DP of  $1.2 \times 10^6$  units.

**Simulation of Multichain Systems.** The search for crystallinity was carried out according to the Windle approach,<sup>6,7</sup> for copolymers with two crystallizable components. The present approach for stereochemical copolymers parallels that taken earlier for some chemical copolymers of diphenylsiloxane with dimethylsiloxane.<sup>8-10</sup> These searches were carried out using 100 chains, each containing a hundred units with stereochemical structures simulated as described in the preceding section. Each unit in these chains was given the opportunity to be involved in the crystallization process, and each simulated chain retains no information on the origin of the units with regard to the contributing *cis*- or *trans*-F<sub>3</sub> cyclics. All units would thus have the same probability of being involved in the crystallization process so long as they occurred in a sequence of a minimum length suitable for crystallization and had matches with other sequences on neighboring chains. The minimum number of units in a sequence required for crystallization is estimated from experimentally obtained melting points, as described in the following section.

**Melting Points.** The extent to which the melting point of the crystallizable units in a polymer is de-

**Table 1.** Predicted Relative Probabilities for Triads for Various Feed Compositions in the *cis*-F<sub>3</sub> and *trans*-F<sub>3</sub> Copolymers

<i>M</i> <sub>cis</sub> (%)	mm	mr	rr
0 <sup>a</sup>	1.00	4.98	2.99
10	1.00	3.21	1.80
20	1.00	2.29	1.19
30	1.19	2.10	1.00
40	1.66	2.33	1.00
50	2.34	2.66	1.00
60	3.34	3.17	1.00
70	5.04	4.03	1.00
80	8.30	5.66	1.00
90	18.19	10.57	1.00
100 <sup>b</sup>	2.00	1.00	0.00

<sup>a</sup> Corresponds to the *all-trans* polymer. <sup>b</sup> Corresponds to the *all-cis* polymer.

pressed by the presence of the other units is given by<sup>11,12</sup>

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} [\ln(L)] \quad (1)$$

where  $T_m^0$  and  $T_m$  are the melting points of the pure crystallizable polymer and the polymer under study, respectively,  $\Delta H_u$  is the enthalpy of fusion per mole of crystallizable units,  $R$  is the gas constant, and  $L$  is the degree of crystallinity. The depressed melting points observed experimentally<sup>4</sup> can be compared with those obtained from the simulations. The sequence length and the number of exact sequences giving the best fit of the experimental data can be taken as the minimum value required for crystallization of the MTFPS units.<sup>8-10</sup>

**Chain Matching.** Sequences on neighboring chains were scrutinized for matches in stereochemistry, for example, occurrences of units consisting of the sequence ...mmrm... on chains positioned alongside one another. Sliding the chains past one another longitudinally to search for the largest possible matching densities was done to model annealed samples.<sup>6,7,9</sup> The longitudinal movement ( $\langle r \rangle$ ) of the chains relative to one another, out of register, approximately models the lateral sorting out of sequences in polymeric chains during slow crystallization (generally with some annealing). However, in typical polymers with significant degrees of crystallinity, the crystallites formed during relatively rapid ("cold") crystallization will lock some sequences in place, thus restricting the movement of the chains and decreasing the efficiency of the chain-matching process. This can also be simulated by adjusting the extent of the chain movement to smaller values, thus restricting the freedom of the chains to slide by one another.

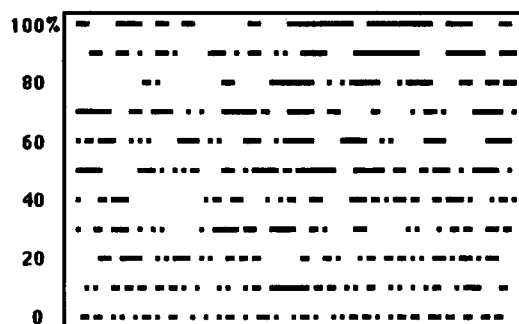
## Modeling Results

**Stereochemical Structures.** As described above, two triad and four pentad configurations in the case of *cis*-F<sub>3</sub> and three triad and nine pentad configurations in the case of *trans*-F<sub>3</sub> are expected. Values of their predicted relative probabilities were found to be in excellent agreement with those calculated analytically,<sup>4</sup> specifically to within a few tenths of a percent. The analytically calculated values, in turn, were in good agreement with the experimental NMR results.<sup>4</sup> The excellent agreements obtained support the assumptions used in simulating the stereochemical structures. The simulated results have the advantage in that actual sequences were generated for determining them, and these or similarly-generated sequences can then be directly used in the subsequent chain-matching parts

**Table 2. Predicted Relative Probabilities for Pentads for Various Feed Compositions in the *cis*-F<sub>3</sub> and *trans*-F<sub>3</sub> Copolymers**

$M_{cis}$ (%)	mmmm	mmmr	rmmr	mmrm	mmrr	rmmr	rmrr	mrrm	rrrm	rrrr
0 <sup>a</sup>	0.00	1.00	2.00	2.49	2.51	4.47	5.49	1.75	4.49	2.75
10	1.00	3.56	3.20	4.82	5.13	7.03	7.95	3.03	7.00	3.95
20	1.00	2.29	1.33	2.44	2.52	2.76	2.89	1.32	2.76	1.46
30	1.42	2.48	1.09	2.40	2.27	2.09	2.00	1.09	2.08	1.00
40	2.60	3.66	1.38	3.52	2.90	2.29	1.97	1.29	2.29	1.00
50	4.72	5.40	1.84	5.40	3.69	2.55	1.98	1.56	2.55	1.00
60	8.68	8.15	2.70	8.83	4.73	2.95	2.01	1.91	2.92	1.00
70	16.60	12.77	4.41	15.63	6.08	3.40	2.01	2.37	3.34	1.00
80	34.56	21.93	8.10	30.47	7.66	3.89	1.99	2.88	3.89	1.00
90	98.74	50.29	20.94	82.13	10.04	4.63	1.95	3.65	4.68	1.00
100 <sup>b</sup>	5.01	1.99	1.00	3.99	0.00	0.00	0.00	0.00	0.00	0.00

<sup>a</sup> Corresponds to the *all-trans*-polymer. <sup>b</sup> Corresponds to the *all-cis*-polymer.

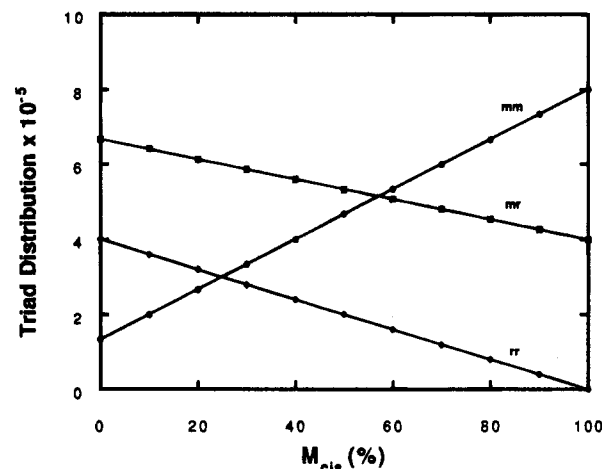


**Figure 3.** Graphical representation of simulated chains of poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) having various compositions of the *cis* cyclic trimer, *cis*-F<sub>3</sub>. Black and white squares represent the *d* and *l* stereoisomers of the units, respectively.

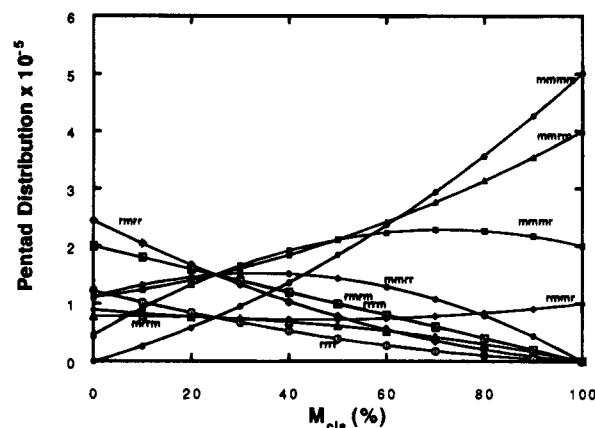
of the investigation. Another advantage of the simulation methods is their ability to predict sequence distributions in polymers prepared with different *cis*-F<sub>3</sub>/*trans*-F<sub>3</sub> feed composition ratios, and even with cyclics having different degrees of polymerization. Some examples are given in Tables 1 and 2, which list predicted probabilities of triad and pentad configurations, respectively, in polymers with various feed compositions of *cis*-F<sub>3</sub>. These results, for example, indicate that *rmmr* and *rrrm* pentads have almost the same distribution at all concentrations.

Figure 3 is a graphical representation of simulated chains of various compositions of *cis*-F<sub>3</sub>, where each row represents a chain having the specified composition. Black and white squares in the figure refer to stereoisomers (*d* and *l*) of MTFPS units, respectively. As expected, even the 100% *cis*-F<sub>3</sub> polymer has both types of stereosequences of different lengths. As discussed in the following section, sequences of a minimum length can lead to the formation of crystallites regardless of their stereospecificities. The dependences of the triad and pentad distribution on the feed composition are illustrated in Figures 4 and 5, respectively. Of particular interest here is the polymer prepared from a feed composition of 25% *cis*-F<sub>3</sub>. At this composition, symmetric pentads (e.g., *mmmm*, *mrrm*, *rmmr*, *rrrr*) have similar distribution values, and these values are half the values of the unsymmetric pentads, which are again quite similar. This circumstance gives rise to some special thermodynamic and mechanical effects, as described below.

**Simulated Multichain Structures.** Comparison of the simulation results with the experimental melting point depressions<sup>4,9</sup> indicates that three MTFPS units is the minimum number for a sequence to participate in the formation of a crystallite. It was also assumed



**Figure 4.** Dependence of the triad distribution of the polymers (degree of polymerization  $DP = 1.2 \times 10^6$ ) on the feed composition of *cis*-F<sub>3</sub>.



**Figure 5.** Dependence of the pentad distribution of PMTFPS polymers on the feed composition.

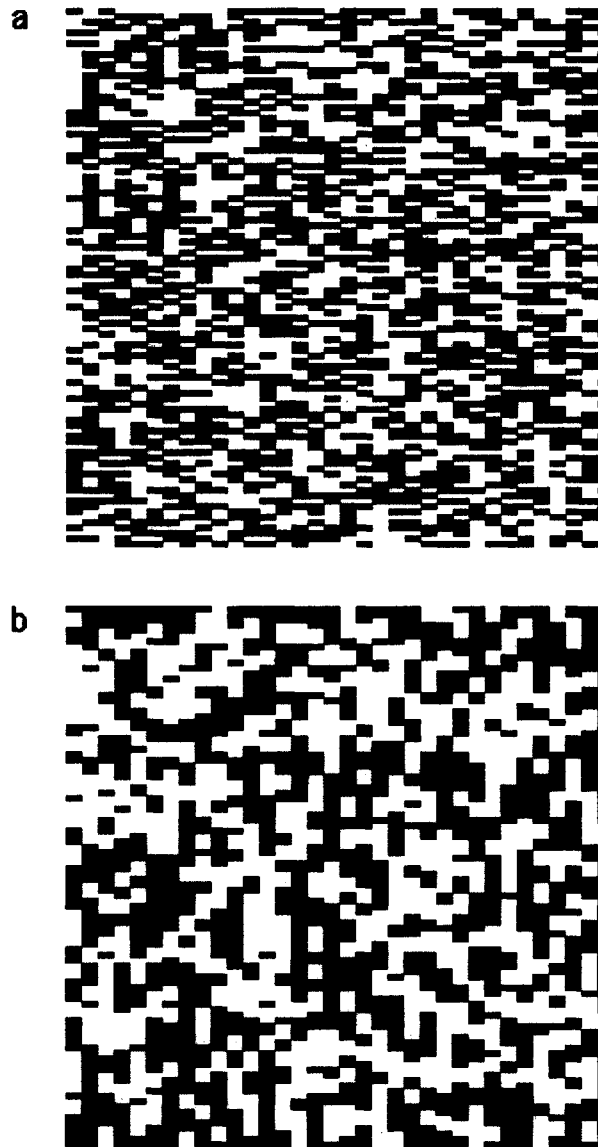
that three matching sequences on three neighboring chains are also required. The simulations are for two-dimensional arrangements and thus represent only slices through an actual three-dimensional sample. It can be expected that the minimum number of units per sequence must be less than or equal to four, the longest stereoregular sequence of samples prepared from *trans*-F<sub>3</sub>, since these samples do exhibit a melting transition at  $-4.4$  °C.<sup>4</sup> Some graphical representations of the simulated results are shown in Figures 6 and 7, which are for polymers prepared from *trans*-F<sub>3</sub> and *cis*-F<sub>3</sub>, respectively. In the a sections of the figures, the black squares represent the *d* isomer and the white squares the *l* isomer. These chains were then slid by one another to maximize the number of "like" squares



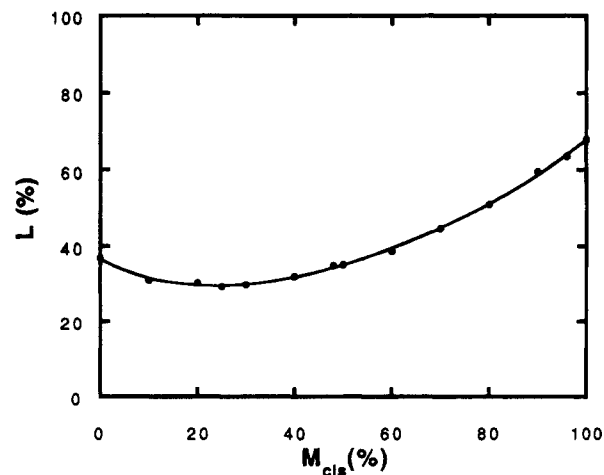
**Figure 6.** Simulated stereochemical structures (a) for the *trans* polymer and the corresponding crystalline regions (b) after annealing. See text.

neighboring one other in the same row and thus coalescing into blocks, the lengths of which are under scrutiny. The b sections show the extent of these annealed crystallized regions. The crystallites are now represented by the white blocks, with the black regions in this case representing sequences that were not long enough to participate in the crystallization. The figures indicate that crystallinity is present in both cases of *trans*- and *cis*-F<sub>3</sub> polymers but is much more extensive in the latter, as expected. The crystallites thus generated presumably act as cross-links and reinforcing domains, thus explaining the observed solidity of the samples prepared from higher *cis*-F<sub>3</sub> feed contents.<sup>4</sup> More specifically, the larger amounts of crystallinity generated in the case of the *cis*-F<sub>3</sub> polymer can be attributed to the longer stereosequences resulting from the *ddd* or *lll* ring opening of the *cis*-F<sub>3</sub> cyclics.

**Degrees of Crystallinity.** Values of the degree of crystallinity  $L$  of the various simulated samples were determined by counting the units involved in the melting sequences relative to the total number of units (10 000) of the samples. The results are shown in Figure 8 as a function of *cis*-F<sub>3</sub> feed composition  $M_{cis}$  (%). The degree of crystallinity changes with composi-



**Figure 7.** Simulated stereochemical structures (a) for the *cis* polymer and the corresponding crystalline regions (b) after annealing. See text.



**Figure 8.** Degree of crystallinity of the polymers as a function of the amount of *cis*-F<sub>3</sub> in the feed composition.

tion, as expected, with a minimum value at the 25% *cis*-F<sub>3</sub> composition. Specifically, the degrees of crystallinity ranged from 37% at 0% *cis*-F<sub>3</sub> (which agrees with the low melting point of the *trans*-F<sub>3</sub> PMTFPS polymer),<sup>4</sup>

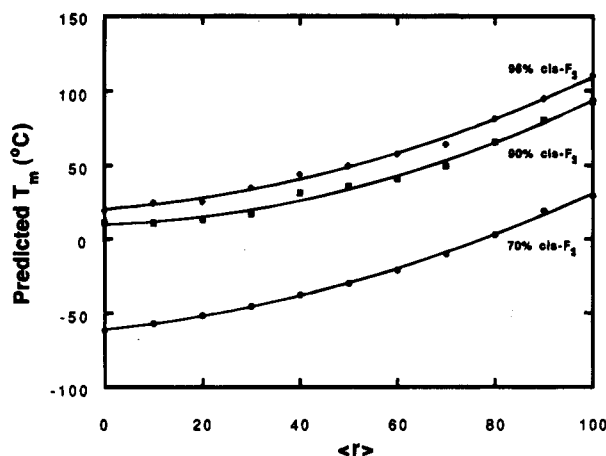


Figure 9. Effect of the search sliding length on the predicted melting points.

Table 3. Some Thermodynamic Information on the *cis*-F<sub>3</sub> and *trans*-F<sub>3</sub> Copolymers As Determined Experimentally<sup>4</sup> and As Predicted from Melting Point Depression Theory and from the Simulations

cis/trans	<r> <sup>a</sup>	exptl		T <sub>m</sub> (°C)	
		T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	eqn 1 <sup>b</sup>	simulation
0/100	100	-4.4	1.7	2.39	-4.08
48/52	100	2.8	12.9	92.5	-2.56
70/30	88	14.7	12.5	137.5	14.1
90/10	56	38.8	16.2	184.0	38.6
96/4	49	48.0	26.2	194.4	47.5

<sup>a</sup> Extent of chain sliding. <sup>b</sup> Melting point depression equation.<sup>11</sup>

to 68% at 100% *cis*-F<sub>3</sub> (which agrees with experimental observations that PMTFPS polymers prepared from *cis*-F<sub>3</sub> are highly crystalline and solid materials at room temperature).<sup>4</sup> The minimum value of the degree of crystallinity at the 25% composition suggests an even lower melting point at this composition.

**Melting Points.** All of the simulated melting points were obtained for the annealed case, with the chains permitted to slide past one another for a specified length to locate the best matching density nearest to the starting points. The chain sections were relocated from one end to the other so as to keep the number of comparison pairs constant. Figure 9 shows the effect of the average extent of movement <r> of a single chain along its length on the predicted melting points, at three different feed compositions. Table 3 presents the melting points of various polymers of different compositions that were determined experimentally or predicted theoretically. Column two of the table gives the extents of chain movement that were found to give the best agreement with experimental results. As expected, higher *cis*-F<sub>3</sub> contents required the choice of smaller chain movements, since the larger degrees of crystallinity expected would restrict the movements of the chains. Column three gives the melting points of the polymers as determined experimentally from DSC measurements, and the next column, the enthalpies of fusion.<sup>4</sup> Column five gives the values predicted by eq 1, the melting point depression relationship.<sup>11,12</sup> The melting points predicted from eq 1 are seen to be much larger than those determined experimentally, which could be explained by the fact that only part of the crystallizable component can actually undergo crystallization.

Using the simulated values of the percent crystallinity in eq 1 should therefore provide more reliable predicted values of the melting points. These values are given in

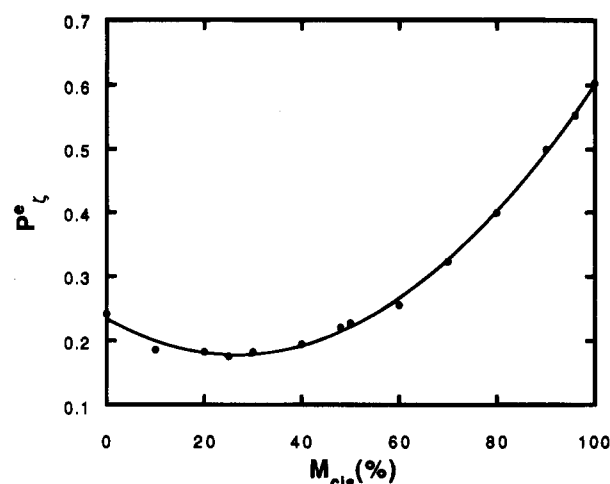


Figure 10. Probability of additional crystallizable units in the polymers as a function of feed composition.

column six of Table 3. It should be recalled that it was the comparison of experimental values and simulated values for the polymer that was used to estimate the minimum sequence length for crystallization. These relationships can now be used to predict melting points at other compositions or for polymers prepared from cyclic monomers having different degrees of polymerization.

**Thermodynamics of Crystallization.** The Flory theory<sup>11</sup> also provides equations for several physical quantities associated with crystallization. The arguments are based on the assumption that matching sequences of a minimum sequence length ζ of neighboring chains would coalesce to form a crystallite. It is also suggested that addition of a sequence of crystallizable units of length equal to or greater than ζ to a growing crystallite depends on (i) the availability of neighboring sequences in the amorphous region and (ii) the decrease in standard free energy gained by incorporation of amorphous polymer units into the crystalline state.

Also of interest is the probability P<sub>ζ</sub> of finding a unit residing adjacent to a terminal unit of the crystallite and belonging to a sequence of ζ units. Its values P<sub>e</sub>ζ measured under equilibrium conditions were calculated from the simulated results by counting the units adjacent to a crystallite, with potential for crystallization, as a function of M<sub>cis</sub>(%). The values of this probability are shown in Figure 10 and do exhibit a minimum value for the polymer prepared from 25% *cis*-F<sub>3</sub> in the feed. As expected, the values increase with an increase in the degree of crystallization and are much greater for polymers prepared from *cis*-F<sub>3</sub>.

**Interfacial Free Energies.** Another important crystallization variable is σ<sub>e</sub>, the interfacial free energy per unit, which represents the excess free energy per mole associated with a unit at the end of a crystallite. Values of this quantity were also calculated from the simulation results. Specifically, the standard free energy of fusion per mole of units ΔF<sub>u</sub> was calculated from

$$\Delta F_u = \Delta H_u - T\Delta S_u \quad (2)$$

and σ<sub>e</sub> from

$$\Delta F_\zeta = \zeta\Delta F_u - 2\sigma_e \quad (3)$$

Estimates of the required values of ΔH<sub>u</sub> and ΔS<sub>u</sub> were obtained from the literature.<sup>4</sup> The values of σ<sub>e</sub> thus obtained are shown in Figure 11. This interfacial free

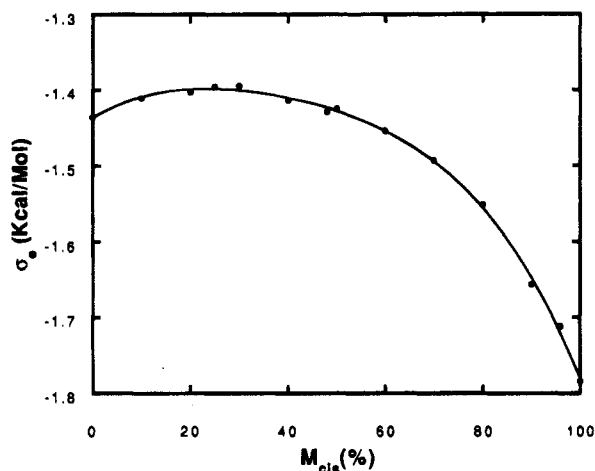


Figure 11. Interfacial free energy per mole of units as a function of feed composition.

energy is an important variable since it takes into account the decreased stability of the shorter crystallites. It can be used as an indicator of the status of the predicted crystallinity in the copolymers. For example, it suggests that in all cases the shorter crystallites in the polymer would be unstable and be reincorporated into the melt. This conclusion is in agreement with experiment, in that even at 95% *cis*-F<sub>3</sub> polymer, only 50% of the material occurs in the crystalline phase.<sup>4</sup>

**Moduli of the Elastomeric Networks.** Although the simulated chains for the matching comparisons are shorter than those typically serving as network chains in an elastomer, it is possible to use the theory of rubberlike elasticity<sup>9,11,13,14</sup> to obtain some semiquantitative results on the mechanical properties of these materials. This can be done by relating the modulus of elasticity to the number of crystalline sequences acting as cross-links, with the sequences in the amorphous state contributing as elastomeric chains. If the number of crystalline sequences per unit volume is represented by  $\nu_c$ , then Young's modulus at infinitesimal deformations is given by

$$Y_0 = 3RT(\nu_c/N_1) \quad (4)$$

where  $N_1$  is the number of units actually participating in the formation of the crystallites. Values of Young's modulus predicted from the simulated values of  $\nu_c$  are shown in Figure 12. The only experimental values of the modulus for such polymers<sup>15</sup> is for chemically cross-linked systems, but more relevant results should be forthcoming.

The minimum value in the curve appearing in Figure 12 corresponds to a sample prepared from 25% *cis*-F<sub>3</sub>, whereas the fact that there is a maximum in the curve is probably due to the coalescence of crystallites as the length of the stereoregular sequences increases. Beyond

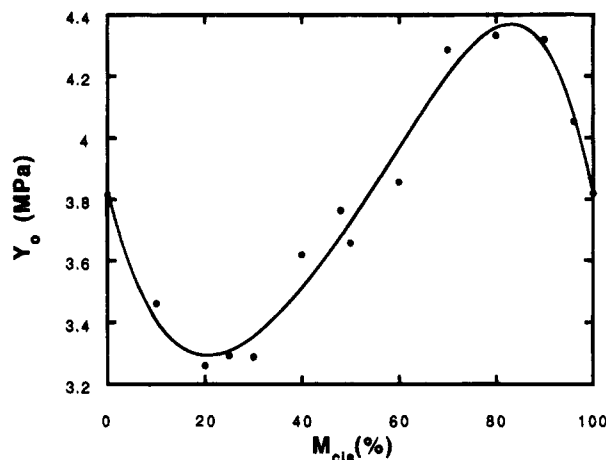


Figure 12. Young's modulus at infinitesimal extension as a function of feed composition.

a certain composition, increasing the number of crystallizable units may result in connecting already-formed crystallites, thus decreasing rather than increasing the number of effective cross-links.

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